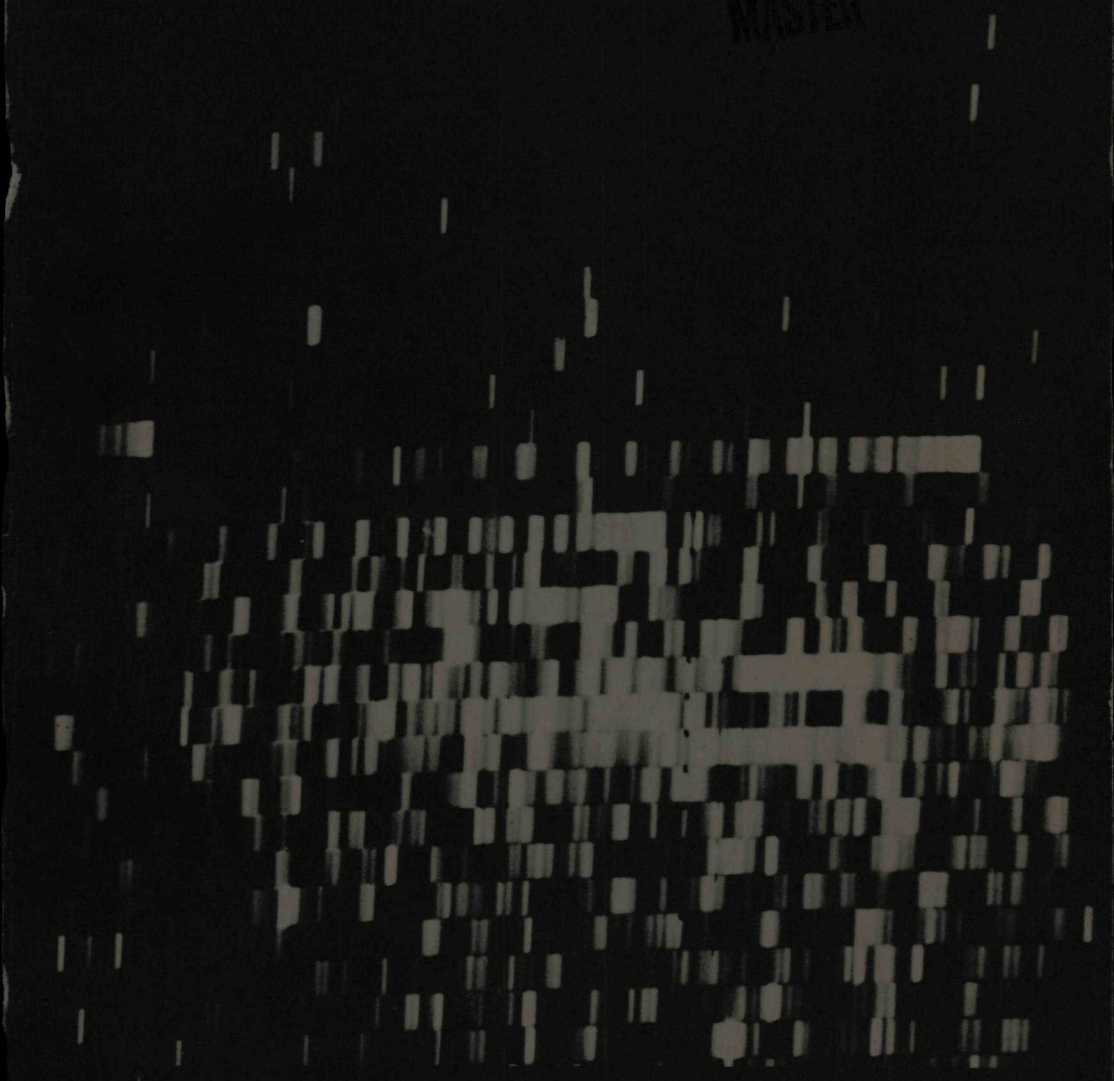
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ANALYSIS OF ESSENTIAL NUCLEAR REACTOR MATERIALS

C. J. RODDEN

MASTER



DIVISION OF TECHNICAL INFORMATION
U. S. ATOMIC ENERGY COMMISSION

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ANALYSIS OF ESSENTIAL NUCLEAR REACTOR MATERIALS

Contributing Editor

CLEMENT J. RODDEN

NEW BRUNSWICK LABORATORY

U.S. Atomic Energy Commission

Prepared under the auspices of the

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PREFACE

It has been barely two decades since the first nuclear reactors went into operation. During this time both the number of reactors and the analytical chemistry problems of the materials used in these reactors have increased considerably. The present book is a collection of published and unpublished information that could be of assistance in the analysis of the essential materials used in nuclear reactors.

In the writing of this book, an attempt was made to provide the analytical chemist with the information needed to carry out many analyses involved in nuclear technology without the necessity of further literature searching. The effort to make this book a laboratory reference book is not without disadvantages, the foremost of which is that much of the information included had to be strictly practical in nature with the physical and inorganic chemistry aspects of the subjects held to a minimum.

A forewarning must be given to readers in search of a specific method of analysis. The chapters on uranium and thorium, for example, are concerned with the determination of the element only; the analyses of uranium and thorium metals for impurities are discussed in the trace-element chapter. On the other hand, the beryllium, plutonium, and boron chapters cover both the determination of the element and the analysis of the metal for impurities. Another example should also be given. If the reader were to look for a specific method of determining uranium in an alloy, the chapter on alloys and ceramics might be consulted as well as the chapters covering specific techniques, such as X-ray emission spectrography. This apparent disorder arises from the many different types of material concerned plus the free rein given to the authors of individual chapters in covering subjects. Some of the duplications that have arisen cause of overlapping coverage have been allowed to remain for ease in locating information.

The concentration expressions (1+2), (1+9), etc., used frequently in the detailed procedures should be defined: the first numeral indicates the volume of reagent; the second numeral indicates the volume of water. For example, ammonium hydroxide (1+2) denotes 1 volume of ammonium hydroxide (specific gravity, 0.90) diluted with 2 volumes of water. If no dilution or concentration is specified, the concentrated reagent is meant. The many concentration expressions

found in the text are a result of describing as closely as possible the procedures as written by the original authors.

For additional information on analytical methods for reactor materials, the reader's attention is directed to *Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle*, compiled and edited by Ralph J. Jones and published by the Division of Technical Information, United States Atomic Energy Commission in 1963.

The chapters have been written by workers in the various fields covered. The exceptions to this are the sections in the Reactor Coolants chapter that were written by the editor.

W. C. Judd and D. Dutina acknowledge the aid of L. P. Pepkowitz, whose understanding and foresight made the writing of the section on sodium and sodium–potassium alloy coolants possible.

Charles Stevens, one of the authors of the Mass Spectrometry chapter, has the following acknowledgments: "Appreciation is due Mark Inghram and David Hess, who pioneered surface-ionization isotopic analysis, in general, and high-sensitivity isotopic analysis and who designed the basic 12-in.-radius mass spectrometer. Special appreciation is also due my colleague, Andrew Lee Harkness, for many pleasant years as an associate in the work on which this chapter is based. Thanks are extended to Barbara Ann Swartz, Matthew Laug, Geraldine Baentelli, Virginia Dickey, and Myrna Heinen for taking much of the data. This writeup is the first fairly detailed description of the instruments built at Argonne; therefore I take this opportunity to give credit for the excellent work done by all the people at Argonne involved in constructing these instruments."

The editor specifically wishes to acknowledge the assistance of Dr. Morris Lerner of the New Brunswick Laboratory, who reviewed essentially the entire book and whose criticism and comments were especially helpful, and of Marian Fox, Special Publications Officer, Publishing Branch, Division of Technical Information Extension, Oak Ridge, who handled the arduous task of editorial revision.

The editor's thanks go to the authors of the various chapters, who, in spite of a heavy workload, spent a great deal of time and effort in preparing their chapters. The editor also wishes to thank S. Sapirie, manager of the Oak Ridge Operations Office, for his understanding in allowing the editor to spend the time necessary for this undertaking.

CLEMENT J. RODDEN
New Brunswick, N.J.
March 1964

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CHAPTER 1

URANIUM

by C. J. Rodden*

1-1 THE CHEMISTRY OF URANIUM AND ITS COMPOUNDS

A great variety of minerals and ores contain uranium, and they are widespread in geographical distribution. The two most important sources of uranium are pitchblende and carnotite. Pitchblende, UO_2 (generally between UO_2 and U_3O_8), is of igneous origin and contains variable amounts of other elements, whereas carnotite is a sedimentary mineral of granitic origin and contains potassium, vanadium, and uranium in the proportions approximately represented by the formula $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$. Carnotite usually occurs in sandstone admixtures.

Uranium metal has a melting point of approximately 1130°C and a density of about 19.00 g/cm³. It can be machined, hot-drawn, and cold-worked. The surface takes a high polish and is silvery in appearance; however, it slowly tarnishes in air.

Uranium forms intermetallic compounds with many other metals. The metal, which lies near beryllium or aluminum in electropositivity, is a strong reducing agent, and it forms binary compounds with most other elements. In the dry state compounds in which the valence of uranium is (III), (IV), (V), or (VI) are well known. However, in aqueous solution U(V) disproportionates into U(IV) and U(VI); whereas the strong reducing agent U(III) is rapidly oxidized by dissolved oxygen and also slowly reduces water to liberate hydrogen. Uranium(VI), the most stable form in aqueous solution, usually exists in, and is separated from, acidic or neutral solutions as the uranyl ion, $(UO_2)^{+2}$. Uranium(VI) often separates from alkaline solutions as the diuranate, $(U_2O_7)^{-2}$, as, for example, $(NH_4)_2U_2O_7$. It may also separate as the uranate, $(UO_4)^{-2}$, as, for example, Na_2UO_4. Variable amounts of hydrous oxide may also be present in such precipitates.

The uranyl ion exhibits a green-yellow fluorescence, which is weak in aqueous solution but strong in the crystalline state.

Important binary compounds include the hydride, carbides, silicides, nitrides, oxides, and halides.

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The hydride, a pyrophoric dark-gray powder, is formed by the action of hydrogen on the metal at 250°C at atmospheric pressure. Uranium hydride serves as a starting material for the preparation of many compounds. For example, uranium trichloride is readily prepared by the action of hydrogen chloride.

$$UH_3 + 3HCl \rightarrow UCl_3 + 3H_2$$

Decomposition of the hydride leaves the finely divided metal in an exceedingly reactive state.

The three carbides UC, U_2C_3, and UC_2 form high-melting-point crystals with metallic luster. Silicides that have been reported are USi, αUSi_2, βUSi_2, USi_3, U_3Si, and U_3Si_2.

The nitrides UN and UN_2 are unreactive dark powders. The UN is not decomposed when heated to 2500°C in an inert crucible at low pressures.

The common oxides of uranium are UO_2, a dark-brown or black powder; U_3O_8, ordinarily a black but sometimes an olive-green powder called "black oxide"; and UO_3, the color of which varies from red to yellow, depending on the crystal modification and particle size. Uranium peroxide, $UO_4 \cdot 2H_2O$, which is yellow, can be precipitated in slightly acidic solution by hydrogen peroxide. It dissolves in alkalis, yielding peruranates. Hydrous uranyl oxide, $UO_3 \cdot H_2O$, dissolves easily in acids, and UO_3 and U_3O_8 are soluble in nitric acid.

The literature lists five fluorides of uranium: UF_3, a black or dark purple colored salt; UF_4, a difficultly soluble compound commonly called "green salt"; U_2F_9, which is black; UF_5, a white substance; and UF_6, a colorless compound that is readily volatile (b.p. 56.4°C). The compounds UF_4 and UF_6 are important. The latter is readily hydrolyzed by water, forming uranyl fluoride. The tetrafluoride is usually prepared from the dioxide and anhydrous hydrogen fluoride at 500 to 600°C.

Uranium forms four chlorides: UCl_3, which is olive-green; UCl_4 and UCl_5, which are green; and UCl_6, which is yellow. The trichloride forms a wine-red unstable solution, and the tetrachloride forms a clear green solution in water. On dissolving in water, the pentachloride disproportionates, forming U(IV) and U(VI), whereas the hexachloride hydrolyzes to UO_2Cl_2. The two higher chlorides are volatile and unstable; the tetrachloride can be sublimed at 550 to 600°C. The tribromide and tetrabromide, triiodide and tetraiodide, and mixed halides are known.

The most common uranyl salts, namely, the nitrate, sulfate, chloride, acetate, and perchlorate, are water-soluble yellow-colored salts. The diuranates, such as $(NH_4)_2U_2O_7$ and $Na_2U_2O_7$, are insoluble. Various U(IV) salts, such as the sulfate, chloride, bromide, and oxalate, are

readily prepared. Most of the uranyl and U(IV) salts form several hydrates.

Uranyl nitrate is of particular importance because, although highly ionized, it can be extracted from a concentrated nitrate solution by organic solvents such as ether and tributyl phosphate. Advantage is taken of this unique property in the separation or purification of uranium.

1–1.1 Valence States

The principal valence states of uranium, are U(III), U(IV), and U(VI). Owing to the relatively low oxidation potential of the U (VI)/(IV) couple, the element can be quantitatively converted to either valence state at will. The alternate use of both valence states permits many separations not otherwise possible. Titrations usually involve a prereduction to U(IV) followed by an oxidation titration to U(VI). Uranium(III) is unstable, but techniques have been developed recently for its use in quantitative analysis.

Acidified uranyl salt solutions are readily reduced by a number of metals or other amalgams, including zinc, aluminum, magnesium, cadmium, lead, bismuth, and silver. In many cases the uranium is reduced to a mixture of the trivalent and quadrivalent states; the proportion of the former ranges up to 40 per cent of the total uranium. Reduction of acidic chloride solutions with silver, cadmium, or lead yields only the quadrivalent form. Uranyl solutions can also be reduced electrolytically to mixtures of U(IV) and U(III). Under the proper conditions tin(II) chloride, titanium(III) salts, and sodium hyposulfite reduce uranyl salts.

The trivalent uranium ion is a powerful reducing agent; exposure to air for a few minutes serves to oxidize it quantitatively to the quadrivalent state. Uranium(IV) solutions are relatively stable in the presence of air. When warmed to 60 to 80°C or when shaken with oxygen, they are oxidized more rapidly. Uranium(IV) in solution is converted to U(VI) by most of the common oxidizing agents.

A detailed description of uranium and its compounds has been given by Katz and Rabinowitch.[1]

1–1.2 Solution of Uranium and Its Compounds

The method best suited for the dissolution of metallic uranium, its alloys, or its compounds depends on the nature of the sample, the constituent to be determined, and the method of analysis. Nitric acid is often employed because it dissolves all, or nearly all, compounds and alloys of uranium. In the analysis of minerals and refractory oxides, it may be necessary to use fusion methods. The presence of nitrates,

690–457 O—64——2

however, cannot be tolerated in many analytical procedures, such as the volumetric determination of uranium following a reduction by zinc. A discussion of available methods of dissolution of uranium and its alloys, taken from Larsen,[2] appears below.

(a) *Uranium and Its Alloys.*[2] Elemental uranium is very reactive; it is comparable to magnesium in many of its dissolution characteristics. The metal in massive form reacts vigorously with 3*N* hydrochloric acid and 12*N* nitric acid and is surface oxidized by air quite rapidly. As turnings and powder, it is extremely pyrophoric, often igniting as a result of mechanical friction, a small addition of acid or water, or even spontaneously. In addition to the usual dangers inherent in handling pyrophoric metal, uranium fires, even when the metal is unirradiated, lead to radioactive contamination.

Metallurgical pretreatment and composition have pronounced effects on dissolution rates. As-cast uranium fuel rods are often preferentially attacked along the major axis, leaving a porous skeleton comparable in size to the original specimen but perhaps containing less then 10 per cent of the uranium. As much or more time may be required to dissolve this portion of the sample as was required to dissolve the first 90 per cent.

The dissolution rates for uranium and uranium alloys that have been highly irradiated are often significantly higher than those for the unirradiated metal. The irradiation effect is ordinarily insignificant when less than 0.1 per cent of the atoms have been fissioned, but when this value is 1 per cent or more, dissolutions can often be carried out at half the usual acidity. Although this effect can in part be ascribed to an increase in surface area resulting from radiation damage, this change in dissolution rate has also been noted when there was little or no metallographically observable loss of surface integrity. These highly irradiated samples may also be more rapidly oxidized and more pyrophoric.

(1) *Nitric Acid.* Probably the most common reagent for the dissolution of uranium metal and its alloys is nitric acid. The dissolution reaction is quite complicated, with the acid reduction products varying from nitrogen dioxide to elemental nitrogen. Generally speaking, those dissolutions that are carried out at acidities of 8*M* or less give nitric oxide as the principal gaseous product; those carried out at higher acidities give nitrogen dioxide as the principal product. The rate of attack on bulk metal by 10*M* acid at 100°C is sufficient to dissolve most 10-g samples in less than 30 min. Powdered samples may react very rapidly and cause ignition of the uranium. If perchloric acid is added even in small amounts, the reaction may be so rapid as to be dangerous.

Zirconium and niobium are two metals that are often added to uranium in low concentrations to improve its radiation and corrosion resistance. Nitric acid and aqua regia dissolve the uranium matrix of these alloys rapidly but do not dissolve the intermetallic crystalloids, which contain the bulk of the zirconium and/or niobium. The finely divided metallic residue that adheres to the metal during the dissolution may oxidize slowly to form an insoluble oxide residue, or it may, after some accumulation, react explosively.[3] Mild agitation may set off the explosion; at times it occurs spontaneously. Explosions, even during the dissolution of 10-g samples, are violent enough to break the beaker in which they are contained and to spray the surrounding area with acid. Samples containing as little as 1 per cent zirconium have exploded violently during a straight nitric acid dissolution.

The addition of hydrofluoric acid or a soluble fluoride salt to a nitric acid or aqua regia dissolution of these alloys can prevent the accumulation of the explosive residue. Two to three times the stoichiometric requirement for the dissolution of the alloying constituent (2 g of fluoride per g of zirconium) is usually added. The precipitation of uranium tetrafluoride may alter the concentration of "available" fluoride, but this can be prevented by adding the fluoride as a complex of aluminum in a 2 to 1 molar ratio. Fluoride that is too securely bound, as in fluosilicic acid, will not prevent explosions.

(2) *Hydrochloric Acid.* Uranium reacts with hydrochloric acid very rapidly to form U(IV) chloride and a black precipitate, which has been described as a hydrated (III–IV) oxide. When 4*M* acid is added to the bulk metal, there is usually a short quiescent period before the rapid evolution of hydrogen begins. For a second or two the solution above the sample is a bright burgundy color, indicating the presence of trivalent uranium, but this color is quickly masked by the dark green of U(IV) and voluminous quantities of the finely divided black precipitate. That the precipitate contains trivalent uranium is shown by the hydrogen equivalents to uranium mole ratio of 3.4 to 3.6 and the continued evolution of hydrogen from the precipitate long after the metal has been consumed. Unfortunately no amount of heating in the acid will dissolve the precipitate completely. In 1*M* acid at 100°C, a 10-g sample can be consumed in an hour; in 12*M* acid the evolution of hydrogen is explosively rapid.

The metal, when removed from the acid after partial dissolution, is covered with a heavy black coating. Most of this is easily scraped away, but next to the bulk metal it is very adherent. This coating is very reactive when dried, often glowing red hot for a moment from sudden air oxidation.

Because the reaction of uranium metal with hydrochloric acid is so rapid, it is usually best to consume the metal with acid alone and then add an oxidizing agent. At 75°C sodium chlorate, hydrogen peroxide, or bromine reacts rapidly with both the U(IV) and the hydrated oxide to form uranyl halide solutions. Excess oxidant can easily be removed by adding strong hydrochloric acid to the solution and boiling it or by evaporating the solution until it is $2M$ or more in uranium. Gaseous chlorine will complete the oxidation of the uranium to the hexavalent state, but, in the absence of a catalyst, the reaction is slow and inefficient, even at 100°C. Small amounts of iron or iodine, $10^{-2}M$ to $10^{-3}M$, promote the rate of oxidation by chlorine very markedly. Other ions such as ferric, dichromate, persulfate, nitrate, etc., will oxidize the uranium to the hexavalent state but will introduce other ions that may be objectionable in subsequent analyses. There is no satisfactory mild oxidant for solubilizing the hydrated (III–IV) oxide to form a U(IV) chloride solution.

The two-step dissolution in which hydrochloric acid attack is followed by an oxidant has definite advantages in the handling of fission-product iodine and bromine. In nitric acid dissolution these fission products are divided between the offgas and the dissolver solution; in a hydrochloric dissolution they are quantitatively retained and may be volatilized at will by the addition of a suitable oxidant.

(3) *Aqua Regia.* Although aqua regia is often used for dissolving uranium alloys where nitric acid or hydrochloric acid and some other oxidant such as hydrogen peroxide would work equally well, it is the only satisfactory reagent for dissolving uranium that is alloyed with the platinum metals. The so-called "fissium" alloys obtained in the pyrometallurgical processing of irradiated uranium which contain 1 per cent or more of the fission elements zirconium, molybdenum, ruthenium, rhodium, and palladium are typical. They present the problem of solubilizing the very reactive uranium matrix material in the same reagent as that used for very inert alloying constituents.

In cases where the dissolution has been made a two-step operation, alloys of this type have been satisfactorily dissolved in aqua regia. The uranium matrix is first consumed in a minimal volume by covering the sample with water and adding the premixed concentrated acids as rapidly as the vigor of the reaction will permit safely. When the gas evolution subsides, a four-fold excess of the concentrated acids is added, and the solution is boiled for about 10 min to dissolve the ruthenium–rhodium residue. If the dissolution is not pushed, appreciable decomposition of aqua regia will occur, and the ruthenium and rhodium will not dissolve no matter how long the solution is boiled. When this occurs, it is necessary to separate the finely divided residue by prolonged centrifugation and to dissolve it separately, e.g., ruthe-

nium residues are dissolved in sodium hypochlorite. Aqua regia having a relatively high hydrochloric acid to nitric acid volume ratio, 4 to 1, is used to prevent the volatilization of ruthenium tetroxide.

Hydrofluoric acid is added in appropriate amounts [see Sec. 1.1.2 (a) (1)] to ensure complete solution of the zirconium. Occasionally, zirconium oxide does precipitate during the dissolution as the result of a reaction between the zirconium fluoride complexes and the silica of the flask, but it can be redissolved readily by a final addition of dilute hydrofluoric acid. If a zirconium analysis is required on the dissolved material, the dissolution must be carried out in quartz ware since both pyrex and Vycor may contain appreciable amounts of zirconium. Polyethylene ware cannot be used because the dissolver solution has to be vigorously boiled.

(4) *Perchloric Acid.* Uranium metal dissolves very rapidly and quite spectacularly in hot 70 per cent perchloric acid. The attack on clean surfaces may begin at 50°C or lower, and once dissolution has started, the temperature rises rapidly to the boiling point, about 190°C. During the temperature rise the solution becomes clouded by a heavy black precipitate, but this soon dissolves to form the characteristic yellow of uranyl solutions. At the boiling point the reaction is very vigorous, but it can be controlled by limiting contact of the metal with the boiling acid. Apparently small particles of metal are dislodged during dissolution, and, in burning in the perchloric acid vapor, they account for a "sparking effect."

There is no attack on uranium metal by 35 per cent perchloric acid even at its boiling point. As the solution is boiled, the concentration and temperature of the solution rise slowly until the dissolution reaction begins at about 150°C. Once initiated, the rate of reaction increases rapidly, and the solution is soon heavily clouded by a black precipitate. Between 160 and 170°C the solution clears and reclouds cyclicly several times a minute. From 170 to 190°C the reaction is very similar to that in 70 per cent acid. The observed behavior between 160 and 170°C is probably the result of chloride attack followed very shortly by perchlorate oxidation.

The character of the perchloric acid dissolution leaves much to be desired from a safety aspect. The dissolution of turnings, chips, or powder should generally not be carried out in perchloric acid. The reactions could be so vigorous that the acid and metal would be forcibly ejected from the flask, and the uranium might be ignited. Any dissolution of uranium should be approached with caution. Perchlorate dissolution should be used only when it is absolutely necessary, and then it should be performed in a closed hood and with no direct handling. Most dissolutions can be slowed quickly by the addition of a diluent; however, the addition of water to boiling perchloric acid would be disastrous.

(5) *Sulfuric Acid.* Unalloyed uranium and most alloys in which uranium is the bulk constituent do not react with sulfuric acid at moderate concentrations and temperatures. When a clean uranium surface is exposed to 6*M* sulfuric acid, there is an initial minute evolution of hydrogen and a visible darkening of the metal surface, but all visible reaction soon ceases. The coating appears to protect the metal from further attack. This is somewhat surprising since U(IV) is strongly complexed by sulfate and U(IV) sulfates are quite soluble. Dilute sulfuric acid is therefore quite useful in removing iron, magnesium, aluminum, and other metals that have been bonded to, or mixed with, bulk uranium metal.

Mixtures of sulfuric acid and hydrogen peroxide attack uranium slowly at 75°C to give solutions of uranyl sulfate. The addition of chloride in catalytic amounts increases the rate of solution very markedly; small additions of fluoride have a similar effect, but it is not as pronounced. Ten grams of uranium can be dissolved in less than 30 min in 100 ml of 6*M* sulfuric acid, 1*M* hydrogen peroxide, and 0.01*M* hydrochloric acid. Since the small amount of chloride is easily removed by evaporating to fumes of sulfur trioxide, a dissolution of this type is particularly useful when a sulfate medium is required in the subsequent analysis.

Anodic dissolution of uranium in sulfuric acid can be carried out very satisfactorily. The uranium metal is placed in a platinum dish or on a flat metal plate and electrolyzed against a platinum cathode. Platinum filter cones are particularly well suited for use as anode cups because the perforations allow the dense uranyl sulfate solution to drain away from the specimen as rapidly as it is formed. There is no gas evolution at the cathode; hydrogen is evolved at the anode. In time, particularly if stirring is employed, appreciable reduction of uranium to the tetravalent state will occur at the anode and some uranous sulfate may precipitate. The precipitate is readily dissolved by hydrogen peroxide. A 10-g piece of metal can be dissolved in 1 hr in 6*M* sulfuric acid with a 6-volt storage cell as a current source. Because the surface of the uranium during an electrolytic dissolution is highly polished, this method is often used in preparing specimens for metallographic examination.

(6) *Hydrofluoric Acid.* Hydrofluoric acid is not used as a prime reagent for the solution of uranium metal because of the insolubility of the reaction product, uranium tetrafluoride. Bulk metal samples react for a short time; they soon become coated, however, and all reaction ceases. Hydrofluoric acid does play a particularly important role in the dissolution of certain uranium alloys [see Sec. 1–1.2(a)(1)] and of zirconium metal and zirconium-uranium alloys. It is also used

as a catalyst in the nitric acid dissolution of thorium metal and thorium oxide.

(7) *Phosphoric Acid.* Cold 85 per cent phosphoric acid attacks uranium slowly, but, after the acid has been concentrated by boiling, a fairly rapid reaction occurs. With an excess of acid, a green solution of U(IV) phosphate is obtained, which gives a gelatinous precipitate on dilution. A glassy substance, which is extremely difficult to redissolve, is formed when the solution is boiled down too far. The solution of uranium in phosphoric acid is accelerated by oxidizing agents such as nitric acid or peroxide and by anodic oxidation.

Fluoride will accelerate the dissolution of uranium in phosphoric acid without condensing the acid. Condensation of the acid leads to low analytical results. The U(IV) is either oxidized by oxygen or complexed by the polyphosphates. In either case it is not available for oxidation by Ce^{+4} or $Cr_2O_7^{-2}$. In the presence of phosphate ions, U(IV) is quite stable to air oxidation. The use of phosphoric acid in uranium dissolutions should be avoided if possible because phosphate in large amounts interferes in many uranium analyses and separations and is very difficult to eliminate.

(8) *Bromine in Ethyl Acetate.* Strong solutions of bromine in ethyl acetate react rapidly with both uranium and zirconium to form uranium(IV) bromide and zirconium bromide solutions.[4] This combination of reagents is particularly useful in dissolving uranium–zirconium alloys if fluoride must be absent in subsequent analyses or in determining oxides, nitrides, and carbides in these metals. The metal salts are easily stripped from the ethyl acetate with water when the dissolution is complete, and carbon tetrachloride scrubs will free the aqueous strip of bromine and ethyl acetate. If desired, some of this bromine can be used to oxidize the uranium to uranyl bromide before scrubbing by heating the solution to 70 to 80°C. Because some hydrogen bromide is formed in side reactions, the aqueous uranium bromide solution will be acidic. The addition of magnesium oxide will prevent this.[5]

Because of what appear to be autocatalytic side reactions between the bromine and the solvent and because of a second-order dependency of the dissolution rate on bromine concentration, the dissolution must be carried out under somewhat restrictive conditions.[6] Dissolution times must be 30 min or less, the uranium product concentration must be 0.5*M* to 1.0*M*, and a 50 to 100% excess of bromine must be used.

Procedure. The sample (10 g bulk) and 25 ml of ethyl acetate are placed in a 100-ml flask equipped with a reflux condenser. The ethyl acetate is heated to near boiling, the heat is removed, and 5-ml increments of an 8*N* solution of bromine in ethyl acetate are added at about 3-min intervals until 40 ml has been added. After an induction period

of several minutes, the dissolution reaction begins and, with the periodic additions of bromine-ethyl acetate, proceeds with sufficient vigor to boil the solution for 15 to 20 min. Some heating is necessary during the last 10 min to complete the dissolution of the metal. The dissolution can be slowed or stopped altogether by the copious addition of ethyl acetate. The surface of the uranium metal during the dissolution has a highly polished appearance very similar to that obtained in electrolytic dissolutions in sulfuric acid.

Chlorine has been tried as a substitute for bromine, but limited solubility and more rapid attack on the solvent made dissolutions with this reagent unsuccessful. With some solvents violent explosions occurred after prolonged treatment.[7]

(9) *Hydrogen Chloride–Ethyl Acetate.* Hydrogen chloride solutions in ethyl acetate react with uranium at a moderate rate to form uranium tetrachloride solutions. In a $3M$ solution, which is close to saturation, a 10-g bulk sample will dissolve in 4 to 5 hr. Soon after the sample has been introduced, hydrogen evolution begins, and the solution takes on the characteristic green of tetravalent uranium. With no agitation other than the gas evolution, the green is masked after several minutes by the deep burgundy of trivalent uranium. When dissolution is complete, or during the dissolution if desired, the trivalent uranium can be oxidized easily by aeration.

The ethyl acetate–hydrogen chloride dissolution of uranium is unique in that uranium metal is dissolved completely in a relatively mild reagent. Its action is similar to that of hydrochloric acid, but it does not lead to the insoluble hydrated oxides. With this procedure, it has been possible to selectively dissolve the metal in metal–oxide mixtures and to separate certain intermetallic compounds by dissolving only the uranium matrix.

Other solvents can be used in place of the ethyl acetate. Acetone has been used extensively by workers at Oak Ridge National Laboratory. The choice of solvents depends primarily on whether or not immiscibility is important in the procedure to be used subsequent to dissolution.

(10) *Sodium Hydroxide–Hydrogen Peroxide.* Occasionally it is necessary or convenient to dissolve a uranium sample in a basic medium, i.e., when a particular alloying constituent is not soluble in acid or when a solution is desired which can be quickly converted to any acid medium. The dissolution in sodium hydroxide–hydrogen peroxide mixtures will usually meet this need.

Uranium metal reacts at a moderate rate with $1M$ sodium hydroxide–$5M$ hydrogen peroxide mixtures to form a clear solution, highly colored by the uranyl peroxide complex. A 10-g sample will dissolve in less than 1 hr in 50 ml at 100°C. The sodium hydroxide concen-

Table 1.1—REAGENTS FOR DISSOLUTION OF URANIUM AND ITS ALLOYS*

Description	HNO_3	Aqua regia	Nitric–HF	HCl+ Ox	HCl–EtOAc	Br_2–EtOAc	NaOH–H_2O_2
U	S	S	S	S	S	S	S
U-Zr	N	N	S	N	N	S	N
U-Nb	N	N	S	N	N	S	S
U-Fe	S	S	S	S	S	S	N
U-Cr	N	N	N	S	S	S	N
U-Ru	N	S	N	N	N	N	N
U-Mo	N	S	N	S	N	S	S
U-Fission†	N	S‡	N	N	N	N	N
U-Si§	S		S				
U-Pu	S¶	S	N	S	S	S	N

*S = satisfactory; N = unsatisfactory.

†Alloys containing from 1 to 3 per cent zirconium, molybdenum, ruthenium, rhodium, palladium, and cerium.

‡Fluoride must be added to dissolve zirconium.

§Nitric acid dissolutions leave silicon residue, but nitric–hydrofluoric acid dissolutions can easily lead to volatilization of fluosilicic acid.

¶Plutonium itself is not readily dissolved in nitric acid, hydrochloric acid being preferable.

(From R. P. Larsen, *Anal. Chem.*, Ref. 2.)

tration should be kept relatively low since the rate of solution is much more rapid in $1M$ alkali than in $6M$.

In Table 1.1 the more common uranium alloys and the reagents that are used to dissolve them have been summarized. The choice of reagent for the dissolution of a particular sample of uranium or uranium alloy will, of course, depend not only on the ability of the reagent to dissolve the sample but also on what analyses are to be performed on the solution. Many hours of analysis time can be saved if the sample can be dissolved in the medium in which the analysis is to be run, rather than dissolved, whenever possible, in aqua regia, for example, and then converted to the desired medium by fuming.

(b) *Uranium Oxides: Uranates.* Nitric acid dissolves all the normal oxides of uranium (UO_2, U_3O_8, UO_3) with the formation of uranyl nitrate. Uranium peroxide, $UO_4 \cdot 2H_2O$, is readily dissolved in an acidic reducing solution; in hydrochloric acid, uranyl chloride and chlorine are formed. The uranates, diuranates, and uranium trioxide dissolve in the common acids. Neither UO_2 nor U_3O_8 dissolves in dilute hydrochloric or sulfuric acid at a practical rate.[8, 9] Each is slowly oxidized by long heating with sulfuric acid, forming uranyl sulfate. The oxides are readily dissolved by fuming with per-

chloric acid, which results in the formation of uranyl perchlorate. Soluble peruranates are obtained by treatment of uranium oxides with alkaline peroxides.[10, 11]

(c) *Uranium Fluorides.* Uranyl fluoride and uranium hexafluoride are soluble in water. The latter is violently hydrolyzed, forming uranyl fluoride and hydrofluoric acid. Uranium pentafluoride disproportionates and hydrolyzes in water to form hydrofluoric acid, soluble uranyl fluoride, and insoluble U(IV) fluoride. Uranium(IV) fluoride and U(III) fluoride are both insoluble in water.

Uranium fluorides are often converted into U_3O_8 prior to their solution. This conversion can be accomplished by hydrolysis with steam [12] or fusion with boric acid,[13] ammonium oxalate,[14] or potassium pyrosulfate.[15] Uranium tetrafluoride can be readily converted to U_3O_8 by ignition in air [16] or by heating with ammonium carbonate [17] and then dissolving as above. Uranium tetrafluoride is readily dissolved by boric acid solutions that have been acidified with sulfuric, hydrochloric, or perchloric acid, giving U(IV) sulfate, chloride, or perchlorate. When a mixture of nitric acid and boric acid is used, uranyl nitrate and fluoboric acid are formed. Uranium tetrafluoride is also soluble in an EDTA solution. Ferric ion oxidizes UF_4 to uranyl compounds and forms a complex with the fluoride ion. Aluminum chloride dissolves UF_4 by complexing the fluoride ion.[18] Neutral oxalate solutions dissolve uranium tetrafluoride owing to the stability of the U(IV) oxalate complex in neutral mediums. Strongly acidic solutions of ceric sulfate oxidize uranium tetrafluoride to uranyl fluoride. Alkaline peroxides dissolve uranium tetrafluoride and form peruranates. Uranium tetrafluoride is readily dissolved by fuming perchloric acid to form uranyl perchlorate; the hydrofluoric acid is expelled. Long boiling with nitric acid causes slow solution of uranium tetrafluoride, and heating with phosphoric acid results in the formation of U(IV) phosphate and removal of the fluorine. On heating, concentrated sulfuric acid reacts to form a sulfate that dissolves on dilution with water. However, the fluorine is not quantitatively expelled. Treatment with dilute sulfuric acid and powdered quartz yields fluosilicic acid and uranous sulfate. Uranium trifluoride undergoes reactions similar to those of the tetrafluoride with the exception of the reaction in neutral oxalates. The trifluoride is not soluble in neutral oxalates.

(d) *Other Uranium Compounds.* Since uranium chlorides, bromides, and iodides either dissolve in water or react with water, their solution is generally simple. Uranium carbides dissolve on prolonged boiling with nitric acid but are usually oxidized by air or oxygen to U_3O_8 before solution. Uranium sulfates, acetates, and many other salts are soluble in water.

1–1.3 Complex Formation

Uranium forms compounds that may be classified as double salts. The element also forms compounds that are definitely complex. Many of these are of the inner complex or chelate type.

There is a great volume of good analytical information available on the composition of many of the uranium complex compounds. There is still, however, a lack of definite evidence for the formulas for some of the complex ions in solution. Consequently considerable caution must be observed in the interpretation of the formulas of uranium complexes for which the evidence is still indefinite.

The importance of complex ions in the analytical chemistry of uranium lies in their solubility, which makes them useful in separations, or in their color, which makes them useful in spectrophotometric determinations. Some different types of uranium complexes are cited in the following sections to indicate the general nature of the complex-forming power of the uranium atom.

(a) *Inorganic Complexes of U(VI).* Many complexes of the uranyl ion with inorganic substances are known. Among the halide complexes are found the crystalline salts of fluorides such as $(UO_2F_3)^-$, $(UO_2F_5)^{-3}$, and $(UO_2F_6)^{-4}$. The formation of complexes of this type may depend, among other things, on the ratio in which the components are mixed. Salts of the chloride anion, $(UO_2Cl_4)^{-2}$, are also known, and similar complexes with the other halides probably exist.

The sulfate ion forms complexes in which either two or three sulfate ions are attached to a single uranyl ion. Disulfates of potassium, $K_2UO_2(SO_4)_2 \cdot 2H_2O$, and also of organic bases such as ethylenediamine and guanidine are known. The trisulfate series includes compounds such as $Na_4UO_2(SO_4)_3$. The sulfate complex apparently inhibits the precipitation of UO_4 at a pH of 1.5; the amount of interference is roughly a linear function of the sulfate concentration when the ratio [19] of sulfate to uranyl is greater than 1. Sulfate ion also reduces the solubility of uranyl nitrate in ether, which may be a related effect.[20]

The carbonate complexes, formed by the action of ammonium or alkali carbonates or bicarbonates on uranyl hydroxide, alkali uranates, etc., are well known and have been used for many years in analyses of uranium-bearing material.[21] Three molecules of carbonate are associated with each molecule of UO_2, and the complex is an anion of the form $[UO_2(CO_3)_3]^{-4}$. However, when ammonium diuranate is dissolved in ammonium carbonate, a slight excess of carbonate over the theoretical three molecules is required.[22] Although the ammonium salt of the complex is soluble, the barium salt, $Ba_2UO_2(CO_3)_3$, is insoluble.[23]

Ammonium diuranate cannot be precipitated from ammoniacal carbonate solution by ammonium hydroxide; however, sodium diuranate can be precipitated completely from carbonate solution by sodium hydroxide. Ammonium diuranate dissolves in ammonium carbonate at about pH 7.4; if this solution is treated with hydrochloric acid, however, a precipitate of ammonium diuranate [22] appears at pH 5.2.

Polarographic studies indicate that the same complex of the uranyl ion is present in both carbonate and bicarbonate mediums.[24] Electrical transport data lead to the same conclusion. These same studies also indicate qualitatively that the carbonate complex is more stable than the acetate complex because the half-wave potential for the reduction of U(VI) is shifted to more negative values in carbonate or bicarbonate mediums than in the presence of acetate.

Use is made of the solubility of ammonium diuranate in ammonium carbonate in many recovery and separation reactions, particularly in the presence of iron.

Other complexes of the uranyl ion include the cyanide, $[UO_2(CN)_4]^{-2}$, which has been shown by conductance measurements to exist as such in aqueous solution. In the solid state $K_2UO_2(CN)_4$ is known.[25] Complex ammines of UO_2F_2, UO_2Cl_2, UO_2SO_4, and $UO_2(NO_3)_2$ are known in which from two to six molecules of ammonia are held per atom of uranium. Hydroxylamine prevents the precipitation of ammonium diuranate in the separation of uranium and beryllium (or thorium).[26, 27] This may be taken as an indication of the complex formation between the hydroxylamine and the uranyl ion. Hypophosphate and pyrophosphate form soluble complexes with uranyl salts,[28-30] giving compounds such as $Na_2[UO_2(HPO_3)_2]$ and $Na_2[UO_2(P_2O_7)]$. Phosphate ion, like the sulfate, prevents the quantitative extraction of uranium with ether from concentrated nitrate solutions.[31, 32]

Many of the inorganic complexes are of limited interest with regard to the analytical chemistry of the uranyl ion, but their existence should be noted and considered in work involving ionic species, for example, in spectrophotometry and in solvent extractions. In such cases equilibria between simple and complex ions may be important.

(b) *Organic Complexes of U(VI).* Literally hundreds of organic complexes of uranium salts are known, and many survey reports have been written.[33-37] Among the important uses of these compounds are spectrophotometric determinations of uranium, prevention of precipitation, and extraction from aqueous solution.

(1) *Complexes of Aliphatic Acids.* Acetate ion forms a complex with the uranyl ion in which three acetate groups are bound to one uranyl ion; the complex is anionic. The complex is not stable at low pH presumably because hydrogen ion is more firmly bound to acetate

than is uranyl ion.[38] Other aliphatic acids (formic, butyric, etc.) form similar complexes of the type $[UO_2(O_2CR)_3]^-$, where R is an aliphatic radical.

Oxalate ion also forms a uranyl complex sufficiently stable to prevent precipitation of the rare-earth oxalates. In order to precipitate lanthanum oxalate from solutions that contain a uranyl salt, it is necessary to add sufficient oxalate to complex all the uranium before the lanthanum oxalate begins to precipitate.[39]

Tartrate, citrate, and malate ions also form complexes that are stable at a high pH. The uranyl tartrate complex contains one molecule of tartrate per uranium atom, as does the malate complex. Both complexes are anionic, and examples of salts[40, 41] are $K[UO_2OH(C_4H_4O_6)]$ and $Na[UO_2OH(C_4H_4O_5)]\cdot 2H_2O$. Both citrate and tartrate ions prevent precipitation of ammonium diuranate by ammonia. The citrate complex is important in uranium-poisoning therapy.

(2) *Complexes of Aromatic Acids.* Benzoate ion, like acetate, forms a complex anion of the type $[UO_2(C_6H_5CO_2)_3]^-$, of which the ammonium salt is known in the crystalline form. The hydroxybenzoic acids, especially salicylic acid, form numerous complexes, which have been rather carefully studied. Salicylic acid forms two series of complexes, a yellow series and a red series, which contain, respectively, two and three molecules of salicylic acid per atom of uranium. The complexes exist in solution or can be precipitated as insoluble pyridine, aniline, piperidine, and other salts.[42] Aniline salts of the disalicylate series and the trisalicylate series have been made. The salicylate complexes find use in analytical procedures as spectrophotometric reagents or as agents to prevent the precipitation of uranium with the rare-earth oxalates.[43, 44]

Both *p*-hydroxy- and *m*-hydroxybenzoic acids form complexes containing three molecules of acid per atom of uranium; aniline, pyridine, and other salts are known.[41] Cresotinic acid (2-hydroxy-3-methylbenzoic acid) forms an orange-red complex used in spectrophotometric analysis.[45]

With *o*-hydroxynaphthoic acid, complexes of this type are formed:[46] $H_2[UO_2(C_{10}H_6OCO_2)_2]$, red, and $H[UO_2OH(C_{10}H_6OCO_2)]$, yellow. Protocatechuic acid (3,4-dihydroxybenzoic acid) forms complexes of which the guanidine salts have been made. Excess sodium hydroxide is reported to cause no precipitation of uranium from these complexes. Complexes with gallic acid (3,4,5-trihydroxybenzoic acid) forms complexes of which the guanidine salts have been made. Excess sodium hydroxide is reported to cause no precipitation of uranium from these complexes. Complexes with gallic acid (3,4,5-trihydroxybenzoic acid) are also alkali stable and strongly colored; they have been used for

the colorimetric estimation of the uranyl ion.[47, 48] The complex with sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) is also colored and has been used in colorimetric determinations.[49]

(3) *Other Organic Complexes.* Aromatic polyhydroxy compounds, such as catechol and pyrogallol, also form colored complexes with the uranyl ion.[50, 51] Some are orange-yellow in color, and a few are red or violet.

Uranyl salts form complexes with disubstituted dithiocarbamic acid, RR'NCSSH, which are soluble in benzene and other nonpolar solvents.[52] The diethyl derivative is extracted with benzene in the analysis of uranium in thorium.[53] The ethyl phenyl derivative acts in the same manner. Both complexes are readily formed at pH 2.8 or 3.0.

Many other extractable uranyl complexes are known. These include the chelate complexes formed with isatin-β-oxime, quinaldic acid, 8-hydroxyquinoline, 1-nitroso-2-naphthol, and antipyrine. These compounds are insoluble in water and generally insoluble in very weakly acidic or basic solution, but they dissolve readily in such solvents as chloroform, methyl isobutyl ketone, and amyl alcohol. Such complexes are essentially neutral molecules, as contrasted with the soluble ionic type complex formed by the hydroxy acids. Complexes of 1,3-diketones with uranyl salts are also known.[54, 55]

(c) *Inorganic Complexes of U(IV).* The U(IV) ion also forms many complexes, among them complexes of the halide, sulfate, sulfite, carbonate, and phosphate ion.

Of the halide complexes, $(UF_5)^-$ and $(UOF_3)^-$ are known in the form of potassium and ammonium salts, and $(UCl_6)^{-2}$ is known in the form of sodium and lithium salts. Complex sulfate ions are $[U(SO_4)_4]^{-4}$ and $[U(SO_4)_3]^{-2}$. The sulfite complexes include two well-characterized compounds, $(NH_4)_4[U(SO_3)_4]$ and $Na_6[U_2(SO_3)_7]\cdot 20H_2O$. The former resembles the oxalate as well as the sulfate complexes.[56] Phosphate complexes include salts[57, 58] of the ion $[U(PO_4)_2]^{-2}$.

(d) *Organic Complexes of U(IV).* The U(IV) ion forms complexes with many of the same organic compounds that also combine with the uranyl ions. Oxalate, for example, forms a stable, soluble complex of the type $(NH_4)_4U(C_2O_4)_4$ in neutral solutions. Acidification causes U(IV) oxalate to precipitate, and the addition of ammonium hydroxide results in precipitation of U(IV) hydroxide or the hydrated oxides. An acetate complex of the U(IV) ion may also exist since U(IV) oxalate is soluble in solutions of ammonium acetate. However, the solution of U(IV) oxalate in ammonium acetate may occur simply because ammonium acetate buffers the solution to about pH 7, at which pH, U(IV) oxalate is soluble.

Among the salts formed by the carbonate complexes are those with guanidine.[56]

The hydroxy acids, such as tartaric, malic, quinic, citric, lactic, and glycolic, form complexes with U(IV) ion.[59, 60] Some of these, such as citric acid, prevent precipitation of uranium when the solution is made basic with ammonium hydroxide. The polyhydric phenols, such as catechol, also form alkali-stable uranous compounds.[56, 61] The complex ion, of which ammonium, potassium, guanidinium, pyridinium, and other salts are known, is $[U_2(C_6H_4O_2)_7]^{-6}$ or $[U(C_6H_4O_2)OH]^-$. The first complex ion may also be regarded as a dimer of the ion $[U(C_6H_4O_2)_3]^{-2}$ after a seventh molecule of pyrocatechol is added.

Uranium(IV) salicylate is slightly soluble in water and readily soluble in organic solvents, as is U(IV) acetylacetonate. Other U(IV) complexes of the diketones are known, including those of propionylacetone, dibutyrylmethane, benzoylacetone, and furoylacetone.[54, 55] Currently these compounds have limited analytical applications. Highly colored complexes of disalicylal ethylenediamine and its derivates are known and may have value in analytical work.[62]

Uranium(IV) cupferrate, insoluble in water, is soluble in ether and other organic solvents and is an important complex in the chemistry of the U(IV) ion.

1–2 METHODS OF SEPARATION

In the past few years the methods used for the separation of uranium from mixtures have undergone considerable change. In past years the separation of uranium by a precipitation method was quite common. Of these precipitation methods the ones used now to the greatest extent are those employing ammonium hydroxide, hydrogen peroxide, phosphates, and the alkali hydroxides. To a more limited extent oxalic acid, cupferron, and 8-hydroxyquinoline are used. With most of the above reagents a clean-cut separation is not always achieved. This is especially the case with reagents such as ammonium hydroxide, the alkali hydroxides, cupferron, and 8-hydroxyquinoline, where a large number of interfering elements are also precipitated. The precipitation methods are still used to a considerable extent for the separation of uranium from certain interfering anions such as sulfate.

The increased use of solvent-extraction methods for the separation of uranium has, to a large extent, superseded the use of precipitation methods. Many of the solvent-extraction methods of separation make quantitative separations of uranium from interfering elements. In some instances a solvent-extraction method can be used to separate interfering elements from the uranium itself; an example of

this is the chloroform extraction of the cupferrates of certain elements which interfere with the volumetric determination of uranium.

Ion-exchange methods for the separation of uranium have shown considerable promise in the past few years. The separation of uranium by volatilization of either the uranium or the interfering elements is rarely used at the present time.

1–2.1 Precipitation

The addition of a precipitant for uranium to a solution that contains numerous kinds of anions and cations yields in most instances a group separation of uranium along with other elements. If the precipitations can be made in acidic solutions, such as in the precipitation of uranium peroxide or U(IV) oxalate, the separation may be a fairly selective one. Certain nonselective processes are, however, extremely useful, for example, the collection of traces of uranium by coprecipitation with a carrier such as ferric or aluminum hydroxide. If the objective is the gravimetric estimation of uranium, it is generally necessary to use a combination of methods of separation, such as removal of acid-insoluble and hydrogen sulfide groups, extractions, mercury-cathode electrolysis, etc., prior to the precipitation of the uranium.

Trivalent uranium, as is well known, is readily oxidized in solution to U(IV) either by the oxygen of the air or by hydrogen ion. If a salt of U(V) is dissolved in water, a rapid disproportionation to a mixture of U(IV) and U(VI) takes place. It is necessary to maintain reducing conditions by excluding air or by adding a suitable reducing agent when U(IV) is being precipitated as the cupferrate, the oxalate, etc. If an oxidizing attack has been used, the uranium will occur in the U(VI) state.

The formation of a soluble carbonate complex has long been used for the separation of iron, aluminum, etc.,[21] from uranium. At ordinary dilutions 1.15 g of ammonium carbonate prevents precipitation of 1 g of U(VI). When the ammonium hydroxide precipitate is large, repeated precipitations are necessary. The combined filtrates are then acidified, boiled to remove the carbon dioxide, and treated with ammonium hydroxide to precipitate the uranium. Certain rare earths, particularly members of the yttrium group, are somewhat soluble in ammonium carbonate solution.

(a) *Ammonium Hydroxide: Precipitation From Uranyl Solutions.* Ammonium hydroxide precipitates uranium completely from uranyl solutions provided complexing ions such as carbonate, citrate, tartrate, and fluoride are absent.[63, 64] In the presence of phosphate ion, uranyl ammonium phosphate precipitates; however, an excess of phosphate prevents the complete precipitation of uranium.[65]

The ammonium hydroxide precipitation process serves only to separate uranium from many anions and from the alkali metals, the alkaline earths, and the cations that form ammonia complexes, e.g., Cu(II), Ni(II), Zn(II), and others. The latter separations require repeated precipitations and are effective only when the ratio of uranium to the other ions is favorable. Under certain conditions the precipitates will carry more or less completely the anions of phosphorus, vanadium, silicon, and boron. The precipitation with ammonium hydroxide is used quite frequently in the separation of the sulfate ion prior to a solvent extraction of the uranium as the nitrate.

A great number of elements are precipitated in whole or in part by ammonium hydroxide under the same conditions as uranium; these are listed by Lundell and Hoffman.[66] It is therefore obvious that the ammonium hydroxide precipitation method for the determination of uranium can be applied only to solutions that are free from interfering elements.

Ammonium hydroxide precipitation can be used advantageously to collect microgram to milligram amounts of uranium by coprecipitation with ferric or aluminum hydroxide. This method of separation is usually followed by other methods, such as solvent extraction.

Procedure. Since carbonate impurities dissolved in ammonium hydroxide prevent complete precipitation of uranium, the reagent should be fresh. It may be prepared from a tank of liquefied ammonia. If the ammonium diuranate is to be ignited to U_3O_8 for quantitative determination, the ammonium hydroxide should be filtered before use because after it has stood in glass it always contains suspended siliceous material.

To the uranyl solution that is low in fluorides and free of carbonates, tartrates, and other strongly complexing substances, a few drops of methyl red solution are added. Strongly acidic solutions are nearly neutralized with ammonium hydroxide with stirring. Chloride or sulfate solutions that contain U(IV) can be oxidized with a little nitric acid. To the weakly acidic solution is added 5 to 10 g of ammonium nitrate or chloride per 100 ml of solution. Addition of macerated filter paper is advisable. The solution is boiled, and ammonium hydroxide (1+4) is added slowly, with stirring, until the solution smells of ammonia. The solution is filtered, and the precipitate is washed with a hot solution containing 2 g of ammonium nitrate or chloride per 100 ml of water, made basic with ammonium hydroxide.

(b) *Peroxide.* Although the separation as peroxide is rarely used for the quantitative recovery of uranium, it serves a very useful purpose in two ways. It separates the uranium from many impurities, and it is also useful in concentrating impurities from a uranium solution before determining these impurities by spectrophotometric, spectrographic, or other means.

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The usual peroxide precipitation is made at pH 0.5 to 3.5. In general, the higher the pH, the more impurities are precipitated. In certain instances, a gelatinous, poorly filterable product is obtained. Iron affects the precipitation because it catalyzes the decomposition of hydrogen peroxide.[67] The interference of iron is largely eliminated by the addition of maleic acid and by maintaining the pH of the solution [68, 69] between 1 and 3. Lactic acid can also be used.

A Canadian report [70] gives conditions for achieving a good filterable product and purity.

> *Procedure.*[70] The uranium compound is dissolved in hydrochloric acid so as to obtain a solution containing 10 g of uranium per 100 ml of acid. The pH is adjusted to 1.5, and the solution is cooled to 25°C. To this solution 120 per cent of the theoretical amount of 30 per cent hydrogen peroxide is added, with constant stirring, and the precipitate is allowed to settle. The precipitate is filtered or centrifuged and washed with 0.01*N* hydrochloric acid and then with water.

The precipitation of peroxide at the Union Carbide Nuclear Corporation is made from a nitrate solution at a somewhat lower pH.

> *Procedure.* One hundred grams of the U_3O_8 is weighed into a 4000-ml beaker. The oxide is dissolved in a minimum amount of 2*N* nitric acid. When all the oxide has dissolved, the solution is filtered through a Whatman No. 42 filter paper into a clean always-safe 5-in. container. (An always-safe container is one in which a nuclear excursion cannot take place regardless of the U^{235} concentration.) The volume of the solution should not exceed 2000 ml.
>
> With freshly prepared ammonium hydroxide (made by bubbling ammonia gas through distilled water), the pH of the solution is adjusted to a reading of 1.0 on a pH meter. (Ammonium hydroxide prepared in the above manner contains a minimum amount of silica.) The electrodes are removed from the solution when a pH of 1.0 has been reached.
>
> The amount (in milliliters) of 30 per cent reagent hydrogen peroxide which must be added to precipitate the uranium is obtained by multiplying grams of uranium by 1.3. The calculated amount of reagent peroxide to be used for the precipitation is diluted with four times its volume of nitric acid solution at a pH of 1.0. Then the acidity is readjusted to a pH of 1. (The purpose of this dilution is to avoid a localized precipitation of the $UO_4 \cdot 2H_2O$.)
>
> While the uranium solution is being mixed with a motor-driven glass stirring rod, the diluted hydrogen peroxide is added slowly to it. After 30 min the pH of the solution is again readjusted to 1.0 with ammonium hydroxide prepared by bubbling ammonia gas through distilled water. [This has to be done because the formation of $UO_4 \cdot 2H_2O$ from $UO_2(NO_3)_2$ and H_2O_2 results in an increase in acidity.] The $UO_4 \cdot 2H_2O$ is allowed to settle at least 16 hr. The solution is kept covered during this time.
>
> The supernatant solution is decanted. The precipitate is washed with two 1000-ml washes of hydrogen peroxide diluted with 99 times its volume of nitric acid solution at a pH of 1.0. The precipitate is allowed to settle between washes, and the supernatant solution is decanted. Then the precipitate is vacuum filtered through a 9-in. Buchner funnel

and a No. 42 Whatman paper. When all the uranium is on the filter paper, it is washed three times by covering the filter cake with a solution of hydrogen peroxide diluted with 99 times its volume of nitric acid solution (pH of 1.0). Suction should not be continued after the cake becomes dry because this practice might introduce air-borne impurities unless the funnel is covered with a filter paper held tightly with rubber bands. The filter paper is dried in the funnel until the precipitate can be separated from the paper easily.

The elements that form insoluble peroxides, such as scandium, thorium, and zirconium, will not be removed. Ethylenediaminetetraacetic acid (EDTA), however, has been used [71] to complex scandium so that it does not precipitate with peroxide, whereas the uranium compound does precipitate. A single experiment at the New Brunswick Laboratory indicates that thorium and zirconium behave in like manner. The following procedure [71] was designed for the analysis of samples containing from 1 to 10 mg of scandium and 1 g of uranium. Less than 1 mg of uranium is left in solution. If concentrations are changed, it becomes necessary to change the peroxide and EDTA concentrations also, i.e., to use a 100 per cent excess of both reagents.

Procedure. The 1-g sample of uranium is dissolved in 2 ml of nitric acid and warmed to remove oxides of nitrogen. To the cooled solution, 200 mg of EDTA as the disodium or diammonium salt is added in a minimum amount of water so that the sample solution can be diluted to 35 ml. The solution is stirred at a moderate rate with a magnetic stirrer (Teflon-covered bar), and the pH is adjusted to 2.5 by the dropwise addition of ammonium hydroxide and finally by the addition of 5*N* ammonium hydroxide. Any momentary precipitation is disregarded. The peroxide is precipitated by the dropwise addition of 0.5 ml of 30 per cent hydrogen peroxide, and the solution is maintained at pH 2.5 by the addition of 5*N* ammonium hydroxide. (About 3 to 4 drops of 5*N* ammonium hydroxide is added after every drop of hydrogen peroxide.) After the dropwise addition of the 0.5 ml of hydrogen peroxide, an additional 0.5 ml is added in excess, and the final pH is adjusted to 2.5 with 5*N* ammonium hydroxide. After settling has taken place, the supernatant liquid from the peroxide precipitation is filtered through a fritted-disk funnel of medium porosity. The peroxide is washed and transferred with a wash solution containing 2 ml of 30 per cent hydrogen peroxide in 100 ml of water, acified to a pH of 2.5 with nitric acid. The filtrate and washing from the above are used for the scandium determination.

(c) *Phosphate.* Solutions containing uranyl ions, when treated with phosphoric acid, readily precipitate uranyl monohydrogen phosphate, UO_2HPO_4, and, when treated with diammonium phosphate, they precipitate ammonium uranyl phosphate, $NH_4UO_2PO_4$. The control of pH is somewhat critical since in solutions of low pH incomplete precipitation occurs and since both salts are soluble in excess phosphoric or other strong acids. The optimum pH for the precipitation

is 1.7; the pH should be at least in the range 1.2 to 3.3. The precipitate formed in the absence of ammonium salts is fine and may pass through the filter paper. By slowing the rate of precipitation of the ammonium uranyl phosphate, Swinehart [81] obtained a precipitate that was readily filtered. Ammonium hydroxide was added until precipitation of the uranyl ammonium phosphate started. The solution was then set aside 5 to 10 min before the neutralization was completed.

In recent years an increasing number of articles have dealt with the separation of uranium as ammonium uranyl phosphate. The most important advance has been the precipitation of uranyl ammonium phosphate in the presence of EDTA. It appears that Tillu [72] first published this method, although G. A. Rampy had done work along these lines which was reported by Vita, Trivisonno, and Voss.[73] Carter and Weber [65] made a rather complete study of the method and applied it to a variety of materials. Milner and Edwards [74] applied this method of separation to uranium–bismuth alloys, whereas the Mallinckrodt Chemical Works uses it in routine analysis of uranium-ore concentrates.[75, 81]

Unlike the precipitation of uranyl phosphate, the precipitation of uranyl ammonium phosphate in the presence of Versenol (*n*-hydroxyethylenediaminetetraacetic acid) is not very dependent on pH. Carter and Weber [65] showed that over the pH range of 4.3 to 9.3 the precipitation with Versenol is essentially complete; whereas with Versene the pH control is more critical, and a pH of 9.5 appears to be more satisfactory. Other workers, however, work at a lower pH [73, 74] with satisfactory results. A more rapid precipitation was obtained at pH 9. The presence of large amounts of phosphate causes incomplete precipitation. Concentrations of diammonium phosphate greater than 5 g per 350 ml of solution appear to result in incomplete precipitation. The concentration of complexing agent was also found to be important, although less so with Versenol than with Versene. With 100 mg of uranium in solution, amounts of complexing agent greater than 25 ml of 50 per cent complexing agent in 350 ml of solution resulted in loss of uranium. From the work of Carter and Weber,[65] it would appear that Versenol is preferable to Versene for use as a complexing agent. No complete separation is made from solutions containing tin(II), tin(IV), molybdenum, or tungsten.[74] Beryllium and titanium accompany the uranium.[76] Large amounts of fluoride or carbonate interfere, and silica, if present in large amounts, coprecipitates.[65] The precipitate is rather difficult to filter. Paper pulp can be used to aid filtration, or the precipitate can be separated by centrifuging.

The following procedure is used for the assay of uranium-ore concentrates.

Procedure.[75] A sample solution containing not more than 0.4 g of uranium is placed in a beaker, and a saturated potassium permanganate solution is added to it to produce a permanent pink color. Then about 10 ml of macerated filter pulp is added. Twenty milliliters of a solution of the tetrasodium salt of EDTA (made by dissolving 34 g of sodium–EDTA in water and diluting to 100 ml) is added. Then 35 ml of phosphate reagent is added. (The phosphate reagent is made by mixing the following in a 5-pint bottle: 920 ml of hydrochloric acid; 600 ml of a solution containing 23 g of ammonium acetate per 100 ml of solution; and 600 ml of a solution containing 15 g of diammonium hydrogen phosphate per 100 ml of solution.) The solution is then heated on a hot plate until the beaker is hot to the touch. After the beaker has been removed from the hot plate, 3 to 4 drops of 0.1 per cent bromphenol blue is added. Concentrated ammonium hydroxide is added dropwise until a purple or blue color appears. After the solution has been heated to boiling on a hot plate, it is filtered through S and S No. 589 White Ribbon paper with macerated filter pulp. The precipitate is transferred to the filter. The filter is washed three times with 2 per cent ammonium acetate solution, and the filtrate is discarded.

The separation of tetravalent uranium with phosphates has been employed for the isolation of small amounts of uranium prior to a fluorimetric[77] or titrimetric[78] determination. Zirconium[77, 78] or thorium[79] is used as a carrier. Strandell[80] indicated that the precipitation of U(IV) orthophosphate from acid solution depended on the concentration of aluminum salts in solution. Presumably double complexes are formed between uranium, aluminum, and phosphate ions. It was shown by Alimarin et al.[79] that U(IV) ion can be precipitated completely with sodium hexametaphosphate from a 3*N* solution of perchloric acid. Thorium is used as a coprecipitating agent for small amounts of uranium. The following procedure[78] has been suggested for the separation of U(IV) ions from niobium and tantalum. Oxalic acid or a high concentration of tartaric acid prevents complete reduction of uranyl ion.

Procedure.[78] The solution containing at least 0.5 g of tartaric acid in 100 ml is reduced with amalgamated zinc. One milliliter of a solution of zirconium nitrate, made by dissolving 2 g of zirconium nitrate in water and diluting to 100 ml, is added as a collector. The uranium, together with the zirconium, is precipitated by the addition of a 10 per cent solution of $(NH_4)_2HPO_4$ (containing 10 g of diammonium hydrogen phosphate per 100 ml of solution). After 1 hr in the cold, the precipitate is collected and washed with a solution prepared by mixing 50 ml of *N* sodium acetate, 70 ml of *N* hydrochloric acid, and 130 ml of water.

Hypophosphate and pyrophosphate form soluble complexes with uranyl salts[28-30] and form insoluble salts with U(IV) solutions.[57, 58] In general, these two ions precipitate quadrivalent metals from acid solution; examples are titanium, zirconium, thorium, and

uranium(IV) salts. Free hypophosphoric acid, $H_4P_2O_6$, or its disodium salt, and sodium pyrophosphate, $Na_4P_2O_7$, can be used.

(d) *Alkalis.* Precipitation of uranyl solutions with sodium hydroxide yields a precipitate of uncertain composition. Increasing proportions of sodium or potassium diuranate, which are insoluble even in the presence of carbonates, are formed under more strongly alkaline conditions. The substances precipitated by strong alkalis are not easily filtered.[82]

Although strong alkalis have been used to recover uranium from such materials as uranyl phosphate,[83] the presence of a large excess of phosphate prevents complete precipitation. The sodium hydroxide has to be at least $9N$, and the precipitate must be separated by centrifuging.

(e) *Oxalic Acid.* Oxalic acid precipitates quadrivalent uranium as the dioxalate. Certain anions and organic compounds such as fluorides and lactic acid interfere by complexing the uranium ion. Sulfates and large amounts of phosphates should be absent. In a solution previously reduced either electrolytically in a mercury-cathode cell or by zinc amalgam, no cations in moderate amounts interfere except thorium and the rare earths.

Precipitation should take place in a hydrochloric acid solution. Acidities up to $3N$ hydrochloric acid are permissible.[84–86] If the concentration of hydrochloric acid is lower than $2N$, other oxalates may precipitate: zinc, iron(II), copper, etc. The solubility varies from 5 mg per liter in $0.12N$ hydrochloric acid to 500 mg per liter in $6N$ hydrochloric acid. If the precipitate is filtered immediately, from 0.5 to 1 per cent of the uranium passes into the filtrate.

Traces of iron, nickel, and manganese are carried down but no chromium, copper, or phosphate. There is a poor separation from niobium and the rare earths and none at all from thorium. The $U(C_2O_4)_2$ can be redissolved in nitric acid and hydrogen peroxide, in sulfuric acid, or in sodium hypochlorite at pH 9 to 10.

Procedure.[87] The reduced solution (reduced electrolytically or with 3 per cent liquid zinc amalgam until the red color of trivalent uranium is formed) is filtered into 2 to 6 g of oxalic acid through acid-resistant filter paper, such as Whatman No. 52. If 1 g of uranium is present, if the volume exceeds 250 ml, or if the iron and chromium content is expected to exceed 2 g, then at least 4 g of oxalic acid is used. The reductor and the paper are washed with $3N$ hydrochloric acid, and 4 ml of stannous chloride solution, 120 g of $SnCl_2 \cdot 2H_2O$ per 100 ml of $6N$ hydrochloric acid, is added through the filter paper. The solution is stirred for at least an hour at room temperature. The precipitate is filtered on Whatman No. 42 paper and washed 10 times with 10-ml portions of 1 per cent oxalic acid in $3N$ hydrochloric acid.

(f) *Cupferron.* Ions of the following metals are precipitated by cupferron from strong-acid solutions: iron, gallium, zirconium, niobium, tin, antimony, hafnium, titanium, vanadium, tantalum, and uranium(IV). Among others, the following elements are not precipitated: aluminum, chromium, beryllium, phosphorus, manganese, nickel, zinc, uranium(VI), boron (borate or fluoborate), the alkaline earths, and the alkali metals. The cupferron separation has been used chiefly as a means of separating interfering elements from uranyl solutions before volumetric analysis. Precipitation of the U(IV) cupferrate has been used by several laboratories.[88, 89]

Nitric acid should be absent in cupferron separations, and, if precipitates are to be ignited, perchloric acid should also be absent. Sulfuric acid solutions are suitable. Hydrochloric and organic acids can also be used. The two valence states of uranium make possible the double cupferron procedure in which iron, titanium, and others are precipitated from uranyl solutions; after reduction uranium is precipitated from the remaining elements. It has been found necessary to have a reducing agent present to ensure complete precipitation. Both hydroxylamine[90] and sodium hyposulfite[91] have been used for this purpose. After the second step the U(IV) cupferrate, $U(C_6H_5N_2O_2)_4$, can be either filtered or extracted with an organic solvent. The precipitate is flocculent and fairly easily washed.

Procedure.[90] The acidity of the solution is adjusted to 5 per cent sulfuric acid by volume. Five grams of hydroxylamine hydrochloride is added, and the solution is cooled for 10 min in an ice bath. A 6 per cent cupferron solution is added slowly with stirring until precipitation is complete. Vigorous stirring is continued for 2 min, an additional 5 ml of cupferron solution is added, and the mixture is stirred vigorously for a second 2 min. The precipitate is allowed to stand in the ice bath for another 5 min and then is filtered with suction and thoroughly washed with a freshly prepared cupferron wash solution. (Two solutions are prepared; they are kept cool in an ice bath and mixed prior to use. The first is 100 ml of a 7.5 percent by volume sulfuric acid solution; the second is a 50-ml solution containing 0.8 g of cupferron and 3 g of hydroxylamine hydrochloride.) The precipitate is dried at 70°C and slowly ignited until the organic matter has burned off; after this it is heated to 900 to 1000°C.

(g) *Tannic Acid.* Uranyl salts in buffered acetate solution react with tannic acid (digallic acid) to yield a deep-brown voluminous precipitate. The precipitation is quantitative. Carbonates and tartrates cause no interference.[92] This method ranks with the ammonium diuranate method in usefulness. Tannin, the glucose ester of tannic acid, also precipitates uranium from hot solutions. Oxalates prevent the precipitation of uranium by tannic acid in slightly acid solution.[93]

The following elements are precipitated by tannic acid, or tannin, and are listed in the order of decreasing ease of precipitation: tantalum, titanium, niobium, vanadium, iron, zirconium, hafnium, thorium, uranium, and aluminum.[93] It is impracticable to separate adjacent members of this series with tannic acid, at least without the aid of complexing agents such as oxalates or carbonates. Tannic acid separations of uranium from vanadium are also unsatisfactory.[94] The alkali metals are not carried down.

Milner and coworkers used tannin for separating uranium from the aqueous solution after a cupferron extraction in the analysis of uranium–zirconium alloys[95] and uranium–titanium alloys.[96] The precipitate is ignited to U_3O_8. Colin[97] has used it in alkaline solutions to separate uranium from titanium under certain circumstances.

Procedure.[92] To the uranyl solution, usually containing less than 200 mg of uranium, ammonium hydroxide is added until most of the mineral acid has been neutralized. Any excess ammonium hydroxide is neutralized with acetic acid. Smaller quantities of strong acids can be converted to acetic acid by addition of ammonium acetate. After weakly acidic conditions are obtained, 2 ml of 2 per cent tannic acid is added for each 12 mg of uranium. The mixture is heated to boiling, and an ammoniacal 10 per cent ammonium acetate solution is added until the precipitate settles and the upper part of the liquid is clear. The very voluminous chocolate-brown precipitate is filtered and washed with slightly ammoniacal 2 per cent ammonium nitrate solution. Washing by decantation prior to filtration is desirable when separation from large quantities of other elements, e.g., alkali metals, is being made.

(h) *8-Hydroxyquinoline (Oxine).* Under basic or weakly acidic conditions, oxine precipitates hexavalent uranium quantitatively as a reddish-orange compound. The uranyl 8-hydroxyquinolate forms an addition compound with an extra mole of reagent, precipitating[98, 99] as $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. The pH range for complete precipitation has been given as 4.1 (Ref.[100]) to 13.5 (Ref.[101]). The compound is easily filtered or extracted and can be titrated with bromine. Uranium(IV) is also precipitated by oxine.

Uranium can be separated from phosphates with oxine, if the phosphates are not present in large amounts, by performing the precipitation at a high pH (10 to 12) and by using an excess of the reagent.[101] Small amounts of fluorides, oxalates, lactates, and hydroxylamine do not interfere. Uranyl 8-hydroxyquinolate is precipitated from tartrate-complexed solutions[102,103] but is dissolved by ammonium carbonate. Advantage is taken of the latter factor in separating aluminum from uranium.[104] It is necessary to keep in mind, of course, that under the conditions where oxine precipitates uranium, many

other elements, including copper, aluminum, zinc, and thorium, are precipitated.

Procedure (Weakly Acidic Conditions).[96, 99] The acetate–acetic acid buffered solution (pH 5 to 6) of uranyl chloride, sulfate, or nitrate (but not perchlorate if the compound is to be ignited), which is free from interfering ions and contains less than 100 mg of uranium per 100 ml of solution, is treated with an oxine solution (2.5 g of oxine in 5 ml of glacial acetic acid diluted to 100 ml) with stirring until an excess of the reagent is known to be present. At least 2.5 ml should be used per milligram of uranium. The mixture is heated to 60°C, digested for 15 to 20 min, and filtered. The precipitate is washed with 2 per cent ammonium nitrate solution made slightly ammoniacal.

Procedure (Basic Conditions).[101] The uranium concentration and reagent solution described above are satisfactory. The uranyl solution is made nearly neutral with ammonium hydroxide, and the precipitate that forms is just redissolved with dilute sulfuric acid. To the cold solution, 10 g of ammonium chloride, nitrate, or sulfate is added. The oxine solution is then added. Silica-free 6*N* ammonium hydroxide is added until the solution is just basic. Then 20 ml of silica-free ammonium hydroxide is added, and the mixture is digested at 60 to 65°C for half an hour. If the supernatant solution appears turbid after standing for 15 min, more ammonium salt is added. The mixture is filtered hot, and the precipitate is washed as in the above procedure.

(i) *Quinaldic Acid.* A number of metals, including uranium, are precipitated by quinaldic acid (quinaldinic acid, 2-quinolinecarboxylic acid, C_9H_6NCOOH).[105] Precipitations with this reagent are generally comparable to those with 8-hydroxyquinoline. The reaction is carried out in the presence of ammonium chloride.

Procedure.[105] The uranyl solution is prepared for precipitation in the same way as for 8-hydroxyquinoline. The pH should be between 6 and 7, and 5 to 7 g of ammonium chloride should be present per 150 ml of solution. To the boiling solution, an excess of the reagent, 3.5 per cent sodium quinaldate in water, is added. After it has cooled, the mixture is filtered on a sintered-glass crucible. The precipitate is washed with 5 per cent hexamine and 5 per cent ammonium nitrate until free of chloride.

(j) *Benzenearsonic Acid.* Benzenearsonic acid [phenylarsonic acid, $C_6H_5AsO(OH)_2$] is more or less specific in that it forms precipitates with ions of quadrivalent metals from solutions of various acidities. Uranium(IV) benzenearsonate precipitates as a fine very light-green compound, whereas uranyl salts are not affected. Various derivatives of benzenearsonic acid may also be useful. These include the *m*-nitro-*p*-hydroxy, *p*-*n*-butyl, and *p*-dimethylaminobenzeneazo derivatives.[106]

Uranium (IV) is quantitatively precipited by benzenearsonic acid in a weakly acidic solution. Thorium, zirconium,[107] hafnium, tin (IV), niobium, and tantalum are also quantitatively precipitated.[108]

Zirconium benzenearsonate also precipitates quantitatively from strongly acidic solutions. Titanium and cerium(IV) are partially precipitated.

Procedure. The acidity of the U(IV) solution, free of thorium, zirconium, the earth acids, and other interfering ions, is adjusted with ammonium hydroxide and sulfuric acid until the pH is 1 to 3. The solution is heated nearly to boiling, and a 2.5 per cent solution of benzenearsonic acid or its sodium salt is added in excess. The precipitate is filtered off and washed with 0.01*N* to 0.1*N* hydrochloric acid.

1–2.2 Carrier Precipitations

Gathering agents have been used in analytical chemistry for many years to collect a small amount of a precipitate distributed through a considerable volume of liquid.[106]

For example, hydrous manganese dioxide has been used to gather ferric hydroxide,[109] and microgram quantities of copper have been collected by the addition of a few milligrams of lead and precipitation of both as sulfide.[110]

In general, an ion is more completely carried the greater the insolubility of the compound on which the ion is being carried, the greater the insolubility of the compound formed between the ion itself and the precipitating agent, and the greater the similarity in size and chemical behavior of the carrying and carried ions. The more nearly two ions are alike, the more apt they are to form isomorphous compounds, and, in turn, the more likely they are to coprecipitate.

Carriers were used to isolate traces of uranium prior to its determination. The carriers for uranium that have been used to the greatest extent for analytical purposes are ferric hydroxide,[111-115] aluminum hydroxide,[112, 113, 116, 117] calcium hydroxide,[118-121] magnesium oxide,[122] and thorium peroxide.[123] Other carriers that have been used for the separation of uranium are barium carbonate [124] and calcium fluoride.[125]

(a) *Ferric Hydroxide.* Ferric hydroxide has been used as a carrying agent for uranium in the analysis of effluents.[115, 125] In general, 2 to 10 mg of iron (0.005 wt. %) was added as ferric chloride, followed by an ammonium hydroxide precipitation. The iron residue obtained could then be examined by spectrographic, fluorescence, or colorimetric methods. In one investigation [125] it was found that the concentration of uranium left behind after precipitation did not exceed 1 or 2 parts per 100 million parts of solution, which roughly represented the limit of experimental error. The presence of substantial amounts of carbon dioxide, up to 0.01 wt. %, did not alter the results measurably.

Nakanishi,[126] using hydrous ferric oxide as coprecipitator, separated uranium from an aqueous solution prior to a fluorometric determination.

(b) *Aluminum Hydroxide.* In a few instances aluminum hydroxide [112, 116, 117] has been used as a carrier for trace amounts of uranium, chiefly where the presence of iron was not desirable. The reactions are comparable to those obtained with iron. When 5 mg of aluminum was used as carrier [117] and ammonium hydroxide was used as precipitant, it was found that the uranium content of the filtrate was 0.5 to 2.0 μg per 100 ml of solution. Without the aluminum as carrier, the filtrate contained approximately 50 μg of uranium per 100 ml of solution.

(c) *Calcium Hydroxide.* Calcium hydroxide, or lime, has been used both as a precipitant and a gathering agent for the isolation of traces of uranium from solution.[118, 119, 121, 127] It has proved very useful in the presence of carbonate ion [116, 127] with less than 3μg of uranium per liter left in solution. Calcium has been used as a collecting agent in alkaline solution to separate traces of uranium from vanadium. The following procedure has been used for the analysis of sodium vanadate.

> *Procedure.*[118] To a 10-g sample in a 600-ml beaker, enough water is added to make a slurry. To this slurry, 30 ml of 50 per cent sodium hydroxide, 300 ml of water, and a few glass beads are added. The mixture is then covered with a watch glass and boiled vigorously until the volume is about 150 ml. The sample is again diluted with 300 ml of water, heated to boiling, and removed from the hot plate. Ten milliliters of calcium nitrate solution [1.2 g of $Ca(NO_3)_2 \cdot 4H_2O$ per 100 ml] is added. The solution is allowed to stand until the precipitate settles and is then filtered through a Whatman No. 42 filter paper.

(d) *Methyl Violet and Thiocyanate.* Methyl violet and ammonium thiocyanate when added to acidified sea water can be used for the isolation of uranium.[128] Quantitative coprecipitation of uranium in dilutions of 1 in 10^{10} was reported.

(e) *Zirconium Phosphate.* Small quantities of uranium in the tetravalent state are separated from accompanying elements by precipitation as $U(HPO_4)_2 \cdot nH_2O$ on a zirconium carrier.[77] This separation has been used in the analysis of rocks. The uranium is determined fluorometrically.

1–2.3 Ion Exchange

The separation of uranium by means of ion-exchange chromotography has had limited application in analysis although it is used quite widely in plant practice. A literature survey on the use of ion exchange in uranium analysis was made in 1957 by Trivisonno.[129]

The discovery that uranium could be quantitatively absorbed as a complex sulfate on an anion-exchange resin was a significant step

in the separation of uranium. It was found that uranium in a sulfate complex could be separated as an anion from nearly all other metallic ions by absorbing it on a strong-base anion-exchange resin such as Amberlite IRA–400, Permutit SK, or Dowex–1. A survey of this work is given by Kaufman and Lower.[130]

In addition to hexavalent uranium, Fe(III) is also absorbed on the anion-exchange resin as the sulfate complex. If the iron is reduced, by sulfur dioxide or hydrogen sulfide, to the ferrous state, it is not absorbed. Pentavalent vanadium is absorbed as the vanadate ion and interferes with the elution of the uranium. If the vanadium is reduced with sulfur dioxide to the tetravalent state, it is no longer absorbed. Other elements reported to absorb from a sulfate solution are thorium, antimony, manganese as permanganate, chromium as chromate, arsenate, and molybdenum. Permanganate, chromate, and arsenate when reduced are not absorbed. Molybdenum will actually displace uranium from the anion resin, but, when reduced with sulfurous acid, it does not interfere.

Phosphate is absorbed, whereas fluoride decreases the loading capacity of the resin. Uranium is not absorbed from a nitrate solution, whereas from a strong chloride solution uranium is absorbed as the anionic chloride complex.

Uranium can be absorbed as the carbonate complex on quaternary amine type resins. The absorption is decreased in the presence of bicarbonate. No special advantage is gained in analytical work with the carbonate complex system.

Nitric,[131, 132] perchloric,[133, 134] and hydrochloric [135, 136] acids have been used as eluting agents to remove the uranium sulfate in analytical applications.

The techniques used in general analytical applications of ion-exchange chromatography have been given in detail by Samuelson.[137] Of the analytical applications for the separation of uranium, the absorption as the sulfate complex followed by elution with perchloric acid has been employed by Fisher and Kunin [134] and Seim and coworkers.[133, 138] Milner and Nunn [135] used a 5*M* hydrochloric acid solution on De-acidite FF (a Permutit product similar to Amberlite IRA–400 and Dowex–1) to separate uranium and thorium in an alloy containing bismuth, the thorium going into the eluate and the bismuth and uranium being retained on the column. The uranium is eluted from the resin with 0.2*M* hydrochloric acid. Banerjee and Heyn [139] used a quaternary amine type anion-exchange resin to separate trace amounts of uranium from bismuth. The sulfate complex of uranium is retained at pH 1 to 1.5, whereas the cationic bismuth passes through the column. The uranium is then eluted with dilute perchloric acid (1+10). For the analysis of uranium in sea water [136] an Amberlite

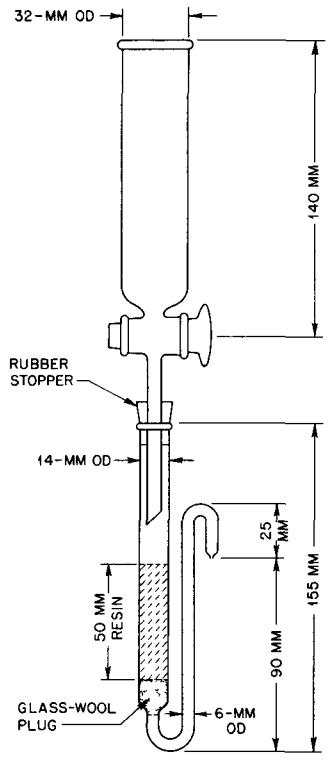


Fig. 1.1—Ion-exchange apparatus. (From Seim, Morris, and Frew, *Analytical Chemistry*, Ref. 133.)

IRA–400 resin is used for the sea water direct at a pH range of 3 to 9. After being washed with a buffer at pH 5 and water, the uranium is eluted with 0.8*N* hydrochloric acid. For the separation of uranium from the rare earths, a solution [132] 0.01*N* in sulfuric acid was absorbed on Dowex–1 resin. The uranium was eluted with normal nitric acid.

The following procedure is indicative of those employed for ores.[133]

Columns. A special column (Fig. 1.1) was made to facilitate the handling of a larger number of samples. This design was advantageous in keeping the liquid level above the resin bed, in providing for easier control of drop rate, and in facilitating the loading and washing of the columns.

Resin. The resin is a quaternary–ammonium anion–exchange type and is a modification of Amberlite IRA–400, consisting of 40- to 60-mesh beads and purchased under the name Amberlite XE–117, type 1 or 2. Before use, the resin is converted, batchwise, to the sulfate form by treating it for 20 min with three times its volume of 10 per cent sulfuric acid. The treated resin is then washed several times by decantation with distilled water. A final 50-ml wash is given the resin in the column. No difficulties have been encountered in storing the sulfate form of

the resin under distilled water for several weeks. Because the resin is inexpensive, it may be discarded after use.

Procedure. An appropriate weight of sample containing 0.5 to 40 mg of uranium oxide is treated on a hot plate for about 10 min with 15 to 30 ml of 12*M* hydrochloric acid. Then 5 to 10 ml of 16*M* nitric acid is added, and heating is continued until acid-soluble minerals have been dissolved. The samples are then fumed strongly with 5 to 10 ml of 9*M* sulfuric acid. The larger volume of acid in each case represents the amount used for 5-g samples. After the samples have been fumed, the residues are taken up in 50 ml of water and boiled gently for 5 to 10 min. The solutions are then filtered and washed with hot water. For samples containing appreciable phosphate, the washing is done with hot 0.1*N* sulfuric acid instead of hot water. The solutions are then adjusted to a pH of 1.0 to 1.5 with 6*M* sodium hydroxide. An estimation of the amount of iron present can be made in this step, and an appropriate amount of 6 per cent sulfurous acid (10 to 30 ml) can be added to effect complete reduction of the iron. After the solutions have been allowed to stand for about 10 min, they are passed through the ion-exchange columns at a rate of about 1 drop/sec to absorb the uranium. The beakers and dropping funnels are then rinsed three times with hot water, after which the resin is washed with 50 ml of hot water.

The uranium is then eluted with 50 ml of 1*M* perchloric acid that has been heated to boiling. The elution rate is again maintained at 1 drop/sec. Under these conditions the temperature of the resin bed varies from 60 to 70°C. After being eluted, the resin is allowed to stand 10 min in contact with the last of the eluent. The columns are then blown out with air to remove all possible eluent.

1–2.4 Solvent Extraction

Of the various separation techniques for uranium which have appeared in the past decade, the one that has been used almost universally is liquid–liquid extraction.

The present view of the extraction of metals into an organic solvent indicates that an uncharged species is required.[140] Complexing of metal ions leading to the formation of uncharged species falls into two main categories, one involving coordination and the other, ion association. Since most extractable species involving coordination are chelates, it is common to term these as belonging to the chelate extraction system. The other system is that of an ion association, in which the extractable species are formed by the association of ions.

Usually, the chelate systems lack specificity and generally require multiple steps in extraction and scrubbing, addition of washing agents, and control of pH and valence states. This results, in most cases, in an increase in analysis time. The double cupferron system and the 8-quinolinol system are examples of this. The cupferron system gives only 99 per cent recovery and is time consuming, whereas the 8-quinolinol system lacks specificity.

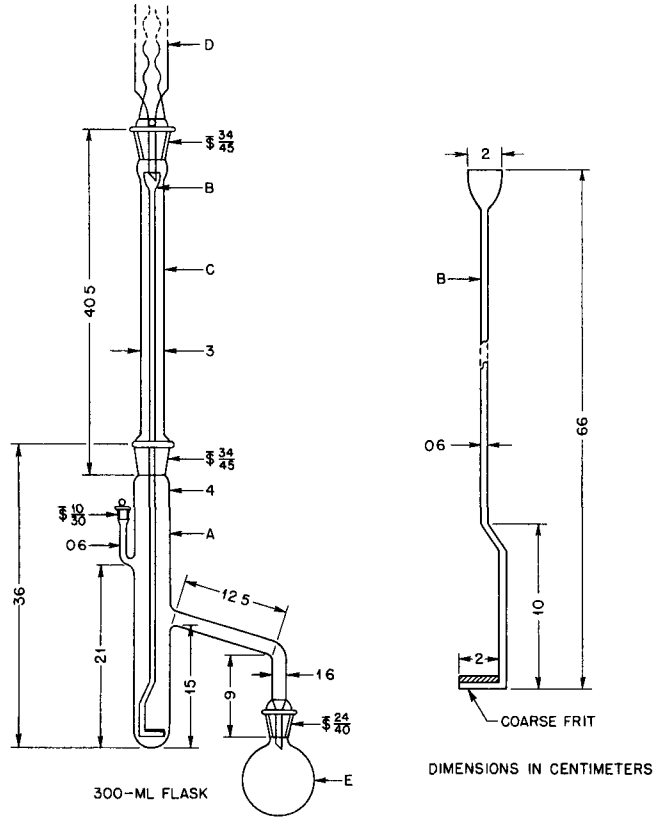


Fig. 1.2—Continuous extractor.[146] A, side-arm extraction apparatus. B, frit with thistle tube. C, condenser column surrounding B. D, condenser. E, receiving flask.

Extraction of uranium utilizing the ion-association systems tends to be more specific than extractions utilizing the chelate systems. The extraction of nitrate complexes is probably the most specific system. Examples are the ethyl acetate-nitrate salting system, the ether-nitrate salting system, the tributyl phosphate system, the phosphine oxide systems, and the methyl isobutyl ketone system.

For general information on solvent extraction, the book by Morrison and Freiser[140] contains a comprehensive coverage. The apparatus and general techniques used are discussed in detail. In general, for batch extraction the usual separatory funnels have been adequate, and for continuous extraction an apparatus similar to that shown in Fig. 1.2 has generally proved satisfactory.

The toxicity and flammability of many solvents should be considered in all solvent-extraction work.

The following sub-sections have been divided into ion-association extraction systems and chelate extraction systems.

(a) *Diethyl Ether.* Diethyl ether was used for the separation of uranyl nitrate by solvent extraction to a great extent in the early phases of the work on nuclear energy problems both in plant processes and in analytical chemistry. Although this solvent is not used to the extent that it formerly was, it is still employed in some separations in analytical chemistry. (Diethyl ether is a liquid having a boiling point of 34.6°C with a flash point of −45°C. The solubility in water is 7.5 g per 100 ml at 20°C, whereas the solubility of water in diethyl ether is 1.3 percent. The specific gravity is 0.715 g/cm^3, and the viscosity is 0.23 centipoise at 20°C. The material is not corrosive. The low boiling and flash point make it a hazardous material to work with, especially in hot climates and in mountainous regions. Precautions have to be taken, and laboratory facilities have to be constructed with the fire and explosion hazards in mind at all times. It is also essential that water be present when ether solutions containing nitrates are being evaporated. Otherwise explosive mixtures may be obtained.) Hecht and Grunwald [141] were the first to use diethyl ether in analytical separations. The early work of Furman and coworkers [142, 143] described the effects of various salting agents and analytical applications. Scott [144] made a rather thorough study of the effects of salting agents, acid concentration, and interfering anions as applied to analysis.

Uranyl nitrate is soluble in diethyl ether, but, for complete recovery of it from interfering elements, it is necessary to use salting agents. Calcium and ammonium nitrate have been used extensively for this purpose, with ammonium nitrate being preferred in cases where ignition to U_3O_8 is the final step in the analysis. Zinc, copper, ferric, lithium, and aluminum nitrates are very effective as salting agents.

Table 1.2—METAL NITRATES AS SALTING AGENTS WITH DIETHYL ETHER

Formula	NO_3^- normality from salting agent	U distribution coefficient (organic/aqueous)	U extracted, %
NH_4NO_3	10. 07	1. 31	56. 7
$NaNO_3$	7. 72	2. 85	74
$LiNO_3$	10. 5	85. 02	98. 8
$Ca(NO_3)_2$	10. 57	165. 4	99. 4
$Zn(NO_3)_2$	10. 68	259	99. 6
$Cu(NO_3)_2$	9. 31	162	99. 4
$Mg(NO_3)_2$	3. 03	0. 448	30. 9
$Th(NO_3)_4$	5. 54	1. 71	63. 2
$Al(NO_3)_3$	4. 85	3. 95	79. 8
$Fe(NO_3)_3$	7. 37	74. 7	98. 7

The efficiency of various salting agents is given in Table 1.2. The nitric acid content is also important. With increasing nitric acid content, up to about $5N$, the percentage of uranium extracted increases.[144] Acidities higher than $6N$ nitric acid may lead to reaction between the ether and the nitric acid. The elements which extract in varying amounts and which may cause trouble are cerium(IV), vanadium, iron, if present in large amounts, thorium, zirconium, and molybdenum, if present as silico or phosphomolybdic acid. Nitric acid is also extracted, and additional nitric acid should be added either to the extraction funnel or to the continuous extractor, depending on which method is used.

Certain anions cause trouble in the separation either by extracting other elements, such as ferric ion when chloride is present, or by decreasing the uranium distribution, such as happens when fluoride, sulfate, and phosphate ions are present in certain amounts. The effect of interfering anions is shown in Fig. 1.3, taken from Scott.[144] Solutions containing varying quantities of the common anion, introduced as the sodium salts, were made $3N$ with nitric acid and $1M$ with respect to ferric nitrate, and the percentage of uranium extracted was determined. Provided foreign anions do not reduce the percentage of uranium extracted below 79 per cent in a single extraction, no modification of the routine procedure using three extractions is required to achieve 99 per cent recovery of uranium. Al-

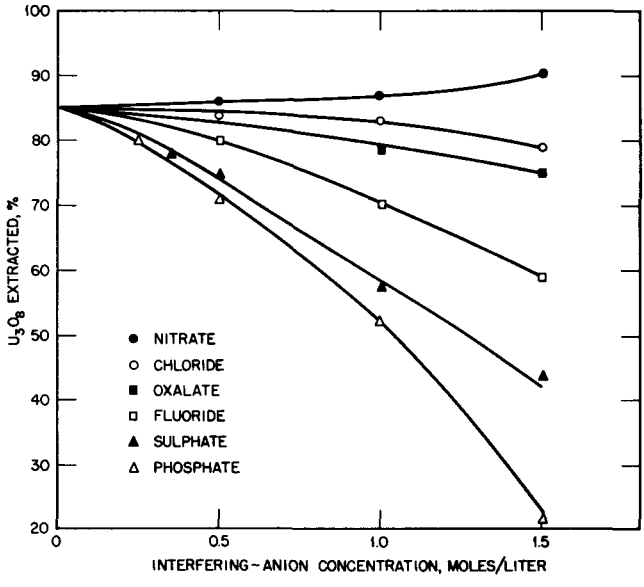


Fig. 1.3—Effect of various anions on percentage of uranium extracted. (From Scott, *The Analyst*, Ref. 144.)

690-457 O—64——4

though calcium nitrate can be used to offset the effect of sulfate, it is the usual practice to precipitate the uranium with CO_2-free ammonium hydroxide and redissolve the precipitate in nitric acid. In the presence of phosphate ion, the separation as the hydroxide is not always complete. The phosphate can also be removed by precipitation with zirconium nitrate in a nitric acid medium.[143] The zirconium phosphate precipitate is inclined to be gelatinous, and some uranium may be occluded. Aluminum nitrate or ferric nitrate can be used to overcome the influence of phosphate. A saturated ferric nitrate solution as the salting agent has proven satisfactory for this purpose.[148]

Both continuous extraction and batch extraction have been employed. The following are representative procedures.

Procedure for Continuous Extraction (Macro).[145] A continuous extractor (Fig. 1.2) is used. A nitric acid solution of the sample, which has been saturated with ammonium nitrate, is transferred to A of the extractor. Some solid ammonium nitrate should be present. Ether is added to the solution in A to the level of the side arm, and ethyl ether is poured into the thistle tube portion of the frit (B).

The thistle tube (B) is then placed into position with the frit end at the bottom. The receiving flash (E) is filled one-fifth full with water and enough ether is added to form a layer 1-in thick. The receiving flask (E) is then attached to the extractor, and the glass stopper is placed in the small side arm on A. Column C and condenser D are then attached to A. At this point, cold water is started through the condenser. A hot-water bath is placed around receiving flask E, and the flask is heated on a steam bath. After the ether has refluxed for about 15 min, column C is raised, and the water solution in A is stirred by raising and lowering B. This is repeated every 15 min. After 45 min (or before, if any precipitation occurs) 5 ml of concentrated nitric acid saturated with ammonium nitrate is added through the small side arm in A. After 90 min the flask is removed from the water bath, and flask E is allowed to cool. The contents of the flask are then transferred to a 250-ml beaker, the flask is rinsed with most of the ether layer from A, and the washings are added to a 250-ml beaker. The flask is washed once with water, and the washings are added to the beaker. The beaker is then placed on the steam bath, and the solution is evaporated to dryness.

Procedure for Continuous Extraction (Micro).[146] A sample containing 0.05 to 0.2 g of uranium is transferred to the lower compartment of a clean microextractor (shown in Fig. 1.4). The extractor is rinsed with 1*M* nitric acid immediately before the analysis is started. If a mircopipet is used, the pipet is also washed thoroughly 1*M* nitric acid, and the washings are added to the extractor. The extraction apparatus shown is designed for a total volume of the aqueous phase between 4 and 8 ml. To the extractor (lower compartment), 1 ml of saturated aluminum nitrate solution and a suitable volume of 6*M* nitric acid are added. The acidity of the aqueous phase should be 2*M* to 4.0*M* nitric acid, and sufficient liquid should be present to cover the sinter. The lower com-

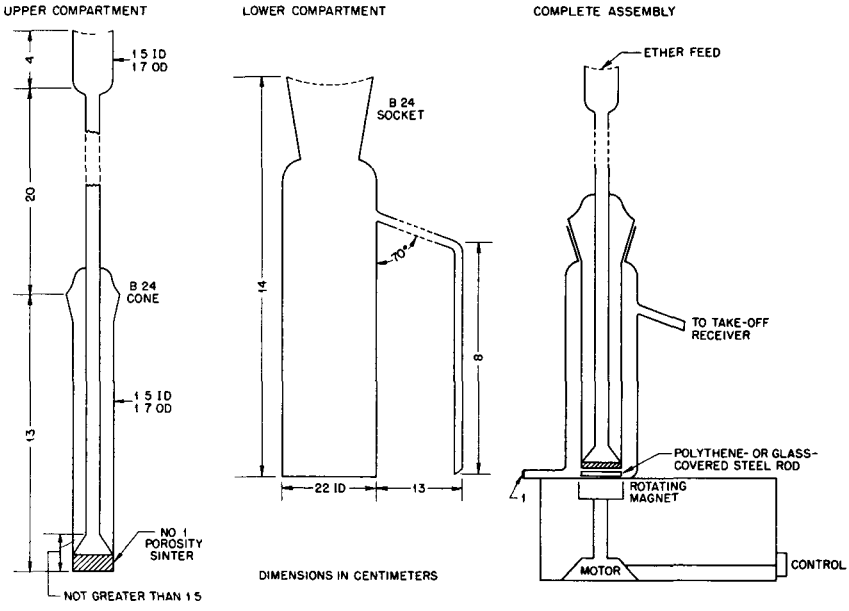


Fig. 1.4—Ether-extraction microapparatus. (From Ref. 146.)

partment of the extractor is placed into position on the magnetic stirring unit, and stirring is started. About 0.2 g of solid ammonium nitrate is added to the solution, allowing complete dissolution to take place after each addition, until a saturated solution is obtained. The upper portion of the extraction apparatus, which has previously been rinsed with 1*M* nitric acid and acetone and allowed to dry, is inserted. A 250-ml conical flask containing 10 ml of water is placed in position below the outer tube of the extraction apparatus. Nitric acid–conditioned ether (2 volumes of ether is mixed with 1 volume of nitric acid, and, after settling, the organic phase is separated) is added through the feed tube at the rate of 3 to 4 ml/min, and the ether phase is collected in the conical flask until a volume of about 100 ml has been obtained. The ether flow rate and the stirrer should be under constant control during this operation. A fine cloud of dispersed ether droplets should circulate continuously throughout the aqueous layer. When the apparatus is assembled, the volume of the aqueous phase should be such that there is a difference of at least 1.5 cm in level between the aqueous ether interphase and the delivery tube. The extraction usually takes 25 to 35 min. The ether layer remaining in the extractor is tested with potassium ferrocyanide test paper to ensure that it is free of uranium. A brown coloration is given by uranium, and the extraction must be continued until this test gives a negative result. The conical flask is then transferred to a boiling-water bath, and the ether phase is evaporated completely. Steady boiling is promoted by the presence of a small spiral of platinum wire. The solution in the flask is transferred to a clean 400-ml beaker, the flask is washed with water, and the washings are added to the beaker. The solution is then made up to 100 ml with water.

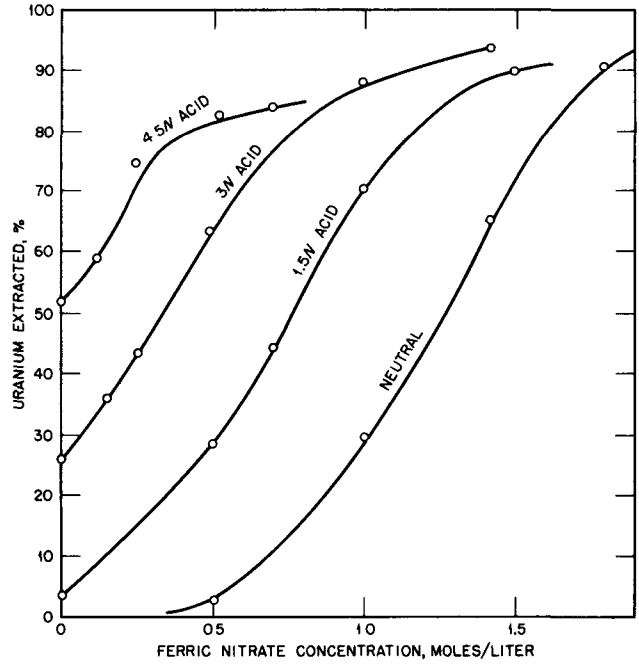


Fig. 1.5—Variation in percentage of uranium extracted with change in nitric acid and ferric nitrate concentrations. (From Scott, *The Analyst*, Ref. 144.)

Procedure for Batch Extraction.[144] A suitable aliquot of the uranium solution is added to a separatory funnel, after ensuring that the solution is 3*N* with respect to nitric acid and 1*M* with respect to ferric nitrate. It is convenient for solutions to contain 1 to 20 mg of U_3O_8 when uranium is to be estimated finally by the peroxide colorimetric method. The final volume of solution is then brought to 50 ml for the lower, and 200 and 250 ml for the higher, concentrations.

The recommended concentrations of ferric nitrate and nitric acid need not be rigidly adhered to, but for other concentrations it is necessary to compute from Fig. 1.5 the number of ether extractions and the amount of acid required in the course of the analysis. With the recommended concentrations, however, it has been established that three extractions give 99 per cent recovery. No account is taken of other nitrates present in solution, but they help to increase the percentage of uranium extracted and to ensure that the routine procedure gives even better than 99 per cent recovery.

A volume of ether equal to, or slightly greater than, the initial aqueous layer is added to the funnel, and the funnel is shaken, with periodic releases of ether vapor, for 1 min. Settling is allowed for 1 min, and the aqueous layer is drained into a small beaker.

Before the second and third extractions, the beaker that has contained the aqueous extract is rinsed with the ether to be used for the next extraction. It is advisable to use a volume of ether slightly greater than that of the initial aqueous layer so that, after shaking, the volume of the ethereal layer will not be less than the volume of

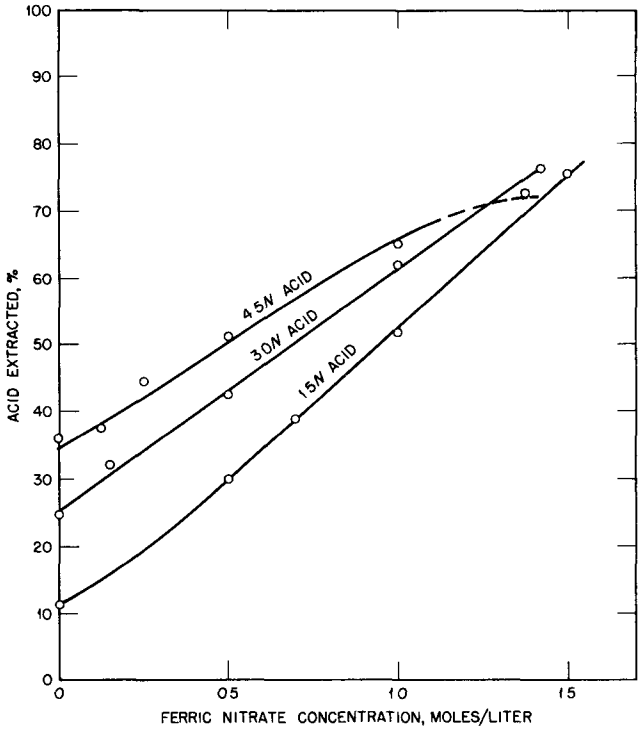


Fig. 1.6—Variation in percentage of nitric acid extracted. (From Scott, *The Analyst*, Ref. 144.)

the aqueous layer despite losses due to evaporation and solution of ether in water. This ensures that efficiency of extraction is not less than that provided by use of Fig. 1.5.

The ether layer is swirled around the inside of the funnel and then allowed to stand for 1 min; then the small amount of aqueous layer that has collected is drained off. The ether layer is transferred to a beaker containing 30 to 50 ml of water.

The aqueous layer is returned to the funnel, the beaker is rinsed out with the calculated quantity of nitric acid, and this too is added to the funnel. A second and a third extraction are made following the same procedure.

With the recommended concentrations of salt and acid, 1.2 ml of nitric acid (sp. gr. 1.41) for every 10 ml of uranium solution should be added, before the second and subsequent extractions, to restore the normality of the aqueous layer to 3*N*. For other concentrations the quantity of acid can be estimated from Fig. 1.6.

The beaker containing the accumulated ether layers and water is left to stand in the draught of a fume cupboard until all the ether is evaporated.

This method is rapid and convenient and eliminates the need for heating the ether layer. It is advantageous if the draught can be augmented by lowering the sash of the fume cupboard.

The residual aqueous solution is neutralized with sodium hydroxide (a small piece of litmus paper is used as the indicator). Sufficient nitric acid is added to make the solution just acid. Sodium carbonate is then added to give a final solution containing between 1 and 5 per cent of Na_2CO_3.

A few pieces of porous pot are added to the alkaline solution, and the solution is heated on the hot plate to remove dissolved ether. Finally, the solution is boiled for 15 min and allowed to cool to room temperature.

Boiling has the effect of increasing the rate of coagulation of small quantities of ferric hydroxide, etc., which may be present. These impurities are not generally extracted by the ether but are introduced by admixture of small amounts of the aqueous layer, an effect very difficult to avoid. The quantities of precipitate are so small, however, that solutions can be made up to the desired volume before filtering without causing significant errors. It is often useful to add 1 ml of 30 per cent hydrogen peroxide before boiling to ensure the precipitation of impurities such as manganese, but boiling must then be continued for 45 min to decompose completely the peruranate formed.

If the acid–ether extract is evaporated over sodium carbonate solution instead of water, bicarbonate may form and lead to large errors in the colorimetric estimation with peroxide in alkaline solution when the absorbancy is measured at 360 to 370 mμ.[144] Moreover, once sodium bicarbonate is formed under these conditions, it cannot be completely decomposed, even with prolonged boiling. Neutralization with sodium hydroxide and the addition of sodium carbonate ensure that this source of error is eliminated. An alternative procedure is to measure the intensity of the yellow color in the range 440 to 450 mμ, where the absorption is not affected by the presence of bicarbonate; the sensivity, however, is much reduced at this wave length.

Other procedures employing ether extraction are given by Jensen and Bane,[147] Lindh, Rynninger, and Skaraeus,[148] Kienberger, Greene, and Pepper,[149] Helger and Rynninger,[150] Reid,[151] Ribley, St. John, Hunt, DeVries, and Mellon,[152] Stevenson,[153] Käärik,[154] and Nagy and Almâsey.[155]

Another application of solvent extraction of the nitrate using diethyl ether is considered under cellulose-column chromatography in Sec. 1–2.5(a), where a solution of the nitrates is absorbed on a cellulose column and the uranyl nitrate is then eluded with diethyl ether.

(b) *Ethyl Acetate.* The use of ethyl acetate as a solvent for the extraction of uranium nitrate appears to have been first used by Grimaldi and Levine.[156, 157] Since ethyl acetate has a flash point of $-2°C$ compared to $-45°C$ for diethyl ether, the fire hazard is lessened. The method has been used primarily for batch-extraction procedures after the solution has been saturated with aluminum nitrate. The aluminum effectively complexes phosphate, sulfate, and fluoride, which normally interfere with the quantitative extraction of uranium. The use of ethyl acetate in a continuous extraction is not recommended because of the possibility of hydrolysis of the ethyl acetate.

Vanadium, cerium(IV) and zirconium are partially extracted. Thorium nitrate will extract to a large degree. The method has been applied to traces of uranium in ores,[156, 159-161] in uranium concentrates,[162] in ferrous metals,[163] and in low-grade uranium-acid solutions.[164]

The procedure of Grimaldi and Levine is characteristic of those usually employed. In most instances the uranium is determined fluorometrically.

Procedure.[157] The sample (0.15 g) is completely decomposed by fusion with a sodium hydroxide–sodium nitrate mixture. This flux will decompose shales and phosphate rocks. After fusion the melt is leached with water and acidified with nitric acid, and 7.5 ml of nitric acid is added in excess (present practice is to employ 3.5 ml of excess nitric acid). Silica does not separate out if the acid is added to the cool solution. Any hydrolytic precipitate that may form is not filtered off. The solution is then made up to 50 ml, and a 5-ml aliquot is transferred to a test tube. To this are added 9.5 g of aluminum nitrate (enough to saturate 5 ml of solution) and 10 ml of ethyl acetate, and the mixture is shaken for 30 sec. After the layers have separated, about 8 ml of the ethyl acetate layer is drawn off and filtered through a dry filter paper.

(c) *Methyl Isobutyl Ketone* (*Hexone*). The use of methyl isobutyl ketone for the extraction of uranium from nitrate solutions was used as far back as 1945 by Kraus.[165] The use of this reagent in plant separations has been quite extensive,[166] but only recently has this reagent been used for analysis.

A comprehensive evaluation of the properties of hexone in relation to its use for uranyl nitrate extraction has been made by Bradley.[167] Paley [168] used methyl isobutyl ketone in a nitrate solution with ammonium nitrate as a salting agent to separate uranium prior to a colorimetric determination with thiocyanate. Nietzel and DeSesa [169] modified this procedure for the same use. Booman and coworkers [170, 171] also made a rather complete study on the use of methyl isobutyl ketone for its use in analytical chemistry. This work was concerned with the separation of uranium from fission products. From their studies it appears that the use of aluminum nitrate as a salting agent is preferred. The acidity of the aluminum nitrate salting solution affects the distribution of fission products in a liquid–liquid extraction system. At constant aluminum nitrate concentration, fission-product extraction is increased 50-fold between 0.1*N* acid deficiency and 0.1*N* free acid. An acid-deficient nitrate solution is defined as one that contains less nitrate ion than a solution of the stoichiometric salt, i.e., it contains hydrolyzed species. Zirconium and niobium hydrolyze in an acid-deficient solution to give a difficult-to-extract species. Ruthenium and rhodium are also re-

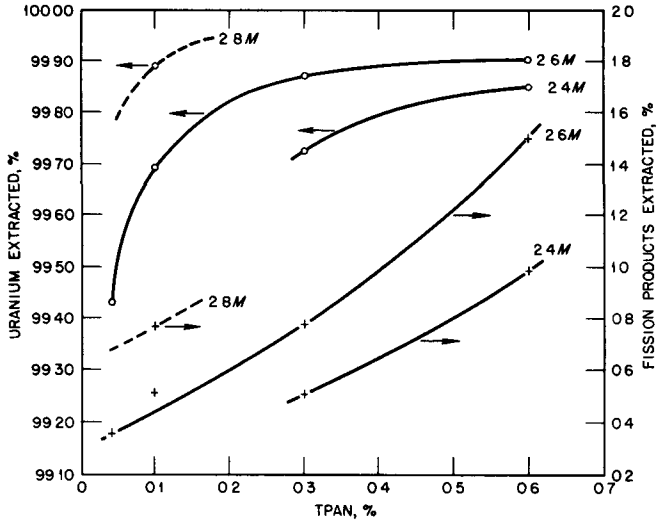


Fig. 1.7—Effects of tetrapropylammonium nitrate and aluminum nitrate concentrations on extraction of uranium and fission products. (From Maeck, *Analytical Chemistry*, Ref. 171.)

ported to have lower extractability from an acid-deprived solution. A value of 1*N* acid-deficient aluminum nitrate was chosen as the level for the system because in the range of aluminum nitrate concentration from 2.4*M* to 2.8*M* it provided the degree of buffering required for

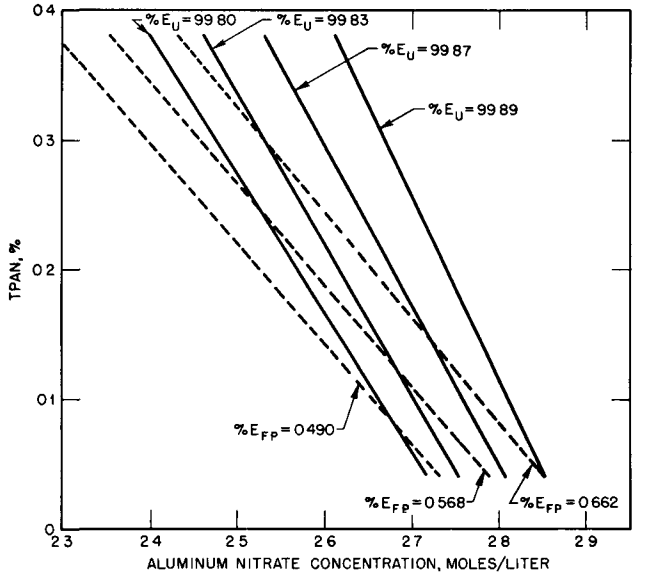


Fig. 1.8—Plot for selecting optimum extraction conditions. (From Maeck, *Analytical Chemistry*, Ref. 171.)

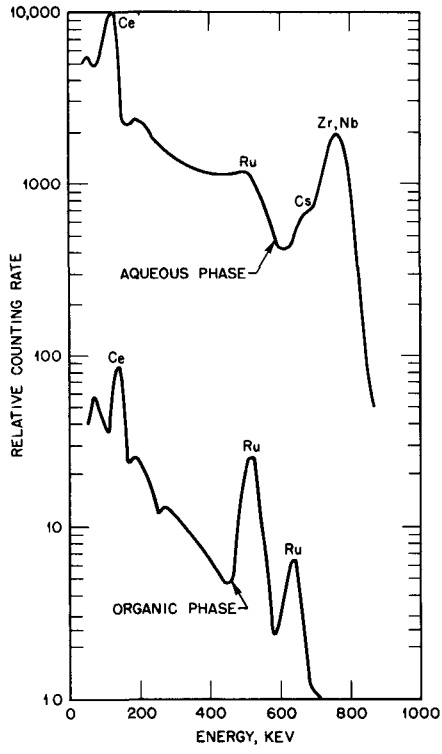


Fig. 1.9—Gamma-energy spectra of extraction phases for 1-year-cooled fission-product mixture. (From Maeck, *Analytical Chemistry*, Ref. 171.)

the range of acidity expected in samples and it did not cause emulsification of the two phases as did more highly acid-deficient solutions.[171]

The effect of salting-agent concentrations on the extraction of U(VI) is well known. Increasing amounts of aluminum nitrate increase the extraction of uranium; however, increasing amounts also tend to increase the extraction of the fission products. The addition of the quaternary amine salt, tetrapropylammonium nitrate (TPAN), increased the uranium extraction. The separate effects of TPAN and aluminum nitrate concentration on the extraction of uranium and fission products are shown in Fig. 1.7, and the optimum TPAN–aluminum nitrate extraction conditions are shown in Fig. 1.8.

Indications are that as much as 100 mg of uranium can be extracted in 2 ml of hexone by increasing the TPAN concentrations to 5 per cent wt/vol).

Studies were made [171] to determine the distribution of fission products from a typical Materials Test Reactor (MTR) type dissolver

solution and of 49 individual cations. The upper curve of Fig. 1.9 is the gamma-energy spectrum before extraction of a fission-product mixture cooled for one year. The lower curve is the gamma-energy spectrum of the organic phase after extraction. Of the active gamma-emitting isotopes, only fission-product cerium and ruthenium extract.

Only a few elements, such as mercury, technetium, ruthenium, plutonium, neptunium, and thorium, extract to any extent. Chlorides tend to increase the extraction of ions that form anionic chloride complexes. This is especially notable in the case of Au(III), Cr(III), and Fe(III). Only tungstate, and to a lesser extent ferrocyanide, seriously hindered the extraction of uranium. Ferrocyanide forms an insoluble complex with uranium. Tungstate evidently forms a complex with uranium, preventing its complete extraction. Phosphate, fluoride, and sulfate, although they do interfere with many liquid–liquid extraction systems for uranium, did not interfere at the levels tested (anion to uranium ratio, 10/1). Although thiocyanate and dichromate enhanced the extraction of uranium, they also increased the extraction of fission products.

The following procedure has been used for the separation of uranium from highly radioactive solutions prior to its determination by a controlled-potential coulometer. With this procedure recoveries of 99.87 per cent of the uranium present have been reported.

Procedure. The aluminum nitrate salting solution is prepared by placing 1050 g of reagent-grade aluminum nitrate nonahydrate in a 2-liter beaker and adding enough water to make a volume of approximately 900 ml. The mixture is placed on a hot plate, and, after dissolution has been completed, 67.5 ml of concentrated ammonium hydroxide is added, and the solution is stirred until the hydroxide precipitate dissolves. This will require several minutes. With the temperature of the solution less than 50°C, 10 ml of 10 per cent TPAN solution is added, and the solution is stirred until dissolution is complete. The solution is transferred to a 1-liter volumetric flask and made to volume with water. If this solution is to be used to determine microgram quantities of uranium, a preliminary extraction with hexone is suggested to remove uranium contamination. Following the extraction TPAN will again have to be added to the salting solution before it is used.

Aqueous samples containing up to 2 mg of uranium and as much as 8*M* in nitric acid can be quantitatively extracted with a salting solution containing 0.1 per cent TPAN. Samples of higher acidity should be neutralized to less than 8*M* acid before extraction. The extraction of larger amounts of uranium is feasible provided the salting solution contains proportionately larger amounts of TPAN.

A 0.500-ml sample is pipetted directly into a test tube containing 4.0 ml of aluminum nitrate salting solution. Two milliliters of hexone is added, the tube is stoppered, and the uranium is extracted for 3 min. The solution is centrifuged to facilitate phase separation. An aliquot of the organic phase can be removed, and the uranium can be determined by any

suitable procedure. If U(III) or U(IV) is suspected, boiling the sample with sufficient nitric acid before sampling will oxidize the uranium to the VI valence state.

Hardwick and Moreton-Smith [172] used hexone to separate U^{233} from irradiated thorium. Ammonium nitrate was used as a salting agent. The thorium that is extracted with the uranium is separated by washing after the addition of sodium diethyldithiocarbamate. Some alpha activity, which is extracted with the hexone, is also removed with the thorium when it is washed with an aqueous phase at pH 2.8 containing sodium diethyldithiocarbamate.

Procedure.[172] When 1 to 100 μg of U^{233} per liter is to be separated, a suitable aliquot (0.1 ml is suitable for 100 μg of U^{233} per liter) is placed in a 40-ml centrifuge tube. This is made up to approximately 1.5 ml with *N* nitric acid, and the solution is saturated with ammonium nitrate by adding the solid reagent. To this solution is added 3 ml of hexone, and the solution is stirred for 5 min. The mixture is centrifuged, and the hexone layer is transferred to a clean 40-ml centrifuge tube. The extraction is repeated with two further 3-ml portions of hexone, and the three hexone layers are combined. To the combined layers are added 5 ml of 2*M* ammonium nitrate solution and 1 drop of a mixed (screened) methyl orange indicator solution (1 g of methyl orange and 1.4 g of xylene cyanol FF in 500 ml of 50 per cent alcohol), and the mixture is stirred. The solution is made alkaline by the addition of ammonium hydroxide and 0.5 ml of sodium diethyldithiocarbamate solution (freshly prepared and filtered 20 per cent aqueous solution). At this stage ammonium nitrate is added until the aqueous layer is mauve (not red), and the solution is stirred for 4 to 5 min. If necessary, more acid is added during this time to maintain the mauve color. The mixture is centrifuged, and the hexone layer is transferred to a 50-ml beaker. The surface of the aqueous layer is washed with 0.5 ml of hexone, and the washings are added to the hexone in the beaker. The U^{233} is generally determined by a counting technique.

(d) *Tri-n-butyl Phosphate.* The use of tri-*n*-butyl phosphate (TBP) as a separating agent in the solvent extraction of uranium has developed to a considerable extent in the past 10 years. Among the various solvent-extraction methods that are current, the ones employing this reagent are quite numerous. An excellent review by Wright [173] gives much pertinent information on the use of TBP for the separation of uranium.

(TBP is a liquid having a boiling point of 177 to 178°C at 27 mm Hg. Its flash point is 294°F, its viscosity is 3.41 centipoises, its solubility in water is 0.4 g/liter at 25°C, and the solubility of water in TBP at 25°C is about 7 per cent. The specific gravity at 20°C is 0.973, and the color of the pure compound is water-white. The material is not very corrosive and can be stored in most common laboratory containers.)

The separation of uranium from other materials with TBP is based on the fact that inert diluents decrease the distribution coefficients in general; thus, if the proper TBP to diluent ratio is selected, the uranium distribution coefficient although decreased will still be significantly higher than the coefficients of the metals that extract similarly to uranium. In this way the absolute amounts of impurities extracted will be decreased.

The uranium complex $UO_2(NO_3)(TBP)_2$ with TBP appears to be stronger than those of thorium, plutonium, cerium(IV), and zirconium, which extract in a manner similar to uranium.

Since extractions are usually made from nitric acid solutions, the stability of TBP in the presence of nitric acid is important. Acid concentrations up to 16*M* at room temperature were found to have no effect. The hydrolysis rate of TBP is important since some of the hydrolysis products, notably dibutyl and monobutyl phosphates, markedly decrease the efficiency of the re-extraction of the uranium from the solvent because of the rather stable complexes of these hydrolysis products with uranium. (In one instance [174] dibutyl phosphate, because of its high distribution coefficient, was used for the determination of uranium in sea water. The uranium is not stripped but is obtained by ignition of the solvent.) The rate of hydrolysis at room temperature is very slow. Prolonged heating at 105°C in 3*M* nitric acid resulted in 0.23 per cent hydrolysis. Pretreatment of the TBP with 1*M* sodium hydroxide effectively removes hydrolysis products.

The type of solvent used to dilute the TBP affects the distribution of uranium. Table 1.3 shows this effect. A 0.2*M* uranyl nitrate solution in 3*M* nitric acid was extracted with a 20 per cent solution of TBP in the various solvents listed. In general, kerosene type solvents, such as Varsol, carbon tetrachloride, hexane, and hexone (methyl isobutyl ketone) are employed in chemical analysis.

Table 1.3—EFFECT OF DILUENTS ON URANIUM EXTRACTION [173]

Solvent	Uranium extraction coefficient (organic/aqueous)
Kerosene	9. 32
Isooctane	8. 45
Methylcyclohexane	10. 4
Benzene	13. 2
Chloroform	3. 22
Carbon tetrachloride	20. 1
Trichloroethylene	6. 8

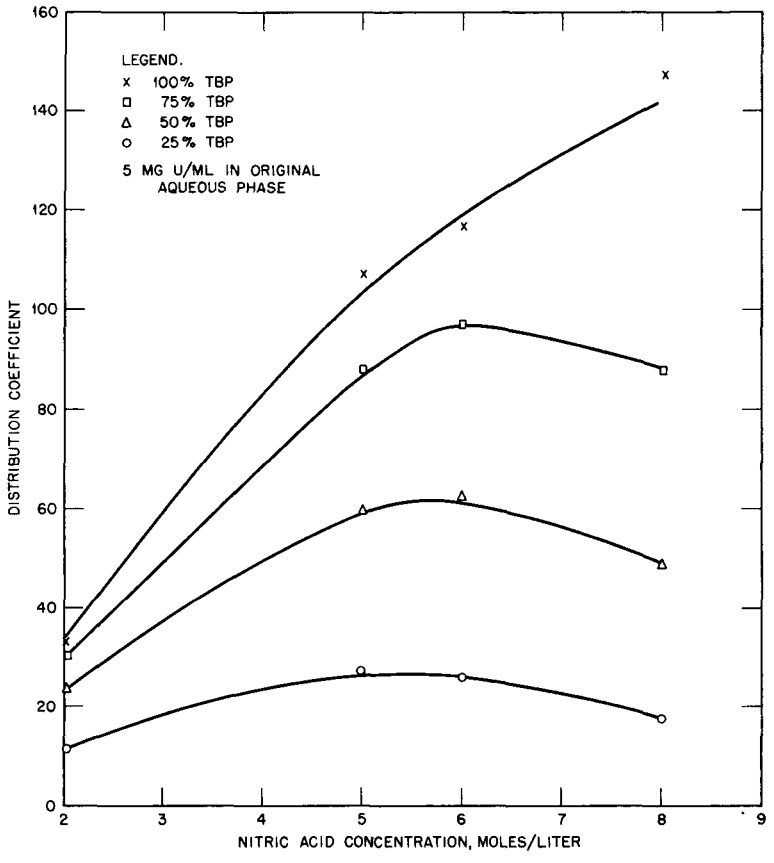


Fig. 1.10—Effect of nitric acid and of TBP concentration on the distribution coefficient of TBP.[175]

Consideration has to be given to the toxicity and density of the solvents used, as well as to the uranium distribution.

Various factors influence the extraction of uranium. The extraction efficiency varies inversely with the temperature. However, the distribution coefficient of uranium changes by a factor of only 2 when the temperature is varied from 10 to 50°C. Equilibration time has no effect. The uranium distribution coefficient, when no salting agent is present, increases with the concentration of nitric acid up to about $5M$, as shown in Fig. 1.10, but it is also a function of the total nitrate concentration.

Salting agents have a marked effect on the uranium distribution coefficient. Various salting agents, such as aluminum nitrate, ammonium nitrate, calcium nitrate, ferric nitrate, and sodium nitrate, have been used with the results shown in Table 1.4.

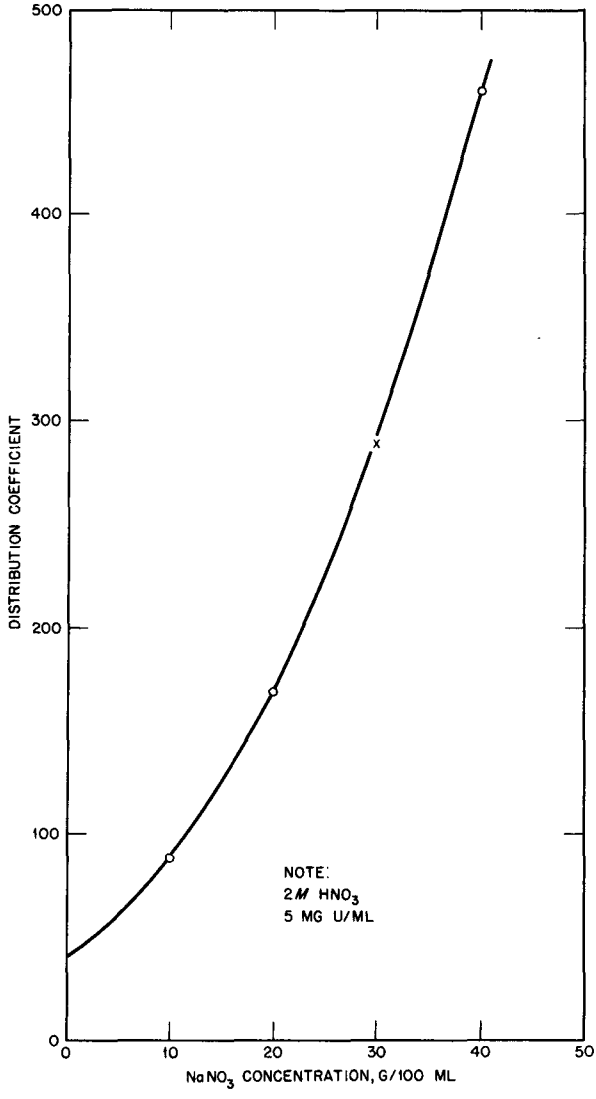


Fig. 1.11—Effect of $NaNO_3$ on TBP (undiluted) extraction of uranium.[175]

The effect of the concentration of sodium nitrate as a salting agent is shown in Fig. 1.11. In the presence of a salting agent, nitric acid depresses the distribution coefficient of uranium,[175] as shown in Fig. 1.12. However, the distribution is still adequate for analytical separations.

The distribution coefficient of uranium is reduced by dilution of the TBP with an inert solvent, as shown in Fig. 1.10. The distribution coefficients of metals with extraction mechanisms similar to uranium show a similar reduction with decreased TBP concentration. There-

Table 1.4—METAL NITRATES AS SALTING AGENTS*

Formula	Concentration, g/100 ml	Nitric acid, molarity	Uranium distribution coefficients (organic/aqueous)
		2	35
NH_4NO_3	70	2	370
$NaNO_3$	40	2	460
$NaNO_3$	66	0	1800
$Ca(NO_3)_2 \cdot 4H_2O$	58	2	370
$Fe(NO_3)_3 \cdot 9H_2O$	53	2	430
$Al(NO_3)_3 \cdot 9H_2O$	60	2	1000

*Conditions: 20 per cent TBP in hexane; 5 mg of uranium per milliliter in original aqueous phase; volumes, 25 ml aqueous, 10 ml organic.

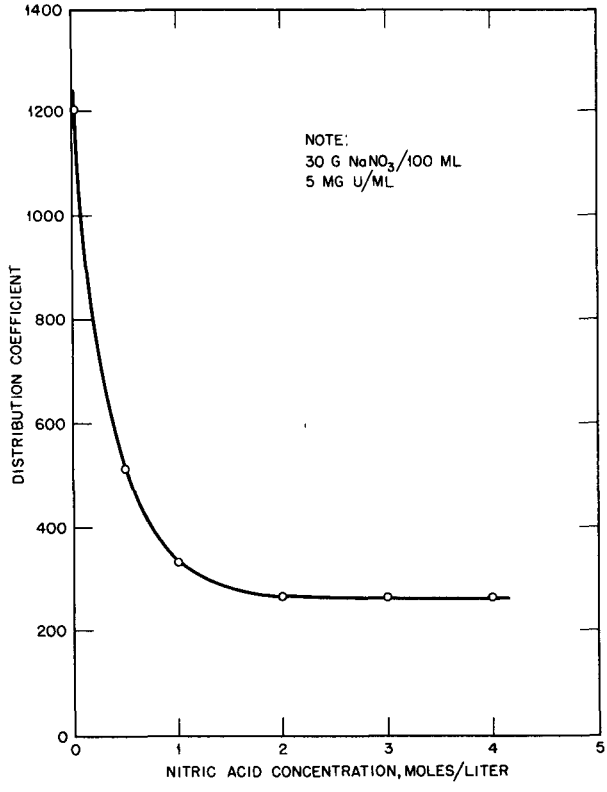


Fig. 1.12—Effect of nitric acid on the TBP (undiluted) extraction of uranium from $NaNO_3$ solution.[175]

fore, it is possible to separate uranium from these metals by diluting the TBP sufficiently. In analytical work concentrations have ranged from 20 to 100 per cent TBP.

The extraction of zirconium is inhibited by oxalate, fluoride, fluosilicate, and citrate. Experience at the New Brunswick Laboratory indicates that an extraction with 100 per cent TBP from 6*N* nitric acid followed by a backwash of the organic layer with 5*M* nitric acid and a second backwash with saturated oxalic acid removes zirconium. Sulfate, phosphate, fluoride, and silicate, especially when present in large concentrations, may interfere with the extraction of uranium with TBP.[173, 176] Aluminum nitrate has been used to complex fluoride,[175, 177] phosphate,[178] and sulfate.[179, 180] Ferric nitrate is also fairly effective in reducing the interference by sulfate, phosphate, and fluoride.[175] It is usually the practice to backwash with 5*M* HNO_3 to remove traces of salting agents and impurities which might extract. Thorium, zirconium, and cerium are not entirely removed by this washing. If aluminum nitrate is used, it should be tested for uranium since some commercial aluminum nitrate has been shown to contain uranium. The uranium can be removed with TBP before use. Chloride improves the distribution coefficients of certain metals but does not inhibit the extraction of uranium. The use of chloride instead of nitrate systems has been studied by Peppard, Mason, and Gergel [181] and has been applied to the separation of uranium from thorium by Eberle and Lerner [179] and by Larsen and Seils.[182] Waldron and Dowdy [225] have used a hydrochloric acid wash to eliminate the interference of thorium and cerium in uranium determinations. Thiocyanate has also been used

Table 1.5—DISTRIBUTION OF U(IV) AND U(VI) BETWEEN HYDROCHLORIC ACID AND 30 PER CENT TRIBUTYL PHOSPHATE IN CARBON TETRACHLORIDE*

Hydrochloric acid, *M*	Distribution ratio (organic/aqueous)	
	U(IV)	U(VI)
1.0		0. 008
2.0		0. 9
3.0		0. 54
4.0		2. 5
5.0	0. 5	3. 6
6.0	15	9. 0
7.0	50	15
8.0	102	21

*Initial uranium (aq) $= 10^{-2}M$; phase ratio = 1.

with TBP.[183] In the determination of uranium in uranium–plutonium–fission–element alloys,[182] it has been shown that the uranium distribution of both U(IV) and U(VI) is quite dependent on the hydrochloric acid concentration, as shown in Table 1.5. Gill, Rolf, and Armstrong[184] found that the extraction of zirconium and manganese(II) was prevented when ethylenediaminetetraacetic acid (EDTA) was added before the TBP extraction. They separated thorium before extraction by precipitation with oxalic acid.

Various solutions have been used for the recovery of uranium from the TBP solution, such as sodium carbonate, ammonium sulfate,[173] and ammonium acetate,[179] as well as hot water. Contrary to one statement,[76] uranium is rather readily stripped from TBP in a hydrocarbon diluent with sodium hydroxide and hydrogen peroxide[158] or with ammonium hydroxide and hydrogen peroxide. The use of ammonium hydroxide makes further treatment, such as fuming with sulfuric acid prior to a volumetric determination, quite simple.

A different approach to stripping uranium from TBP (20 percent in kerosene) solution has been made by Petrement Eguiluz and Palomares Delgado,[185] who employed 2*N* sulfuric acid and granular metallic cadmium. The cadmium reduces the hexavalent uranium to the tetravalent form, which goes into the sulfuric acid layer. The method was especially applicable for the separation of traces of uranium. No emulsions were found as sometimes happens when sodium or ammonium carbonate solutions are used for stripping. The efficiency of re-extraction with sulfuric acid and cadmium was greater than when water, 2*N* sulfuric acid, sodium carbonate, ammonium carbonate, or sodium sulfate was used.

Procedure. To 50 ml of the TBP phase, containing the extracted uranium, is added 20 ml of 2*N* sulfuric acid and about 20 g of granular cadmium. After the mixture has been shaken for 3 min, the phases are separated.

The TBP can be recovered for reuse by shaking the organic material with ammonia or sodium sulfate solution and then with sodium carbonate solution. The TBP can then be shaken with dilute nitric acid and filtered. Since the TBP may at times show a yellow discoloration, it is necessary to remove this color for certain work, such as that[180] in which the uranium is determined spectrophotometrically in the TBP extract. The removal of the color can be achieved by filtering the TBP through an activated charcoal such as Darco 20X40 grade. (If 1.76*M* sodium sulfate in 0.07*M* sulfuric acid is used as a stripping medium, the yellow colored material is not extracted.[225])

Applications of TBP extraction to analytical separations have been reported by LeStrange, Lerner, and Petretic[180] and by Paige, Elliott, and Rein,[186] who used 25 per cent TBP in isooctane and a 6*M* sodium nitrate aqueous solution. Francois[187] employed 10 per cent TBP in

690–457 O—64——5

isooctane with aluminum nitrate as a salting agent. Guest [158] employed 22 per cent TBP in *n*-hexane and a solution heavily salted with aluminum nitrate. Kimball and Rein [176] used 5 per cent TBP in carbon tetrachloride as the extractant for an ammonium nitrate–nitric acid solution. Clinch and Guy [177] used 32.5 per cent TBP in carbon tetrachloride to extract uranium as a thiocyanate from a solution containing EDTA. Eberle and Peavy [188] used 50 per cent TBP in isobutyl ketone and a saturated aluminum nitrate solution to separate uranium when phosphate was present.

The following procedure is one employed for the analysis of a solution containing: 0.5 g of uranium per liter in a solution of 6 parts hydrochloric acid, 1 part ferric sulfate, 1 part phosphoric acid, 1 part potassium dichromate, and 30 parts water. The usual precipitation methods for separation of the uranium were unsuccessful because of the large phosphate concentration.

Procedure.[188] A 200-ml aliquot of the sample solution is evaporated to dryness on a steam bath. Seventy-five milliliters of nitric acid (3+7) is added, and the mixture is heated until the residue is in solution. Aluminum nitrate is added until the solution is saturated (60 g should be sufficient). The solution is transferred to a separatory funnel, and the beaker is washed with 25 ml of nitric acid (3+7) saturated with aluminum nitrate. Twenty-five milliliters of TBP and 25 ml of methyl isobutyl ketone are added, and, after 1 min of shaking, the aqueous layer is transferred to another funnel. The organic layer is washed with 25 ml of nitric acid (3+7), saturated with aluminum nitrate, and washed again with nitric acid (3+7), both washings being added to the second funnel. The above TBP–methyl isobutyl ketone extraction is repeated with this second aqueous solution. The washings are discarded, and the organic layers from the two funnels are combined. The organic layer is stripped with hot water twice and then with a hot ammonium carbonate solution until all the uranium has been removed.

The following procedure, used for the analysis of monazite sand, describes the use of TBP for the extraction of a chloride solution containing thorium.

Procedure.[179] Ten milliliters of concentrated sulfuric acid is added to a finely ground 0.5-g sample of monazite ore in a 150-ml beaker. The mixture is heated on a hot plate to near dryness. After the mass has cooled, 100 ml of ice water is added and is stirred in until the salts dissolve. The solution is transferred to a 250-ml volumetric flask and, after the addition of 25 ml of nitric acid, is diluted to volume with water.

Samples resistant to this attack may require fusion with sodium peroxide. With samples rich in zirconium and other elements that yield hydrolytic precipitates after decomposition, filtration of the precipitate may be carried out before dilution to volume since occlusion of uranium by these precipitates is generally negligible.

An aliquot of the solution containing 50 to 500 μg of U is transferred to a 250-ml beaker. The solution is diluted to about 200 ml with water, and the hydroxides are precipitated by adding concentrated ammonium

hydroxide until the solution is strongly basic. A small amount of macerated filter pulp is added, and the solution is filtered by means of a Fisher filtrator and a 60-ml sintered-glass Büchner funnel of medium porosity. The hydroxides are dissolved with 50 ml of warm 7*N* hydrochloric acid.

The solution is transferred while still warm to a 250-ml short-stemmed separatory funnel. Twenty-five milliliters of TBP and 25 ml of methyl isobutyl ketone are added. The contents are shaken vigorously for 30 sec. The aqueous (lower) phase is discarded. The organic phase is washed with five 50-ml portions of 7*N* hydrochloric acid. The washings are discarded. The organic phase is washed with four 50-ml portions of 4.7*N* nitric acid, and again the washings are discarded. The uranium is removed from the organic phase by extracting successively with 20-, 15-, and 15-ml portions of a 25 per cent ammonium acetate solution.

The following procedure [189] has been used prior to the fluorometric or spectrophotometric determination of uranium. It employs EDTA to prevent extraction of zirconium. It is used on samples containing 10 to 350 μg of U_3O_8.

Procedure. A sample (up to 1 g) is dissolved in 4 ml of nitric acid (1+3) and heated on a hot-water bath for 2 hr. The volume of the solution is made to 4 ml with water, and the solution is shaken. After the solution has been centrifuged, 2 ml of the clear solution is pipetted into a 6-ml tube and the following are added: 1 drop of an EDTA solution (10 per cent solution of the sodium salt), 1 drop of a 5 per cent sodium sulfite solution, 1 drop of acetic acid, 1 drop of a 20 per cent tartaric acid solution, and 1 drop of 0.04 per cent meta cresol purple. The pH of the solution is adjusted to the color change of the indicator with ammonium hydroxide (1+1) and nitric acid (1+1). To the solution are added 3 ml of aluminum nitrate (1 g/ml) and 2 ml of methyl isobutyl ketone–tributyl phosphate solution (9+1). The container is stoppered and shaken on a mechanical shaker. After the phases have separated, 1 ml of the organic phase is used for analysis.

(e) *Trialkyl Phosphine Oxides.* In the course of a systematic study of organic complexing agents for uranium, workers at Oak Ridge National Laboratory [190] found a number of promising reagents among the organophosphorus compounds. One class of these compounds, the tri-*n*-alkyl phosphine oxides, was found to have an extremely high extraction coefficient for uranium, significantly greater than the coefficients for iron, aluminum, thorium, and vanadium.

On the basis of this work, White and Ross [191] made a qualitative investigation of the extraction of some 40 additional metal ions from acidic solutions by tri-*n*-octyl phosphine oxide (TOPO) to obtain a general picture of the selectivity of these compounds as solvent extractants.

The neutral alkyl phosphine oxides (R_3PO), phosphinates [$R_2(RO)PO$], and phosphonates [$R(RO)_2PO$] can be grouped with the familiar alkyl phosphate, tributyl phosphate (TBP), in their

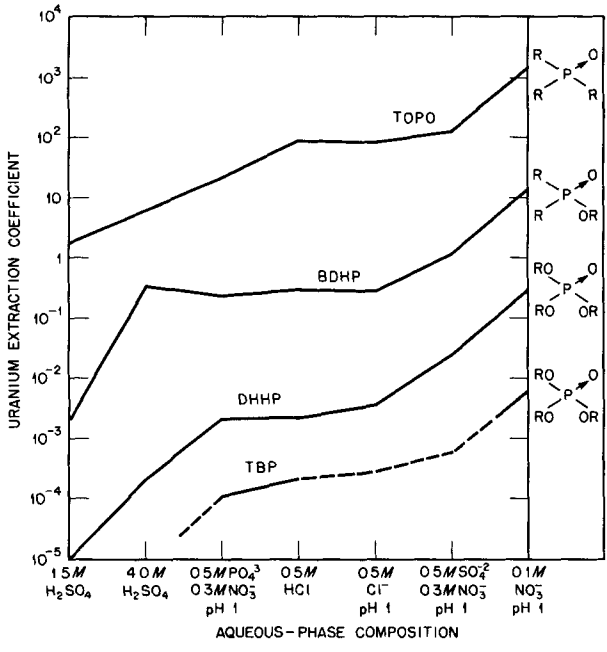


Fig. 1.13—Comparison of neutral organophosphorus reagents.[192] Aqueous phase: As indicated, with 0.004*M* U(VI). Organic phase: 0.1*M* reagent in kerosene. TOPO, trioctyl phosphine oxide; BDHP, butyl dihexylphosphinate; DHHP, dihexyl hexylphosphonate; TBP, tri-*n*-butyl phosphate. Phase ratio (aqueous to organic) = 1; temperature, 25°C.

extraction behavior. Thus, in the extraction of uranyl nitrate by TOPO, the equilibrium

$$UO_2^{+2} + 2NO_3^- + 2R_3PO \rightarrow UO_2(NO_3)_2(OPR_3)_2$$

which is analogous to that proposed for TBP, describes the extraction behavior fairly well. These reagents, however, offer a greatly increased range of extraction power, as shown in Fig. 1.13.

It is seen that TOPO extracts uranium with a coefficient that is five orders of magnitude higher than that shown by TBP and that extractions can be achieved from sulfate and phosphate solutions where TBP is completely ineffective. The phosphinates and phosphonates are intermediate between these extremes. In all cases nitrate is the most favorable aqueous medium, with rapidly decreasing extraction from chloride to sulfate solutions. As with the acid compounds, reagent concentration is an important variable in determining extraction coefficients. Uranium coefficients, for example, vary with the second power of the uncomplexed phosphine oxide concentration.

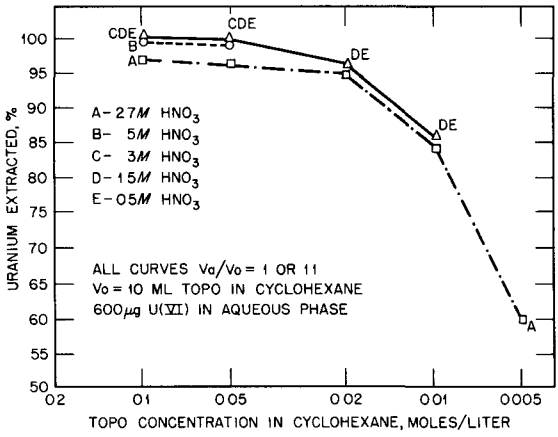


Fig. 1.14—Extent of uranium extraction by TOPO in cyclohexane. (From Horton and White, *Analytical Chemistry*, Ref. 193.)

An important consequence of the high extractability from nitrate solutions is that, by the introduction of relatively small amounts of nitrate in much less favorable aqueous solutions (e.g. sulfate and phosphate), uranium can be effectively extracted by a phosphine oxide. This is to be contrasted with the inhibiting effect that small concentrations of sulfate and phosphate have on extractions with TBP from concentrated nitrate solutions.

It is interesting to note that the variation of uranium extraction with reagent type and with aqueous anion roughly parallels the extraction of mineral acids by these reagents. Thus all these neutral reagents extract phosphoric acid, sulfuric acid, hydrochloric acid, and nitric acid from aqueous solutions, the extraction increasing roughly in that order. In addition, the strength of extraction of a given mineral acid increases in the order phosphate, phosphonate, phosphinate, phosphine oxide. An important property of the dialkyl phosphoric acids is that in combination with neutral organophosphorus reagents a strong enhancement (synergistic) of U(VI) extraction can be obtained.[192]

The extraction of 200 to 1800 μg of uranium by various concentrations of TOPO in cyclohexane was studied by Horton and White.[193] The results obtained are shown in Figs. 1.14 and 1.15. The distribution coefficient for uranium dropped fairly rapidly for less than 0.05 millimole of TOPO even when the original uranium content of the aqueous phase was only about 500 μg. For 0.5 millimole, the aqueous-to-organic volume ratio can be at least 2.5 without decreasing the extent of extraction.

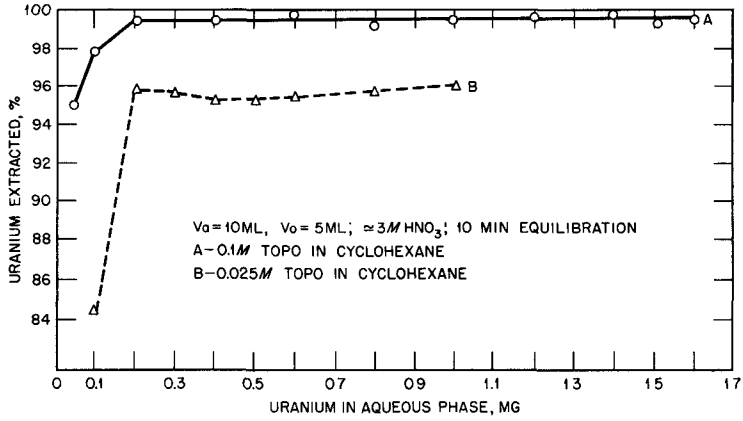


Fig. 1.15—Extraction of uranium by TOPO in cyclohexane. (From Horton and White, *Analytical Chemistry*, Ref. 193.)

Most methods of analysis use TOPO. This material has a melting point of 51 to 52°C and is available from Eastman Kodak Co. (EK-7440).

Tri-*n*-octyl phosphine oxide in hydrocarbons, such as cyclohexane, can be used to extract U(VI) quantitatively from 0.5*M* to 7*M* hydro-

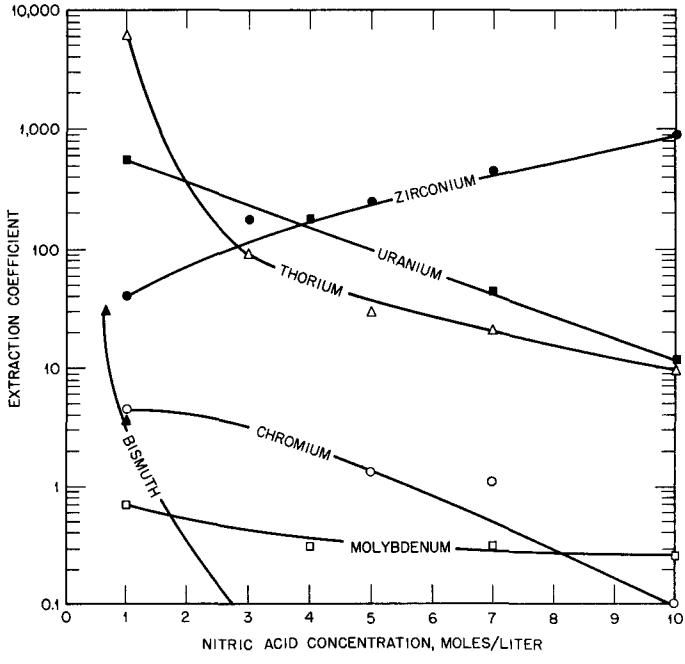


Fig. 1.16—Extraction of some metal ions by 0.1*M* TOPO from nitric acid solutions.[194]

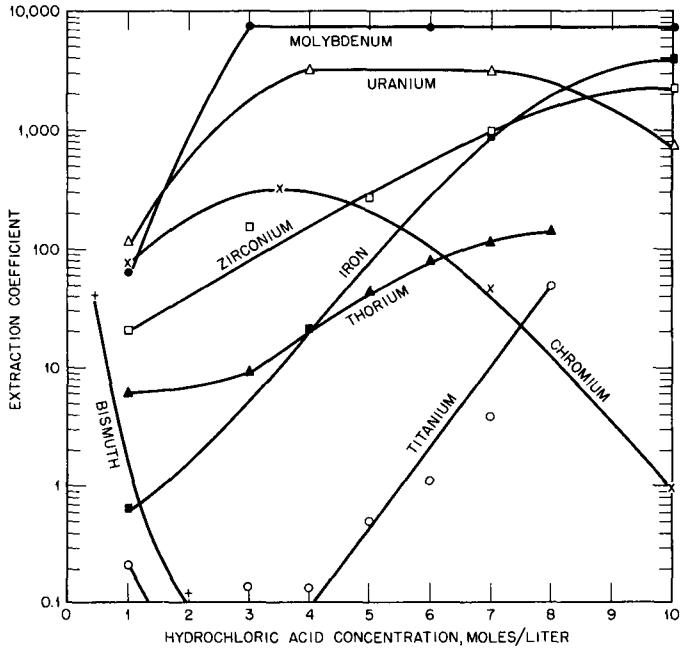


Fig. 1.17—Extraction of some metal ions by 0.1*M* TOPO from hydrochloric acid solutions.[194]

chloric or nitric acid without the addition of salting agents. The only other elements that are extracted to any extent from nitric acid with TOPO are shown in Fig. 1.16. The elements extracted from a hydrochloric acid medium are shown in Fig. 1.17.

The following is the procedure used by Horton and White[193] to separate uranium prior to a spectrophotometric determination.

Procedure. For samples that do not contain interfering ions, a 0.5- to 8-ml aliquot of a solution in nitric, perchloric, or sulfuric acid estimated to contain 15 to 2500 μg of U(VI) is pipetted into the bottom portion of the extraction vessel (Fig. 1.18). The solution is adjusted by the addition of 10*M* sodium hydroxide, nitric acid, or sodium nitrate, so that a total aqueous volume of 10 ml is 1*N* to 3*N* in hydrogen ion and 2*M* to 4*M* in nitrate ion. (For almost-neutral solutions, 2 ml of concentrated nitric acid will give the correct concentrations for a 10-ml aqueous volume.) The total volume is adjusted to 10 ml. Up to 12 ml of aqueous solution can be shaken with 5 to 10 ml of extractant in the apparatus without undue splashing. If the total aqueous volume is greater than 12 ml after the acidity and nitrate content have been adjusted, the extraction is performed in a separatory funnel instead of in the special extraction vessel.

For samples containing Fe(III), Cr(VI), or V(V), a 0.5- to 6-ml aliquot of a solution in dilute perchloric or sulfuric acid medium estimated to contain 15 to 2000 μg of U(VI) is pipetted into the bottom

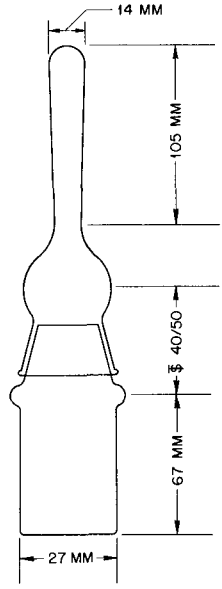


Fig. 1.18—Extraction apparatus. (From Horton and White, *Analytical Chemistry*, Ref. 193.)

portion of the extraction vessel. The Fe(III) is reduced to Fe(II), the Cr(VI) to Cr(III), and the V(V) to V(IV) or V(III), without reducing the U(VI) to U(IV). Sodium bisulfite is a satisfactory reductant if the solutions are boiled to remove excess sulfur dioxide. Hydroxylamine sulfate is also a satisfactory reductant, but amalgamated zinc is unsuitable. Sufficient nitric acid or sodium nitrate and water are added to make the final aqueous volume of 8 to 12 ml 1*N* to 3*N* in hydrogen ion and 2*M* to 4*M* in nitrate ion.

For samples containing titanium, thorium, hafnium, zirconium, or iron(III), but only traces of aluminum, a 0.5- to 6-ml aliquot of a solution in dilute nitric, perchloric, or sulfuric acid estimated to contain 15 to 2500 μg of uranium is pipetted into the bottom of the extraction vessel. Sufficient base, acid, or sodium nitrate and water are added to make the volume of about 8 ml 1*N* to 3*N* in hydrogen ion and 2*M* to 4*M* in nitrate ions. Up to a maximum of 2.5 ml of 1*M* potassium fluoride is added when the concentrations of interfering ions are unknown. If high concentrations of these ions are known to be present, additional fluoride can be tolerated.

For samples containing excessive fluoride or phosphate, an aliquot is pipetted into an extraction vessel, and the acid and nitrate contents are adjusted in the same manner as the samples containing titanium, thorium, hafnium, zirconium, and iron. Sufficient aluminum nitrate is added to complex the fluoride and phosphate estimated to be present. The total volume should be 12 ml or less.

For amounts of uranium estimated to be under about 1400 μg, 5 ml of 0.1*N* TOPO in cyclohexane is pipetted into the extraction vessel containing the treated sample. For 1400 to 3000 μg of uranium, 10 ml of the 0.1*N* TOPO extractant solution is used. The top of the vessel is attached,

and the contents are shaken for 10 min on a reciprocating shaker. The extraction apparatus is inverted for separation of the phases and for removal of the aliquots of the upper organic phase.

(f) *Dibutoxytetraethylene Glycol (Penta Ether).* Penta ether was one of the many solvents developed by C. A. Kraus and his coworkers at Brown University during World War II for the extraction of uranyl nitrate.[226] The method of Kraus[198] was refined by the Analytical Development Section of Tennessee Eastman Company[199, 227, 500] for use in their laboratories. Although its use in the intervening years has largely been replaced by other solvents, it is occasionally used. (Since the flash point of penta ether is 355°F, it is a relatively safe solvent as compared to diethyl ether.)

The use of penta ether to extract uranium as the thiocyanate has been reported.[200]

As with diethyl ether salting agents containing a metal cation give larger distribution coefficients for the extraction of uranium into penta ether. The distribution coefficient of a nitrate solution of uranium employing saturated solutions of the various salts was 450 for ammonium nitrate, 2000 for ferric nitrate, and 3000 for calcium nitrate.[201]

When the uranium was to be determined by a gravimetric method a three-fourths saturated solution of ammonium nitrate as a salting agent was usually employed. The optimum acidity range, using the latter salting agent, was found to be 1*N* to 3*N* in nitric acid. Changes in temperature had a marked effect on the extraction efficiency, the distribution coefficient changing from 430 at 18°C to 330 at 23.5°C.

Iron, in the presence of chloride, will readily extract into penta ether. Tartaric acid can be used to complex iron so that it will not extract. Of course, the chloride ion can be removed with silver nitrate. Thorium is extracted almost quantitatively. (The complex of uranium with thiocyanate will extract into hexone from a sulfate medium, whereas thorium extracts to only a slight degree.) Vanadium in the pentavalent state has a fairly high distribution coefficient into penta ether, but in the quadrivalent form it has a negligible extraction coefficient. Copper, mercury, molybdenum, silver, and cadmium extract to an appreciable extent, but washing the penta ether extract with a three-fourths saturated solution of ammonium nitrate removes the greater portion of the impurities from the penta ether phase. Sulfate and fluoride inhibit the extraction of uranium, whereas phosphate and silicate carry through the extraction. Iron effectively complexes the sulfate, and aluminum complexes the fluoride. Increasing the nitric acid concentration to 3*N* decreases the effect of sulfate.

Essentially all extractions have been made with the batch-extraction technique since the penta ether decomposes if a continuous-reflux-extraction system is used.

Procedure. The nitrate solution of the uranium in 1*N* to 3*N* nitric acid and three-fourths saturated with ammonium nitrate is extracted three times with penta ether. The combined penta ether layers are washed with three-fourths saturated ammonium nitrate to remove impurities that have been extracted. The uranium is then stripped from the penta ether by washing three times with a saturated ammonium sulfate solution.

(g) *Dibutyl Carbitol* [*bis* (*2-Butoxyethyl*) *Ether*]. One of the solvents developed by C. A. Kraus and his coworkers for the extraction of uranium nitrate was Dibutyl Carbitol. The Dibutyl Carbitol method [198] was studied by the Tennessee Eastman Corp. at Oak Ridge and was used quite extensively at that installation. (A high boiling point of 254.6°C at 0.02 mm Hg and a flash point of 260°F indicate that this solvent is very safe for laboratory use.)

As with many other solvents, a salting agent is used. A number of different salting agents have been used, copper, calcium, aluminum, zinc, ferric, and ammonium nitrates being the most common. The distribution coefficient with ammonium nitrate is not very great, and owing to the high boiling point continuous extraction cannot be used. This fact has limited the use of Dibutyl Carbitol as an analytical reagent.

Acid concentration and temperature affect the distribution coefficients. Little information is available on the extraction of other elements. Bromide, chloride, fluoride, phosphate, sulfate, acetate, and malonate lower the uranium distribution coefficients. As with other solvents aluminum or ferric nitrate can be used to complex the fluoride and sulfate ions.

The sample in the form of a nitrate solution is exhaustively extracted with Dibutyl Carbitol. After the combined extracts have been washed with an ammonium nitrate solution, the uranium can be stripped from the organic phase with a saturated ammonium sulfate solution.

(h) *Amines.* Certain long-chain amines (at least 24 carbon atoms) are actually related to anionic-exchange resins and are now considered as liquid ion-exchange systems. Although at the present time no extended use is made of these compounds in analytical chemistry, they may in the future become of considerable importance.

White [194] presented at the First Analytical Chemistry Conference at Gatlinburg, Tenn., a review of the present knowledge of these compounds indicating that uranium can be extracted from many dilute acids with a solution of methyl-di-*n*-octylamine.

Primary amines can be used to extract thorium; tertiary amines cannot In general, the reverse is found to be true for uranium. The rare-earth elements behave, to a lesser degree, in a manner similar to that of thorium. Moore [209] showed that uranium and plutonium

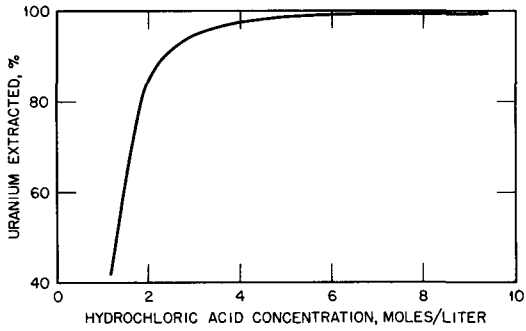


Fig. 1.19—Extraction U^{233} tracer with 5 per cent triisooctylaminexylene from hydrochloric acid solution. (From Moore, *Analytical Chemistry*, Ref. 209.)

can be separated from thorium, the alkali metals, alkaline earths, the rare-earth elements, zirconium, niobium, ruthenium, and other elements that do not form anionic species in hydrochloric acid solution with triisooctylamine dissolved in xylene or hexone. The effect of hydrochloric acid concentration is shown in Fig. 1.19.

In later work Moore [210] used an acetate solution with various concentrations (10 to 30 per cent) of triisooctylamine in xylene, with 3 per cent Butyl Cellosolve as a modifier, for the separation of uranium and plutonium from thorium and fission products. The separation is quite dependent on the acetic acid concentration (Fig. 1.20). Half molar acetic acid was found to be the most satisfactory; as much as 0.1*M* nitric acid can be present. Ammonium hydroxide or 1*M* ammonium bicarbonate were found to be the most efficient stripping agents.

(i) *Diethyldithiocarbamate.* L. A. Haddock in some unpublished work in 1935 found that U(VI) formed a complex with diethyldithio-

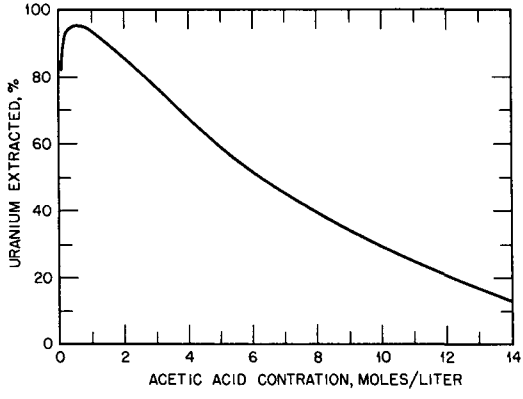


Fig. 1.20—Extraction of U^{233} tracer with 5 per cent triisooctylaminexylene from acetic acid solution. (From Moore, *Analytical Chemistry*, Ref. 210.)

carbamate which was soluble in ethyl acetate and ether but not in carbon tetrachloride.

Jones [195] found that chloroform dissolved the complex and was a more satisfactory solvent than ethyl acetate or ether. Chloride, nitrate, or sulfate did not interfere, but phosphate caused the precipitation of uranium that was not extractable with the chloroform and sodium diethyldithiocarbamate. There were, however, many metal ions, such as iron, copper, nickel, cobalt, and others, which interfered.

Fritz and Johnson-Richard [196] showed that, in the presence of ethylenediaminetetraacetic acid (EDTA), only bismuth, copper, cobalt, mercury, silver, and tin diethyldithiocarbamates are extracted along with uranium. The chief value of this extraction is the separation of uranium from such metals as thorium and iron.

Procedure. To a sample containing not more than 0.08 millimole of foreign metal is added 2 ml of 0.05*M* EDTA and approximately 1 ml of pyridine. A dilution is made to approximately 20 ml, 3 ml of 2 per cent diethyldithiocarbamate is added, and the pH is adjusted to 7 to 8. If thorium is the interfering ion, the solution is allowed to stand for 15 to 30 min at a pH of 7 to 8 before the diethyldithiocarbamate solution is added. The solution is transferred without delay to a separatory funnel, and an extraction is made with 25 ml of chloroform. A few milliliters of a saturated solution of sodium nitrate can be added to clear up the layers. The chloroform layer is drained into another separatory funnel, which contains 50 ml of 0.02 per cent sodium carbonate. An additional 1 ml of diethyldithiocarbamate solution is added to the aqueous layer, and a re-extraction is made with 15 ml of chloroform. This chloroform layer is drained into the same sodium carbonate solution, and the carbonate and combined chloroform extracts are shaken for 30 sec to back-extract the uranium. The chloroform from this back-extraction is drained into another separatory funnel and is back-extracted with a second 25-ml portion of sodium carbonate solution. One milliliter of perchloric acid is added to the combined carbonate solutions to destroy the carbonate. Then 5 ml of triethanolamine buffer and 5 ml of 0.001*M* arsenazo are added, and the pH is adjusted to 7.5. A dilution is made to exactly 200 ml, and the absorbancy is measured at 595 mμ.

Recently Milner and Edwards [197] used the dithiocarbamate reagent for the determination of uranium in a bismuth-base alloy. They found that the bismuth could be extracted readily into a chloroform solution of ethylammonium diethyldithiocarbamate from a nitric acid solution as strong as 3*N*. The uranium remained quantitatively in the aqueous phase. Hardwick and Moreton-Smith [172] used a somewhat similar technique to separate uranium and thorium; however, they adjusted the pH to hold the uranium in the organic layer, whereas the thorium was transferred to the aqueous phase. The uranium was extracted with diethyldithiocarbamate and chloroform from the aqueous phase by adding ammonium acetate and then adjusting the

pH of the solution to 5.5 to 6 with ammonia. The uranium could be determined directly in the chloroform layer by direct measurement of the absorbancy.

Procedure.[197] A 5 per cent diethylammonium diethyldithiocarbamate solution is made by dissolving 50 g of diethylammonium diethyldithiocarbamate in 1 liter of chloroform and keeping it in a dark-glass bottle. The solution is suitably diluted with chloroform when weaker solutions are needed.

A solution of the alloy (bismuth base) is made by warming the sample with 25 per cent nitric acid until solution is complete and then boiling for 2 to 3 min to expel nitrous fumes. The solution is then cooled and diluted to a suitable volume, and more nitric acid is added, if necessary, to make the final solution approximately 1*N* in acid.

To determine the uranium, take an aliquot of the alloy solution, containing up to 1 g of the sample in 25 ml, and transfer it to a 100-ml separatory funnel. A dilution to 25 ml is made, if necessary, with *N* nitric acid, and 50 ml of the 5 per cent diethylammonium diethyldithiocarbamate solution is added. The solution is shaken for 30 sec, and the layers are allowed to separate. The lower chloroform layer is run off and discarded. The extraction is repeated with 5-ml portions of 5 per cent diethylammonium diethyldithiocarbamate solution until the resultant chloroform layer is colorless, signifying the complete removal of bismuth. The aqueous solution is extracted with 20 ml of chloroform, and the chloroform layer is discarded. Ten milliliters of 20 per cent (wt./vol.) ammonium acetate solution is added to the solution in the separatory funnel. followed by the dropwise addition of 0.9*N* ammonium hydroxide until the solution has a pH of 5.5 to 6 as shown by indicator paper. The uranium is extracted with 25 ml of 0.5 per cent diethylammonium diethyldithiocarbamate chloroform solution (if more than 20 mg of uranium is present, use a 1 per cent diethylammonium diethyldithiocarbamate solution). The chloroform layer is transferred to a 100-ml graduated flask, using small volumes of chloroform for washing. The extraction is repeated with 15 ml and then 10 ml of diethylammonium diethyldithiocarbamate solution. The combined extracts are diluted to the mark with chloroform. If the solution contains more than 6 mg of uranium per 100 ml, a suitable aliquot is taken and diluted with chloroform. The absorbancy of the solution is measured in a 1-cm cell against a water blank at 390 to 400 mμ. The uranium content is determined by reference to a calibration graph prepared with standard uranium solutions covering the range 0 to 6 mg of uranium.

(j) *Acetylacetone.* Some preliminary work by Krishen and Freiser [202] indicated that acetylacetone may be of use in the separation of uranium from interfering elements. The selectivity was increased by using ethylenediaminetetraacetic acid (EDTA) as a complexing agent. Although the above work dealt only with uranium in the presence of bismuth, copper, zinc, and lead, it may have other applications. The method was quite effective in removing better than 90 per cent of the uranium when as much as a 5000-fold excess of bismuth was pres-

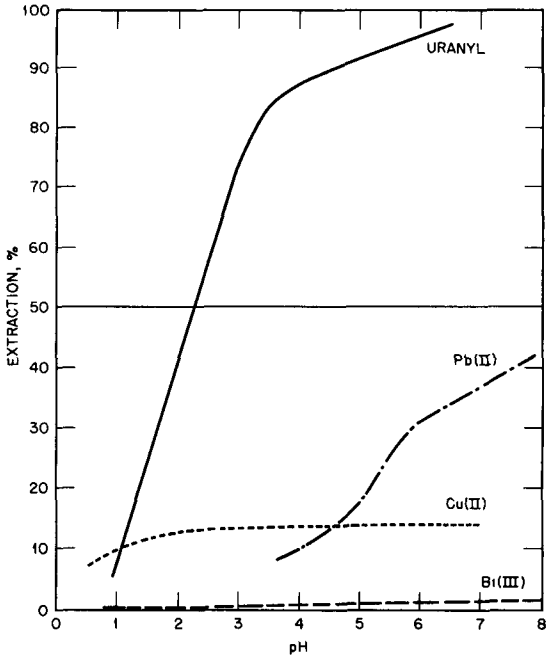


Fig. 1.21—Extraction of acetylacetonates by acetylacetone in presence of ethylenedinitrilotetraacetic acid. (From Krishen and Freiser, *Analytical Chemistry*, Ref. 202.)

ent. The extraction of these elements at various pH intervals is shown in Fig. 1.21.

Solutions of uranyl sulfate were mixed with different amounts of bismuth trichloride solution. A solution of the disodium salt of EDTA was added to give a bismuth to EDTA ratio of 1 to 30. The pH of the solution was then raised to 7.5 by the careful addition of *N* sodium hydroxide. Then approximately 10 ml of acetylacetone was added, and the mixture was shaken for 10 min. The acetylacetone phase was separated, filtered, and made up to a volume of 10 ml. The uranium was determined in the extract by a polarographic method. The separation of uranium from a 5000-fold excess of bismuth did not present much difficulty. The amount of bismuth was limited only by the low solubility of the disodium salt of EDTA, which must be present in 30-fold excess.

(k) *8-Hydroxyquinoline (Oxine)*. A solvent-extraction procedure employing 8-hydroxyquinoline and chloroform has been indicated as a possible means of determining uranium.[203] The extraction of uranium oxinates has been employed for relatively pure solutions,[204] in most instances after a previous separation of interfering elements, of

which there are many. Since only uranium, titanium, vanadium, molybdenum, and tungsten are precipitated by oxine in the presence of ethylenediaminetetraacetic acid (EDTA) from an ammonium acetate buffer,[205] workers in England [206] used oxine in a methyl isobutyl ketone (hexone) solvent to extract U^{233} from irradiated thorium. They found that above pH 6.5 the uranium was completely extracted. Chloroform was also satisfactory as a solvent. Fluoride ions, which are used to catalyze the dissolution of thorium and thoria in nitric acid, had no effect on the extraction. Concentrations of EDTA up to a molar ratio of 2 to 1 of the thorium present could be used under the pH conditions employed. A somewhat similar procedure [183] was used at a pH of 8 to 9 except that chloroform was used as the solvent. One paper of interest [207] describes work in which the uranium is extracted from a carbonate solution using a quaternary ammonium ion and oxine with various solvents. This work indicated that by forming the tri-8-quinolinate ion at a high pH in a carbonate solution and then extracting this ion with a tetraalkylammonium cation in methyl isobutyl ketone a separation of uranium could be made. The most suitable tetraalkylammonium cation was found to be Arquad C [$R_2N(CH_3)_2Cl$ where R averages about a 16 carbon chain]. Vanadium in the oxidized form seriously interferes with the uranium extraction, but it can be reduced before extraction.

The following procedure can be used for 1 to 100 μg of U^{233} per milliliter of solution.

> *Procedure.* A suitable volume of sample solution containing about 10 μg of U^{233} is pipetted into a 40-ml centrifuge tube and diluted to 3 ml with water. Enough EDTA solution (372.9 g of disodium salt of ethylenediaminetetraacetic acid is dissolved in 500 ml of water containing 80 g of sodium hydroxide and then made up to a liter: 1 ml≡232 mg of thorium) is added to give a 10 per cent excess over the thorium equivalent. After the addition of 2 drops of bromothymol blue indicator solution, the pH is adjusted to 7 by adding ammonium hydroxide until the indicator turns blue. The color is returned to yellow by adding *N* ammonium nitrate and then 0.2*N* ammonium hydroxide until the color is just blue again. To this solution is added 5 ml of oxine solution (10 per cent solution of oxine in hexone), and the mixture is stirred for 5 min and finally centrifuged. Suitable aliquots of the hexone layer are taken for counting or fluorometric analysis.

(l) *Cupferron.* The chief use of cupferron in the analysis of uranium is for the separation of interfering elements prior to the volumetric determination of uranium. Solvent extraction of the cupferrates with chloroform from a sulfuric acid (1+10) solution is usually employed.[211] In precise work it is advisable to wash the combined cupferron layers with sulfuric acid (1+10) to remove entrained uranium.

In general, separations are made by oxidizing the cooled solution with potassium permanganate until it is pink and then adding 25 ml of a 6 per cent cupferron solution and shaking the mixture. Twenty-five milliliters of chloroform is added, the mixture is shaken, and, after the phases have separated, the lower layer is drained (a small portion is left in the neck of the extraction funnel). This is repeated until the chloroform layer is clear. An additional 5 ml of the cupferron solution is added, and the extraction is repeated. In the presence of large amounts of zirconium, it has been found advisable to use solid cupferron instead of a solution. The purified solutions are fumed, after being heated on a steam bath to drive off the chloroform, with nitric acid and perchloric acid.

Furman, Mason, and Pekola [212] studied the extraction of cupferrates and found the extraction with chloroform to be a very effective procedure for removing iron, titanium, molybdenum, vanadium, etc. prior to the estimation of other substances. Fritz, Richard, and Bystroff [213] indicated that the pH at which the extraction is carried out is important. If the acidity is too great (pH less than about 0 to 0.2), some of the iron and quadrivalent metal cupferrates remain unextracted in a hydrochloric acid solution. They also indicated that perchloric acid in many cases caused some of the extracted metal cupferrates to bleed back into the aqueous layer. This may explain why Steele [214] found traces of iron, titanium, and molybdenum when he extracted interfering elements using a perchlorate system. This effect does not seem to occur in the sulfuric acid system. It has also been indicated [213] that in separations of iron, where a very acid content is necessary, the aqueous layer should be removed from the nonaqueous as soon as possible after the extraction. The longer the layers are left in contact, the more the ferric cupferrate will bleed back into the aqueous layer.

Although quadrivalent uranium is precipitated with cupferron and can be separated by dissolving in ether,[212] this method is rarely used. The extraction of the U(IV) cupferrates is less satisfactory than the precipitation method owing to losses resulting from the oxidation of the U(IV) to U(VI). Limited success has been achieved with this separation at the microgram level with recoveries of 85 to 94 per cent being indicated.[215]

(m) *1-Nitroso-2-naphthoxide.* Alimarin and Zolotov [208] have used the extraction of uranium with 1-nitroso-2-naphthoxide and isoamyl alcohol from an ethylenediaminetetraacetic acid solution at a pH of 7.5 for the separation of uranium from vanadium and iron. The vanadium has to be reduced and extracted at a pH of 6.5 to 9; iron is extracted at pH 7.0 to 7.5.

(n) *Miscellaneous Solvents.* Methylcyclohexanone has been used [216] for the quantitative separation of uranium from a mixture of thorium and uranium nitrates in a sodium nitrate solution. The presence of nitric acid is detrimental. The uranium is recovered from the solvent with a sodium carbonate solution.

Mesityl oxide, which initially was used for separating thorium from a solution of the nitrates saturated with aluminum nitrate, quantitatively extracts uranium [217] even in the presence of relatively large amounts of phosphate.

The benzohydroxamic acid chelate of uranium is soluble in 1-hexanol [218] and has been used for the spectrophotometric determination of uranium. Thorium, cerium, molybdate, tungstate, acetate, phosphate, chlorate, fluoride, sulfate, or chloride ions did not interfere. The extraction is made at pH 6.2 and is quite acid dependent.

The uranium complex with 1-(2-pyridylazo-2-naphthol) formed in the presence of EDTA and/or cyanide can be extracted with *o*-dichlorobenzene, and the uranium can be determined spectrophotometrically in the extract.[219] Little or no interference was found with copper(II), nickel(II), mercury(II), zinc, iron(III), zirconium, and thorium. Thorium in large amounts, however, may interfere.

1–2.5 Chromatography

Uranyl nitrate can be separated from interfering elements by the use of cellulose-column chromatography or by paper chromatography. Ether in nitric acid is used as the eluting agent. The resolution of mixtures of solutes on paper may depend upon surface adsorption, upon ion exchange, or upon partitioning between solvents.

(a) *Cellulose-column Chromatography.* Uranium can be separated from interfering elements by the extraction of uranyl nitrate with ether containing 5 per cent nitric acid in the presence of cellulose.[220–223] The solvent is allowed to percolate through the column; uranyl nitrate is dissolved and passes quantitatively into the liquid eluate, whereas a large number of other metal nitrates are not appreciably dissolved, or are adsorbed, and remain stationary or move only slowly in comparison with uranium.

The mechanism of the separation process is complicated and is dependent chiefly on the following factors: (1) selective extraction of uranyl nitrate by the solvent, (2) partition between the nitrates dissolved in the organic solvent and water present in the cellulose, and (3) adsorption of metal nitrates on the cellulose.

The method consists in preparing a nitrate solution of the sample for analysis in dilute nitric acid and transferring this mixture to the top of a column packed with cellulose. The ethyl ether–nitric acid

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solvent is percolated through the column to dissolve the uranium nitrate, which passes quantitatively into the liquid eluate.

In the presence of arsenic or molybdenum, which are not retained on cellulose alone, the addition of activated alumina to the top of the column was found to be efficient in retaining these elements. The following nitrates either remained stationary or moved very slightly on a cellulose column on extraction with ether: lithium, sodium, potassium, cesium, silver, beryllium, magnesium, calcium, strontium, barium, radium, zinc, cadmium, aluminum, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, holmium, erbium, gallium, indium, thallium, titanium, hafnium, germanium, tin, lead, niobium, tantalum, chromium, tungsten, tellurium, manganese, iron, cobalt, and nickel. Colloidal gold had a tendency to pass through the column. Mercury in the mercuric state moved down the column but not sufficiently to interfere with the uranium determination. The major portion of the ruthenium and platinum is retained at the top of the column, but small quantities enter the effluent. Indium and rhodium are not mobile, whereas palladium and osmium are readily extracted. Selenium, arsenic, antimony, and bismuth moved down the column. Cerium did not move when in the reduced state. Thorium and scandium moved in the column, but, if the acid concentration of the ether were changed to 3 per cent, the uranium could be separated. Zirconium moves down the column, but the extraction is inhibited by complexing the zirconium with tartaric acid. Phosphates also suppress the movement of zirconium. If phosphate is used, ferric nitrate must be added to complex the excess phosphate. Vanadium does not re-extract except in the presence of ether peroxides. The vanadium peroxy compound can be reduced with ferrous sulfate.

Phosphorous in the form of phosphoric acid was readily extracted; however, ferric nitrate can be used to complex the phosphate ion.

Small quantities of sulfuric acid do not seem to have any appreciable effect on the extraction of uranium. Larger amounts of sulfate retard the extraction. This can be overcome by adding calcium nitrate.

Halides must be absent since many elements are extracted by ether from a hydrochloric acid system. Lebez and Ostanek [224] added light petroleum to the ether–nitric acid solvent to increase the capacity of the cellulose for holding the aqueous phase. Many applications of the cellulose column for the separation of uranium have been made but all are essentially applications of the above procedures to specific problems.

The following procedure has been used for several years in the analysis of ore concentrates.

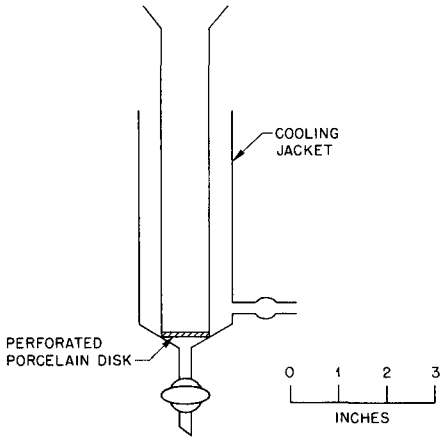


Fig. 1.22—Cellulose column.

Apparatus. A diagram of the cellulose column is shown in Fig. 1.22. The inner surface of the column is made water repellent as follows. The inner tube is cleaned with a sulfuric acid–chromic acid mixture and washed with water. The inside surface of the glass tube is treated with a suitable silicone solution to render it water repellent, and the tube is washed with ether.

Procedure. Activated alumina of 60 to 150 mesh is used as supplied for chromatographic purposes. Whatman cellulose powder of standard grade may be used for the activated cellulose pulp. The pulp may also be prepared from Whatman No. 1 filter paper as follows. Five hundred grams of Whatman filter paper is torn into small pieces, and approximately equal quantities are placed in four 1-gal stainless-steel containers. Three liters of water is added to each container, and the paper is broken up by stirring. The water is heated to boiling, 15 ml of nitric acid is added to each container, and boiling and stirring are continued for 5 min. The liquid is filtered off by transferring the contents of two containers into a Büchner funnel (no paper), washing with five 1-liter portions of water, and drawing off the surplus water. The pulp is returned to the containers, 1.5 liters of alcohol is added to each container, and the mixture is thoroughly stirred and refiltered. The surplus alcohol is drawn off, and the pulp is returned to the containers. Then 1.5 liters of ether is added, and the mixture is stirred and refiltered. The washing is repeated with ether, and finally most of the ether is drawn off. The pulp is stored in well-stoppered containers to ensure that it always remains damp with ether.

The ether–nitric acid solvent is made by adding 50 ml of nitric acid (density 1.42 g/cm^3) to 950 ml of ether (peroxide free). The solvent should not be stored longer than one day since ether in contact with nitric acid is partially oxidized to a nonvolatile peroxide which is left as a residue on evaporation of the solvent and which may explode violently when carried to dryness.

Approximately 1 g of the dried sample is transferred to a suitable beaker, 15 ml of nitric acid is added, and the beaker is covered; after the

initial reaction has subsided, the solution is evaporated to dryness. The residue is redissolved in 7 ml of nitric acid (3+7), and 1.5 g of hydrated ferric nitrate and 1.5 g of calcium nitrate are added. The residue is allowed to cool to room temperature.

The cellulose–alumina column is prepared by thoroughly stirring the cellulose pulp with the ether–nitric acid solvent and allowing it to stand for 10 min. The jacket of the column is filled halfway with the ether–nitric acid solvent. A portion of the pulp is transferred to the column, and, with an up-and-down motion of a plunger (glass rod flattened at one end), any lumps in the cellulose are broken down. The pulp is pressed down to form a smooth unbroken column. This operation is continued until the height of the pulp is 2 in. Approximately 10 g of activated alumina, previously soaked in the ether–nitric acid solvent, is transferred to the top of the column and pressed down lightly. The stopcock is opened, and the solvent is drained to the upper level of the alumina. The column is washed with 50 ml of the ether–nitric acid solvent, and again the ether–nitric acid solvent is drained to the upper level of the alumina. The effluent is discarded.

Sufficient cellulose and/or alumina to absorb the liquid is added to the sample solution. The mixture is transferred to the top of the column, and the beaker is washed with ether–nitric acid solvent and drained thoroughly. The stopcock is opened, and the effluent is received at the rate of about 10 ml/min in a suitable container. About 20 ml of ether–nitric acid solvent is poured into the original sample beaker, the liquid is swirled around the sides of the beaker, and, when the liquid in the tube reaches the top of the alumina, the ether–nitric acid solvent is added to the column. The lip of the beaker is inverted over the top of the column, and the lip is washed with a jet of ether–nitric acid solvent. The addition of about 20 ml of ether–nitric acid solvent to the beaker is repeated, and this is added to the tube each time the level of the solution reaches the top of the column. In all, 180 ml of ether–nitric acid solvent is collected. Fifty milliliters of water is added to the effluent, and the ether is evaporated on a water bath. When the ether has been expelled, the aqueous solution is evaporated on a hot plate to about 20 ml and is transferred to a tared fused-silica or platinum evaporating dish. The solution contained in the evaporating dish is evaporated to dryness. The dish is transferred to a cold muffle furnace, the temperature is raised gradually to 500°C, and the contents of the dish are finally ignited at 900°C for 1 hr.

A variation of the column technique is the decantation method.[228] Activated cellulose is added to a beaker containing 10 ml of 25 per cent nitric acid solution of the sample, and the uranium is extracted by stirring the pulp with ether containing 5 per cent nitric acid, and the solvent is decanted through a filter paper in a silicone-treated funnel. The extraction is repeated with three more portions of the ether–nitric acid solvent. The method is valuable for those samples giving a large amount of gelatinous silica. There are slightly greater amounts of the more mobile elements which go into the ether fraction. The method has not had as wide application as the cellulose–alumina column method.

(b) *Paper-strip Chromatography.* The application of paper-strip chromatography to the separation of uranium was first advocated by Linstead and coworkers.[229] They found that uranyl nitrate could be selectively extracted by an organic solvent containing nitric acid when the extraction was carried out on a strip of absorbent paper. The organic-solvent mixture is allowed to diffuse by capillary action through the paper, and, when solvent movement takes place over a patch of the paper previously treated with a sample of the solution to be tested, uranyl nitrate is dissolved and moves with the solvent front as diffusion proceeds. A wide variety of solvents which dissolve uranyl nitrate could be used, but the best results were obtained with 2-methyltetrahydrofuran and tetrahydropyran.

Thorium is partially extracted and moves with the uranium. Large amounts of phosphate did not interfere after complexing with ferric nitrate. Moderate amounts of chloride, sulfate, oxalate, and acetate did not interfere in the presence of a high concentration of nitrate. This method was later applied [230] to the separation of uranium prior to a polarographic determination. A rather complete investigation of this technique was reported [231] in 1950. This technique was later applied to geochemical prospecting.[232] The technique was modified to use 1.5- by 9-cm strips of Whatman No. 1 filter paper. The solvent used was ethyl acetate containing 10 vol. % of nitric acid and 5 vol. % of water. The uranium is extracted in the solvent front. Many applications of this type technique have been made for the estimation or detection of thorium, uranium, and plutonium. Among the various solvents used are dioxane-antipyrine for the analysis of monazite [233] and 2-butanone from a 5 per cent hydrochloric acid for radioisotopes of uranium,[234-237] specifically U^{233}. Other solvents used have been 2-methyltetrahydrofuran [238] and ether, ethanol, and nitric acid.[239] Uranium has been determined in rocks,[240] in deep-sea sediments,[241] in natural waters after a phosphate separation,[242] and in uranium–plutonium mixtures.[243] As would be expected most procedures have dealt with microgram quantities of uranium. The following procedure is indicative of the type used.

Procedure.[232] A 1-g sample powdered to pass an 80-mesh screen is weighed into a small platinum dish, and 2 ml of nitric acid of sp. gr. 1.42 and 2 ml of 40 wt. % hydrofluoric acid are added. The dish is placed on a water bath, and the contents are evaporated to dryness. One milliliter of diluted nitric acid (1+3) is added and the mixture is stirred with a glass rod. The mixture is allowed to cool and settle. With a capillary pipet 0.05 ml of the clear supernatant liquid is applied to the end of a paper strip cut from a sheet of Whatman No. 1 filter paper. The sample spot is allowed to dry for 1 hr in air. Twenty milliliters of the solvent is prepared by shaking 2 ml of nitric acid (sp. gr. 1.42) and 1 ml of water

with 17 ml of ethyl acetate; the solvent is then poured into a 600-ml beaker covered with a Petri dish.

The paper sheet is rolled and clipped to form a cylinder and is placed in the solvent beaker with the sample spots at the bottom. The solvent is allowed to diffuse upward almost to the top of the strips; then the sheet is removed from the beaker, and the solvent is allowed to evaporate in air. The sheet is spread flat and sprayed lightly on both sides with a 5 per cent aqueous solution of potassium ferrocyanide. The sheet is allowed to dry and is then compared with standard uranium chromatograms.

The uranium can also be determined by spectrophotometric, radiometric, fluorometric, or polarographic means.

(c) *Silica Gel Column.* The chromatographic separation of U(VI), Pu(VI), and Pu(IV) from Zr^{95} and Nb^{95} on a silica gel column has been described.[244] Separations can be carried out from aqueous as well as organic solutions using methyl isobutyl ketone with the nitrates of the above. The Zr^{95} and Nb^{95} are retained on the silica gel.

1–3 METHODS OF DETERMINATION

Gravimetric methods for uranium require, in general, the absence of, or the prior separation of, numerous other elements. They are used chiefly when macroamounts of uranium are available. The normal weighing form is the oxide U_3O_8. This compound is formed upon proper ignition of any one of the following precipitates: ammonium diuranate, uranous fluoride, uranium dioxide, uranium peroxide, uranous oxalate, uranous cupferrate, and uranyl oxinate. Many other precipitates formed by organic reagents on ignition also give U_3O_8. Since many of the procedures used for gravimetric determination are also used for separations, Sec. 1–2.1 should be consulted.

Titration procedures are generally considered to be the most satisfactory ones for the estimation of macroquantities of uranium. Microtitrations can be performed satisfactorily, but spectrophotometric methods and other optical or electrical methods are generally preferable for the estimation of small quantities of uranium. Methods based on the prior reduction of uranium to the U(IV) state have been utilized most frequently. If U(III) is formed during the reduction, aeration serves to convert U(III) to U(IV) prior to the titration. Any one of the oxidants potassium dichromate, ceric sulfate, ferric chloride, or ferric sulfate can be used for the titration in the form of a standard solution. The prior separation of iron, vanadium, titanium, and the hydrogen sulfide metals, especially arsenic, antimony, and molybdenum, is generally necessary. Nickel may interfere with the reducing action of the Jones reductor,[245] but it will not interfere in other methods of reduction. The use of a lead reductor obviates the necessity of oxidizing U(III) since U(IV) alone is formed.

Titrations of uranyl solutions with strong reductants such as chromous or titanous solutions are possible.

Spectrophotometric estimations have been extensively used for the determination of small percentages of uranium, ranging from about 1 per cent down to a few thousandths of 1 per cent or in the concentration range of from several hundred to a few micrograms per milliliter. Of the many spectrophotometric methods, the most sensitive ones are, in general, applicable only to uranium solutions that are substantially pure.

Under optimum conditions as little as 10^{-11} g of uranium in a sodium fluoride bead can be detected by its characteristic fluorescence under ultraviolet radiation. The intensity of the fluorescence can be measured with the aid of suitable filters and a photoelectric photometer. The method has been used extensively for various problems involving trace estimations, including biochemical studies.

The intensities of the various relatively strong lines in the emission spectrum of uranium are too low to make this method as effective as certain other methods for traces of uranium.

Amounts of uranium ranging from 1 mg down to 1 μg can be estimated polarographically. In general, a considerable amount of prior separation is necessary.

Radiation-counting methods are of primary importance with material in which the natural ratio of the uranium isotopes has been altered; they are also important in the chemistry of fission products. Counting methods based on the radium content of uranium ores and minerals have been utilized, especially where thorium was known to be absent.

1–3.1 Gravimetric Methods

Gravimetric methods of analysis are still used to a considerable extent for the determination of uranium, especially by weighing the uranium as U_3O_8 after an ether extraction or after separation with tannin, followed by an ammonium hydroxide precipitation. The precipitates formed with ammonium hydroxide, pyridine, hydrogen peroxide, cupferron, tannin, 8-quinolinol, and oxalate and U(IV) can be ignited to the oxide.

The chief problem with the gravimetric oxide determination is the determination of the temperature of ignition which will form U_3O_8 and not some other oxide containing more or less oxygen. Various temperatures, ranging from 800 to 1200°C, have been suggested. From work done at New Brunswick Laboratory on the stoichiometry of U_3O_8, it appears that at sea level or thereabouts the temperature for ignition should be 850 to 900°C. (Some work at Los Alamos Laboratory at altitudes of about 7000 ft indicates that a temperature of 750°C

might be more suitable.) At lower temperatures more oxygen than the theoretical is present; whereas at temperatures over 900°C an oxygen-deficient compound is obtained. The New Brunswick Laboratory work was performed under conditions normally employed in the laboratory, i.e., heating slowly to about 700°C and then at 850 to 950°C for 2 hr, removing from the furnace, and cooling in a desiccator. The type of compound and its previous history may be of importance. Ammonium diuranate, uranium peroxide, and uranyl or uranous oxalate are readily converted. On the other hand oxide that has been prepared by the ignition of uranium trioxide that contained nitrates could not be converted entirely into U_3O_8 without previous treatment with hydrofluoric acid.

The oxide ignited at 900°C does not appear to be hygroscopic. There is some increase in weight over a period of time which appears to level off at about 0.1 to 0.2 per cent.

Ammonium diuranate, other uranium oxides, uranium nitrate, certain halogen compounds such as uranium tetrafluoride, and organic compounds yield U_3O_8 when heated with free access to air under the conditions stated above. In general, the compounds should be heated slowly. Organic compounds, especially those containing cupferron, should be heated cautiously to avoid mechanical loss or volatilization. The old procedure of covering a compound with oxalic acid before ignition aids in reducing mechanical losses when heating organic compounds. Platinum crucibles are generally preferred to silica or porcelain since some attack of ceramic ware may occur. Under no conditions should the cacodylate [238] be ignited in platinum because the arsenic will react with the platinum. Needless to say this compound should be ignited under a hood because of the liberation of arsenic compounds. No detailed procedures are given for the precipitation and ignition of uranium compounds that can be ignited to U_3O_8 since they are covered under Sec. 1–2.1.

It appears to be the general practice [246] when tannin is used as a precipitant to ignite the precipitate, dissolve the residue in nitric acid, and precipitate the uranium with ammonium hydroxide. The ammonium uranate is ignited to U_3O_8. Uranyl nitrate from an ether extraction is generally ignited to U_3O_8.

The gravimetric determination of uranium as $(UO_2)_2P_2O_7$ is rarely used at present. Other weighing forms for uranium have been suggested, such as $UO_2(IO_3)_2$,[247] cacodylate,[238] and 8-hydroxyquinaldinate $UO_2(C_{10}H_6NO)_2C_{10}H_9NO$.[248] About the only other uranium compound used for a gravimetric determination is uranyl 8-hydroxyquinolate. This compound is dried at 130°C for 2 hr and weighed as $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. It has been stated that at 290 to 380°C, $UO(C_9H_6NO)_2$ is formed.[249–252]

1–3.2 Volumetric Methods

The general volumetric methods for determining uranium are (1) reduction to the quadrivalent state and titration with a standard oxidizing solution, (2) titration of uranyl salts with a precipitating agent such as standard phosphate, ferrocyanide, or alkali, and (3) precipitation of a uranium compound such as the 8-hydroxyquinoline derivative and titration of the precipitating agent carried down. The first method is by far the most common and, in general, the most accurate. The second method is rapid and can be used when approximate results are satisfactory. An attractive feature of the third method is that 12 equivalents of bromine are required to titrate 1 mole of uranium. In a recent publication [253] a method is described in which U(VI) is reduced to U(III) with a Jones reductor in a hydrochloric acid medium.

In many instances, if only the U(IV) content is desired, the sample can be dissolved with the aid of ceric sulfate or ferric salts. The ferrous or cerous ion that is formed, which is equivalent to the U(IV) content, is then titrated in the usual manner. This method is applicable only to certain substances, e.g., UO_2, U_3O_8, UF_4, and UCl_4.

Although uranyl solutions can be titrated directly with standard titanous or chromous solutions, reductimetric procedures are rarely used owing to the rigid precautions required to preserve the standard reductants.

The reduction of uranium is generally accomplished with zinc or lead. Occasionally chromous ion, titanous ion, or electrolytic methods are used. Only in a very few instances is the silver reductor used. With zinc or with electrolytic reduction, a mixture of trivalent and tetravalent uranium is generally obtained. The trivalent uranium is usually oxidized to the tetravalent state by a current of air although occasionally in some potentiometric titrations an oxidant may be used. In the case of the lead or silver reductor, it appears that only tetravalent uranium is found although with the silver reductor carefully controlled conditions must be used. Only rarely is liquid amalgamated zinc employed.

The most common oxidizing agents used for titrating reduced uranium are potassium dichromate or ceric sulfate. Occasionally ferric sulfate is used. End points can be detected either by indicators or by electrometric means. In general, a precision of 1 part per 1000 is obtained when a sample containing 100 mg of uranium is used. When amounts of uranium less than 10 mg are used, the reductors are reduced in size, and microburets are employed. As little as 0.1 mg of uranium has been determined with a precision of ± 2 per cent by titration with dilute ceric sulfate [254–256] or potassium dichromate.[257]

The choice of titrants depends to a great extent on personal preference but includes such factors as speed of reaction at room temperature, effect of catalysts such as phosphoric acid, effect of interfering substances, the stability of the titrant, and the accuracy desired. Room-temperature titrations carried out in the presence of excess iron and/or phosphoric acid or by the addition of an excess of oxidant followed by back-titration with ferrous sulfate are quite satisfactory. The visual end point may be more sensitive in titration with ceric sulfate than with potassium dichromate, but there is less warning of the approach of the end point with ceric sulfate. Potassium dichromate has the advantage of being a primary standard. Most titrations with ferric solution must be made at elevated temperatures and must be protected from air oxidation. This titration has the advantage that samples containing iron can be analyzed without a separation step.

(a) *Reduction of Uranyl Solutions.* The reduction of uranyl solutions to the tetravalent state is a prerequisite for most volumetric methods for the determination of uranium. Of the numerous methods proposed, the ones employing amalgamated zinc or lead are used to the greatest extent.

(1) *Solid-zinc-amalgam Reduction (Jones Reductor).* One of the common ways of reducing uranyl solutions is with amalgamated zinc.[64, 258] In this reduction a mixture of trivalent and quadrivalent uranium is obtained. The reduction must be followed by aeration or other oxidation steps [259] to oxidize the U(III) to U(IV).

Before a Jones reductor is used, it is advisable to review one of the standard reference books, such as Hillebrand, Lundell, Bright, and Hoffman,[260] which consider interferences, techniques of handling (such as avoidance of air in the reductor), the question of hydrogen peroxide formation, and the preparation of the reductor. The amount of amalgamated zinc used in a reductor varies with the amount of uranium in the sample being analyzed.

Large reductors are used for low-grade ore samples to eliminate interferences of traces of some metals by letting them plate out in the upper part of the reductor. Solutions can be passed through large reductors at the rate of 60 ml/min, but more washing is required than for the small reductors. The washing is more efficient if each wash is allowed to drain to the top of the zinc column before the next wash is added. Air should not be allowed to enter the column.

It has been stated that traces of hydrogen peroxide are formed when air reacts with the zinc amalgam, but there is no evidence that this occurs with sulfuric acid solutions. Furthermore, hydrogen peroxide is completely destroyed when a sulfuric acid solution of it is passed through a zinc amalgam reductor.[261, 262]

Sulfate and perchlorate solutions are most commonly used for reduction by the amalgamated zinc in the Jones reductor. Chlorides are also satisfactory if precautions are taken to prevent interference in the titration. Other anions that cause negligible interference are borate and fluoborate.

Microquantities of uranium can be reduced in a small Jones reductor containing a column of zinc about 50 mm in length and 7 mm in diameter. Use of a stopcock can be avoided by having a sintered-glass disk sealed into the bottom of the tube. The uranyl solution, 2 to 10 ml, is drawn through the reductor with suction; no liquid flows otherwise.[254] Other small reductors have been used by Kennedy and Kaufmann.[237]

Substances other than uranium that are reduced by zinc and subsequently titrated must be absent.[66] Nitrates and nitrites are partially reduced to substances such as hydroxylamine which are oxidized by the titrant. Nitric acid or nitrates are often held tenaciously and cannot be removed completely by washing the precipitates or even in some instances by double fuming with sulfuric acid.[88, 263] Acetates in large quantity lead to somewhat high results and are also surprisingly difficult to remove by fuming with sulfuric acid. Polythionic acids, which are sometimes introduced by the prior removal of a metal with hydrogen sulfide, also interfere in the titration. Organic matter, particularly that which is easily oxidized, must be removed. This includes formates, oxalates, tartrates, and alcohol. The solution usually is fumed with sulfuric acid in the presence of potassium permanganate, perchloric acid, or ammonium persulfate, to remove these substances. Ions such as fluorides, oxalates, and hypophosphates which precipitate U(IV) should be absent.[257] The presence of 0.3 to 0.4 g of phosphoric acid per sample of 0.4 to 0.5 g of uranium had little or no effect on the result obtained for uranium.[257] However, if the phosphate content is appreciably greater than this, uranium phosphate precipitates in the Jones reductor and in the reduced solution and gives low values. Phosphate retards the reduction of uranium solutions. Samples that contain 0.1 to 0.5 g of phosphoric acid are increasingly difficult to reduce, and those that contain 1.0 g of phosphoric acid are virtually impossible to reduce satisfactorily. Schreyer and Baes,[264] however, have used a Jones reductor with phosphate solutions in 4.5*M* sulfuric acid to prevent precipitation of uranium phosphate. The addition of large amounts of phosphoric acid [264] as a means of preventing the production of U(III) was not confirmed.[265] The rate of reduction from U(VI) to U(IV) was markedly decreased by phosphoric acid.

There is no interference from the more electropositive metals such as the alkali metals, small amounts of ammonium ion, the alkaline earths, beryllium, aluminum, thorium, and the rare earths, with the

exception of europium. The latter is reduced in the Jones reductor and might be incompletely oxidized by aeration; the low solubility of europous sulfate might also cause trouble.[266] Zirconium, cobalt, zinc, and manganese are also permissible. Metals that may plate out on the zinc and interfere if present in excessive quantities include nickel, cadmium, copper, silver, gold, mercury, arsenic, antimony, bismuth, tin, lead, selenium, tellurium, and platinum. The reductor should be replaced when it begins to show darkening or if it liberates hydrogen readily. Nickel can be tolerated only in amounts less than about 300 mg in a reductor that contains 180 g of zinc amalgamated with approximately 2 wt.% mercury.[245] The plating out of the nickel is accompanied by excessive evolution of hydrogen and incomplete reduction. However, Grimaldi [267] has found that a 10 wt.% mercury amalgam reductor is not poisoned by nickel-bearing solutions; even after 5 g of nickel had passed through, no nickel was found plated out in the reductor. Either hydrochloric or sulfuric acid solutions can be used. The valence changes during the reduction of uranium, iron, vanadium, titanium, and molybdenum are the same for the 10 wt.% reductor as for the 2 wt.% reductor. This amalgam is prepared by shaking 180 g of 20-mesh zinc for about 2 min with 400 ml of a solution containing 23.6 g of mercuric chloride and 10 ml of nitric acid.

Metals that are reduced by the reductor and that interfere in the titration by consuming the oxidizing agent are iron, tin, molybdenum, vanadium, tungsten, and niobium. Titanium and chromium may also be included in this group, but the aeration step completely oxidizes Ti(III) to Ti(IV) and Cr(II) to Cr(III) unless they are present in excessive amounts.

Reductor Preparation. An approximately 2 wt.% amalgam is prepared as follows: 180 g of 20-mesh c.p. zinc is cleaned by washing with 100 ml of nitric acid (1+200) and rinsing three times with water; then it is activated by washing with sulfuric acid (1+19) for about 10 sec. After the zinc has been rinsed rapidly with three 100-ml portions of water, it is amalgamated immediately by stirring for 10 min with 100 ml of 3.6 per cent mercuric chloride solution (23 6 g of mercuric chloride per 400 ml of solution) containing a drop of sulfuric acid. The solution is removed by decantation, and the amalgam is washed several times with sulfuric acid (1+100). The reductor tube, about 16 mm in diameter, is filled with water, the amalgam is introduced about an inch at a time, and each portion is gently tapped in place with a glass rod.

Procedure. A new reductor, or one that has been idle for some time, is washed with four or five 30-ml portions of sulfuric acid (1+19). A clean flask is attached to the reductor, and the sample solution, which contains as much as 17 mg of uranium per milliliter in sulfuric acid (1+19), is drawn through the amalgam at a rate of 15 ml/min. The column is washed with five 30-ml portions of sulfuric acid (1+19) and then with 30 ml of water. Each wash is allowed to drain to the top of

the amalgam before the next is added. (Do not allow the wash to drain below the surface of the amalgam.) This procedure leaves less than 0.05 mg of uranium in a column 19 mm in diameter and 20 cm in length. The rate of flow and amount of washing used vary with the size of the column, the uranium concentration, and the precision desired. For example, with a 25-mm reductor containing 700 g of a .3 wt. % amalgam, the solution can be run through at a rate of 75 ml/min.

(2) *Liquid-zinc-amalgam Reduction.* Liquid zinc amalgams reduce uranyl salts to the uranous condition as do the solid amalgams. However, as reported by Nakazono,[268] hexavalent uranium can be quantitatively reduced to the quadrivalent form by shaking it with a saturated mercury–zinc liquid amalgam in an atmosphere of air. Princeton workers [269] recommended shaking the 5 to 15 per cent sulfuric acid solution of uranium with 5 ml of liquid zinc amalgam for 5 min and separating the amalgam as suggested by Nakazono. Other workers [270] found that 6 wt. % sulfuric acid gave low results but that 10 wt. % sulfuric acid was satisfactory. The interference of nickel and other metals that plate out in the Jones reductor can be avoided by using fresh amalgam for each sample; this is practicable owing to the ease of regenerating the spent amalgam. Microquantities of uranium are also quantitatively reduced to the quadrivalent state by liquid zinc amalgam, but the reduction conditions are critical.[256, 271] With a microtechnique, reduction in air gave a blank, which was apparently due to hydrogen peroxide and was equivalent to about 5 parts of hydrogen peroxide per million parts of solution; [256] a blank equivalent to 8 ppm of uranium was obtained on a macroscale.[269] The microreduction blank obtained in air varies as much as 50 per cent, but, in a carbon dioxide atmosphere, it becomes reproducible and much lower. It can be eliminated entirely if the reduction is followed by a permanganate treatment and then by another reduction, all under carbon dioxide.[256] In the determination of 0.1 to 1.0 mg of uranium in the presence of 20 μg of chromium, increasing amounts of chromium appear to have an increasing inhibitory effect on the reduction of uranium to the quadrivalent state by liquid zinc amalgam.[271] At the present time only occasional use is made of liquid zinc amalgam for the analysis of uranium.

(3) *Silver.* Birnbaum and Edmonds [272] reported that uranium in hot 4*M* hydrochloric acid solution is reduced quantitatively to quadrivalent uranium in the Walden silver reductor. The high acidity raises the U (VI)/(IV) potential; the high chloride concentration lowers the Ag/AgCl potential. There is also evidence that dissolved oxygen may be reduced to form traces of hydrogen peroxide during reduction.[273]

The silver reductor reduces iron, copper, molybdenum, and vanadium but not titanium or chromium. Acetates do not interfere, but nitrates should be absent. Small amounts of silver chloride dissolve in the strong acid and precipitate after dilution, but this does no harm. Unless the procedure is carefully controlled, the results have a tendency to be low owing to aging of the silver column or possibly to exposure to air of the hot reduced acidic solutions before titration. In a modification [274] to prevent the latter, the reduced solution was chilled by attaching a coil condenser immediately below the hot reductor and leading the solution directly into an excess of oxidizing agent. This procedure required that the sample solution be passed through the reductor at a rate of only 3 to 4 ml/min. The precision did not appear to be improved. The silver reductor is rarely used at present for the determination of uranium.

(4) *Lead.* Although Koblic [275] showed in 1925 that lead reduces uranyl salts to the U(IV) state in hydrochloric acid, Bacon and Milner [282] indicated that some U^{+3} is found in solutions from the lead reductor. No extended use of this method was made until Cooke, Hazel, and McNabb [276] applied it to the determination of uranium. (It is not necessary to amalgamate the lead since little or no hydrogen is liberated with acids.) They used a 3*N* hydrochloric acid solution and caught the U(IV) in a 5 wt. % ferric sulfate solution. They used a 25- by 2-cm reductor. Sill and Peterson [277] applied this method to the analysis of milligram quantities of uranium. Sulfate solutions cannot be used because they form an adherent film of lead sulfate, which decreases the efficiency of the reductor. The addition of hydrochloric acid, however, prevents this film formation.[276] Although Cooke, Hazel, and McNabb state that no precautions in regard to air in the reductor need be taken (in fact they state solutions can be run through an air-filled reductor), conflicting statements are found. From the work of Sill and Peterson,[277] it appears that hydrogen peroxide may be formed more readily with the lead reductor than with the Jones reductor if air is allowed to enter the reductor. It is advisable, to be on the safe side, not to allow air bubbles to enter the reductor. The lead reductor has been widely used in the analyses of ores,[278] uranium–zirconium alloys,[279] uranium–thorium alloys,[280, 281] uranium–aluminum alloys,[282] bismuth-base alloys,[283] and other alloy systems. Phosphate in small amounts does not interfere.[284] Nickel does not interfere as with the Jones reductor, but other elements not plated out in the reductor interfere as with the Jones reductor. It appears [285] that perchloric acid in the presence of as much as 50 ppm or more of molybdenum causes erratic results with the lead reductor. In practically all methods ceric sulfate is used as the titrant.

Reductor Preparation.[277] Reagent-grade granulated lead is screened successively through 20- and 100-mesh screens. The middle fraction, that is, the fraction passing through the 20-mesh but not the 100-mesh screen, is then packed into a 12-mm-bore reductor tube sufficiently long to give a 30-cm column of lead. Because the lead is very difficult to remove from the reductor tube, it is advisable to place a 1-cm plug of glass wool at the top of the column as well as at the bottom to protect the column from contamination. A piece of thin-walled rubber tubing should be used on the aspirator to prevent oxygen dissolved in the solutions from building up in the lower part of the column under greatly reduced pressure. A reductor of this size is sufficient for reducing any quantity of uranium likely to be encountered in analytical work. The use of conventional reductor tubes of larger bore results in an undesirable increase in the volume in which the titration must be made but does not affect the extent of the reduction. Hence, the use of reductors larger than that described is to be discouraged.

The size of the lead particles will have a pronounced effect on the rate of reduction. With a 30-cm column of 20- to 35-mesh lead, the reduction of 25 mg of uranium was incomplete when the solution was much below room temperature or was passed through the column very rapidly. The reductor recommended produces complete reduction of uranium over a wide range of conditions, and no instance of over-reduction has been observed. Undoubtedly, either granulated lead or test lead can be used directly as obtained if standard screens are not available. However, a sample of test lead contained such a high proportion of very fine particles that passage of the solution through the column was extremely slow. A 20- to 65-mesh fraction of the material was found satisfactory.

The reductor is preserved under distilled water when not in use. A plug of glass wool is used at the top of the column. When ready to be used, the column is washed thoroughly with 3*N* hydrochloric acid containing a little ferric iron. After the reductor has been washed free of iron with 1*N* hydrochloric acid, a blank is run under the conditions of the determination. If the blank is appreciably higher than the indicator blank when reagent-quality chemicals are used, it must be repeated until it has decreased to the proper value before the reduction of uranium solutions is attempted. It is recommended that a titration of a small known quantity of uranium also be included. If the value after correction of the blank deviates from the theoretical by more than 0.02 ml, contamination of the reductor is indicated. The top of the lead column may become black with use. This deposit will do no harm so long as it is not too extensive.

Procedure.[277] The solution to be analyzed for uranium should have a volume of 80 ml and should contain 20 ml of hydrochloric acid. The solution is reduced by passing it through an air-free lead reductor at a rate of about 100 ml/min at 25°C. The flask and reductor are washed with 80 ml of 1*N* hydrochloric acid, used in small portions to obtain maximum washing efficiency. The last portion of the hydrochloric acid wash should be replaced by water only when the reductor is not to be used for 2 or 3 hr or more.

Steele and Taverner[76] and Steele[214] reduce uranium by boiling a perchloric acid solution with granular lead. The solution is cooled

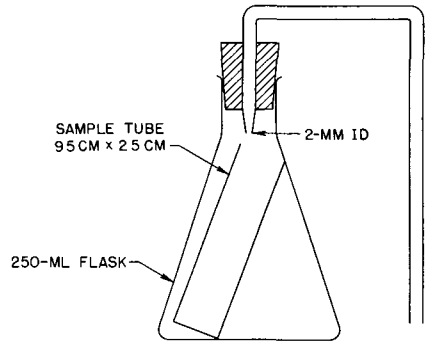


Fig. 1.23—Apparatus for the reduction of uranium. (From Steele, *The Analyst*, Ref. 214.)

under an atmosphere of carbon dioxide and then titrated with potassium dichromate. The procedure allows a number of samples to be analyzed at one time.

Procedure.[214] After a cupferron extraction of interfering elements from a perchloric acid solution (1+3), the organic matter is destroyed by fuming after the addition of 2 ml of nitric acid, cooling, and fuming again. The fuming is repeated to remove the nitric acid. The volume of perchloric acid is reduced to 15 ml by evaporation. It is diluted to about 40 ml, boiled for 1 min to expel chlorine, transferred to a wide-necked 250-ml conical flask, and diluted to 60 ml. A 5-g quantity of granulated lead is added, and a sample tube (Fig. 1.23) containing a piece of marble about the size of a split pea and about 15 ml of diluted perchloric acid (1+1) is inserted into the flask. The flask is stoppered with a rubber stopper carrying a delivery tube and is placed on a hot plate. The solution is then boiled gently for 20 min. The volume should not be reduced by more than about 5 ml during the boiling. The end of the delivery tube is dipped into about 15 ml of 20 wt. % sodium carbonate solution in a test tube without interrupting the boiling. The flask is then cooled in running water. Carbon dioxide is evolved when the sodium carbonate solution is sucked back into the sample tube containing the dilute perchloric acid. When it has cooled, the delivery tube is removed, the sides of the flask are washed down, and the solution is decanted into a 500-ml conical (Phillips) beaker. The lead is not allowed to enter the beaker. The lead is then washed with three or four 10-ml portions of 1 vol. % perchloric acid solution, and the washings are decanted into the beaker. The titration step is made without delay.

(5) *Cadmium.* Cadmium acts as a milder reducing agent than zinc. In one instance small crystals, prepared electrolytically, were used to pack a reductor; a column 70 mm in height was sufficient.[286, 287] In $3N$ sulfuric acid uranyl salts were reduced to U(IV), and only traces of U(III) were formed. The precautions necessary with zinc reductors were observed. Iron, titanium, molybdenum, vanadium, tin,

niobium, chlorates, and other ions were reduced. For small quantities of uranium (10 mg), a pointed cadmium rod served to reduce the metal at 100°C in a centrifuge tube.[288]

Cadmium amalgams can be prepared in the same fashion as the liquid zinc amalgams and can be used to reduce uranyl solutions in an analogous way, only a little trivalent uranium being formed.[289-292] An atmosphere of carbon dioxide in the reduction vessel was recommended.

Bricker and Sweetser[293] used a 90 wt. % cadmium amalgam with a 2*N* sulfuric acid solution for reduction of U(VI) to U(IV). The 90 wt. % cadmium reductor was prepared from fine cadmium filings (20 g of 30- to 60-mesh) which were washed with 1*N* hydrochloric acid and then treated with the proper amount of 2 wt. % mercuric chloride solution to make the amalgam 90 wt. % cadmium. The resulting amalgam was washed thoroughly with 1*N* hydrochloric acid and then tightly packed into a column of 0.5-cm diameter, giving a reductor with a total height of approximately 20 cm. Very dilute sulfuric acid was kept in the column when the reductor was not in use.

The 90 wt. % cadmium reductor was washed before each run with 20 to 30 ml of 2*N* sulfuric acid. If the reductor had not been used for a considerable period of time (overnight or longer), the reductor was washed with 100 ml of the dilute sulfuric acid. An additional 30 ml of the 2*N* acid usually gave no detectable blank titration. Occasionally it was found advisable to wash the reductor with 2*N* hydrochloric acid or 2*N* perchloric acid, followed by 2*N* sulfuric acid.

The uranium sample, if not present as the sulfate, is evaporated with a slight excess of sulfuric acid to fumes of sulfur trioxide and is then dissolved in 2*N* sulfuric acid. An aliquot, of appropriate size, of the resulting solution is passed through the reductor at a rate of about 4 ml/min and, the reductor is then washed with 30 ml of 2*N* acid. The last 20 ml of the wash acid may be passed through the reductor at a much greater rate than specified for the uranium solution.

(6) *Mercury.* In solutions containing hydrochloric acid in sufficiently high concentration, uranyl ion is almost quantitatively reduced to U(IV) ion in a mercury reductor.[294]

(7) *Copper.* It has been reported[295] that, when uranyl sulfate is boiled in 3*N* to 4*N* sulfuric acid with a copper spiral in an apparatus from which air has been excluded, complete reduction to the quadrivalent state takes place in 20 to 45 min.

(8) *Aluminum and Magnesium.* When a uranyl sulfate or uranyl chloride solution that is slightly acid is boiled with either magnesium or aluminum metal, reduction to U(IV) and U(III) occurs.[258] Air must be excluded after all the reducing metal is dissolved to prevent oxidation of the warm solution during cooling. Aluminum in the

form of a spiral [296, 297] is convenient, or the aluminum can be suspended in a glass basket in a flask closed with a rubber stopper holding a Bunsen valve.[298] The method has been used chiefly for the qualitative analysis of uranium although Mechelynck and De Conde [299] have used an aluminum plate for uranium–aluminum alloys.

(9) *Bismuth.* Liquid bismuth amalgams can be prepared similarly to zinc amalgams, and they reduce uranyl salts in either hydrochloric or sulfuric acid.[300, 301] Little if any trivalent uranium was found. Paley [168] reported that bismuth was used for the reduction of U(VI) to U(IV). The reduction occurs more rapidly in more acidic solutions. Perchloric acid appears to prevent complete reduction to U(IV) in a bismuth reductor.[302]

(10) *Stannous Chloride.* Kern [258] used stannous chloride to reduce uranyl salts but had difficulty in removing the excess. Main [303] used 2.00 ml of 0.02*N* iron(III) solution to catalyze the reduction of U(VI) with stannous chloride. It was necessary to heat the solution and remove the excess stannous chloride in the usual manner with mercuric chloride. The indicator correction blank was quite large, in some instances amounting to 10 per cent of the total volume used. Phosphoric acid aided in the reduction. The stannous chloride reduction procedure of Main with minor modifications has been used [285] for the analysis of uranium materials carrying as much as 6 wt. % molybdenum. The molybdenum is determined separately, and the results are corrected accordingly. The results indicated better recovery than was obtained with the Jones reductor when greater than 50 parts of molybdenum per million was present. Although the method may be of use in routine analysis, for precise work the Jones or lead reductor, following separations of interfering elements, is preferred.

(11) *Chromous Solution.*[304, 305] Chromous sulfate can be used for the reduction of uranyl ion to the quadrivalent state prior to a potentiometric titration. It lessens the time required for reduction and allows titration in a smaller volume than usual, with consequent improvement in end points and in the rate of attainment of potential equilibrium. Cupric, silver, lead, stannous, bismuth(III), mercuric, and antimonous ions are reduced to the metallic state by chromous ions, whereas cadmium, ferrous, cobaltous, nickelous, manganous, aluminum, and zinc ions are not. A solution containing 500 mg of uranium and no interfering ions can be reduced with chromous sulfate and titrated potentiometrically with ferric sulfate with a precision better than ± 0.1 per cent. The chromous solutions can be stored under a carbon dioxide atmosphere or over zinc amalgam. The length of time that the chromous sulfate is in contact with the zinc amalgam seems to affect the sensitivity of the indicator platinum electrode dur-

ing the titration; the sensitivity with solutions that had been stored over zinc amalgam for 3, 10, and 21 days was good, poor, and very poor, respectively.

Procedure.[304, 305] A saturated chromous sulfate solution, 5 vol. % in sulfuric acid, is prepared by boiling chromic sulfate solutions over liquid zinc amalgam. The solution is stored under a carbon dioxide atmosphere. The sample solution in 5 vol. % sulfuric acid is placed in the titration cell and heated to 95°C under carbon dioxide with stirring. The saturated chromous sulfate solution is added until the cell potential becomes more negative than −0.200 volt. The sample is then titrated potentiometrically with ferric sulfate.

Lingane and Pecsok [306] give a simple technique for preparing standard chromous sulfate solutions by complete reduction of chromic ion in very dilute sulfuric acid with zinc. The solution is stored under hydrogen and is stable for weeks. Figure 1.24 shows the apparatus used. The zinc used must be very pure and of the mossy type. Before use, the zinc is amalgamated with about 1 wt. % mercury by stirring it in a mercurous chloride solution for a few minutes and then in

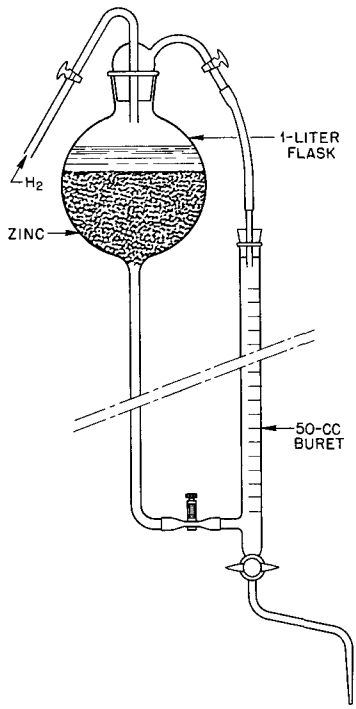


Fig. 1.24—Apparatus for preparation, storage, and dispensing of standard chromous sulfate solutions. (From Lingane and Pecsok, *Analytical Chemistry*, Ref. 306.)

dilute hydrochloric acid and then washing it with water. Potassium dichromate is reduced first with hydrogen peroxide. After the reduced potassium dichromate solution has been heated until the evolution of oxygen ceases, it is cooled and then reduced to the chromous state in the apparatus shown in Fig. 1.24.

Of interest is the work of Cooke, Hazel, and McNabb,[307] who reduced uranyl ion to U(IV) with an excess of chromous chloride. The excess of chromous chloride is destroyed by air oxidation; phenosafranine is used as the indicator to follow the reduction and the air oxidation. Ferric sulfate is added, and the ferrous ion is titrated with dichromate.

> *Procedure.* Solutions containing 1 to 25 mg of uranium are diluted to 5 to 25 ml. Sulfuric acid is added until the solution is 3*N*. The temperature of the solution is kept below 20°C. A pea-sized piece of solid carbon dioxide and approximately twice the theoretical amount of 0.5*N* chromous chloride (prepared by shaking 0.05*N* chromium chloride in 1*N* hydrochloric acid with 15 ml of 2 wt. % zinc amalgam until blue) are added. The solution is allowed to stand about 2 min, and then 2 drops of phenosafranine (0.025 wt. % in water) are added (the phenosafranine is decolorized which indicates an excess of chromous ions). Filtered air is bubbled through the solution at least 1 min to ensure complete oxidation of excess chromous to chromic ions, and 1 ml of phosphoric acid is added. The solution is then diluted with an equal volume of water. The reappearance of the pink color of the indicator at this point indicates complete removal of the excess chromous ions. One to three milliliters of ferric sulfate solution (2.5% solution in 1% H_2SO_4) is added along with 0.05 to 0.2 ml of diphenylaminesulfonic acid, and the Fe(II) is titrated with potassium dichromate. A correction of 0.05 ml of 0.01*N* potassium dichromate is subtracted for each 0.1 ml of indicator used.

Hahn and Kelley [308] used chromous sulfate, prepared by passing a 10 wt. % solution of potassium chromic sulfate through a Jones reductor, to reduce milligram quantities of uranyl solutions. They followed the reduction potentiometrically. They then titrated the U(IV) with ceric sulfate. Chromous chloride solutions have been used [309] to titrate U(VI) chloride solutions to U(IV). It was found that complete reduction could be obtained in 0.1 to 8.0*M* hydrochloric acid at room temperatures when 0.1*M* potassium chloride was present. The titration was followed potentiometrically with a platinum electrode and a saturated calomel reference indicator. The chromous solution was prepared by electrolytic reduction and was kept in an atmosphere of hydrogen. Sharp potential breaks were obtained. The 8*M* hydrochloric acid with 0.1*M* potassium chloride gave the sharpest breaks.

(12) *Titanous Chloride or Sulfate.* Titanous salts readily reduce U(VI) to U(IV).[310] When used to reduce uranyl salts for oxidi-

metric titration, the excess titanous compound can be removed by bismuth trioxide, Bi_2O_3, which is reduced to the metal.[311] The bismuth metal and excess oxide are filtered off, and the filtrate is titrated in the ordinary manner. Wahlberg, Skinner, and Rader[312] used titanous sulfate to reduce uranyl solutions. The use of this reductant is reported to eliminate the need for removal of the hydrogen sulfide group. Selenium interferes with the titration. The cupferrates of interfering elements, which are precipitated by solid cupferron, are removed by filtration. The titanous sulfate is made from titanium dioxide by heating with sulfuric acid and ammonium sulfate. The titanium is reduced to titanous sulfate by using 8 g of zinc and 6 ml of mercury. After the cupferron precipitation has been made from a sulfuric solution, the precipitate is filtered, and the solution is oxidized with nitric and perchloric acid by evaporating to fumes of sulfuric acid. Cupric sulfate is added to the cooled diluted solution, and then the titanous sulfate solution is added until a red precipitate of metallic copper is observed. The solution is allowed to stand for 15 min, and then mercurous perchlorate solution is added rapidly until the metallic copper disappears. The solution is then treated with ferric sulfate and titrated with ceric sulfate in the usual manner.

The results appear to be somewhat low on known amounts of uranium. Whether this is due to the entrainment of some of the uranium in the cupferron precipitate or to some catalytic oxidation of the U(IV) by copper that is present is not known.

(13) *Electrolytic Reduction.* Although electrolytic reduction usually is not rapid or convenient enough for a routine procedure, it does have the advantage of permitting simultaneous reduction and electrolytic removal of impurities.[313, 314] An additional advantage is that no foreign ions are added. A mixture of trivalent and quadrivalent uranium is obtained. Gantz, Barnhart, De Vries, and Mellon[315] described a cell for the simultaneous purification and reduction of uranium. Solutions containing uranium which were 0.5*M* in sulfuric acid were electrolyzed for 30 to 60 min at 6 to 12 volts. The holdup of uranium in the cell was less than 1 part in 5000.

Procedure. The cell used is shown in Fig. 1.25. The anode is 18-gauge platinum wire, 10 cm of which is rolled into a spiral. The stirrer, the blades of which push downward, is air driven. In operation, mercury is run into the cell from the leveling bulb to a depth of 4 to 5 cm. The solution to be purified is transferred quantitatively into the cell using 0.5*M* sulfuric acid. The anode compartment is filled with enough 0.5*M* sulfuric acid that the level of the solution in the compartment will be 3 to 5 cm above the level of the solution in the cell. The blades of the stirrer should just touch the surface of the mercury. The solution is electrolyzed at a potential of 6 to 12 volts. The current can vary from 0.6 to 2 amp, depending on the voltage used. Reduction of the

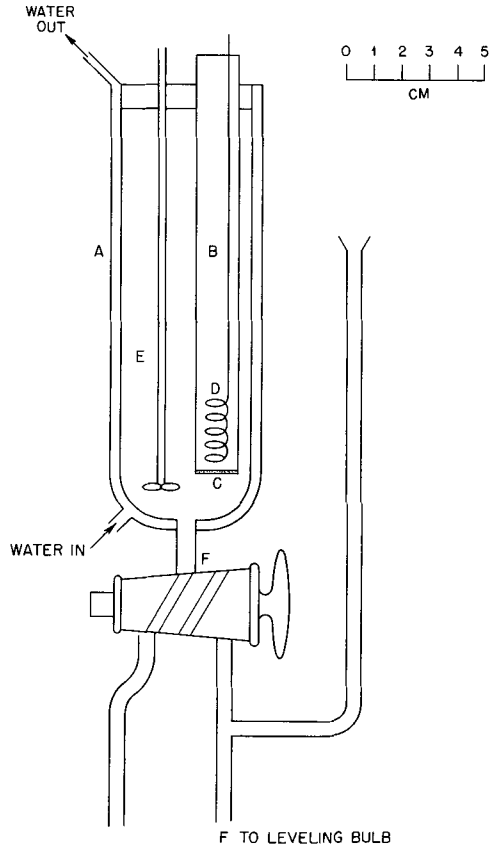


Fig. 1.25—Mercury-cathode diaphragm cell.[315] A, cell. B, anode compartment. C, porous pyrex bottom "M". D, 18-gauge platinum wire. E, stirrer. F, two-way 2-mm stopcock.

uranium will occur in 5 to 15 min. Some of the uranium is reduced to U(III).

After electrolysis the solution is drained from the cell while the current is still on. The cell is washed twice with 0.5*M* sulfuric acid. The solution in the anode compartment is added to the first washing before the wash solution is electrolyzed. Fresh sulfuric acid is added to replace the solution removed from the anode. Each wash solution is electrolyzed for 3 min. The under side of the rubber stopper should also be washed into the cell during the first washing. The method was primarily designed for the removal of iron and chromium impurities from solution, but it also serves to reduce the uranium.

To avoid the possibility of some uranium being retained in a Jones reductor, Kramer and Lerner[316] used electrolytic reduction for the high-precision determination of uranium. A sulfate solution is elec-

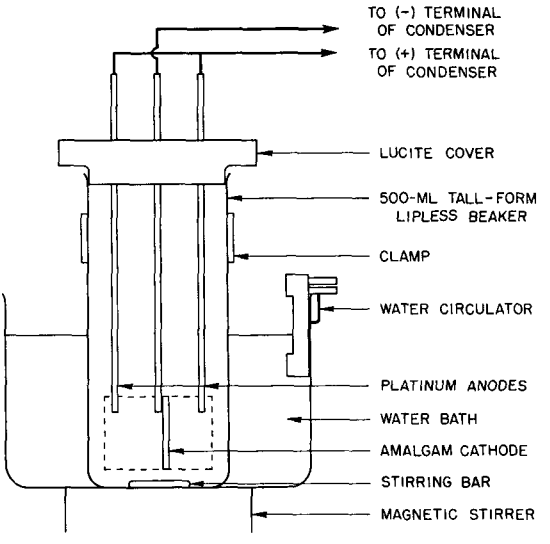


Fig. 1.26—Apparatus for reduction of U(VI).[316]

trolytically reduced using platinum anodes and an amalgamated gold cathode.

Procedure. A sulfate solution containing 5 ml of sulfuric acid in 175 ml of solution is reduced in a tall-form beaker (Fig. 1.26). The stirring bar (pyrex coated) is lowered into the solution by means of a magnet. The beaker is placed in the water bath, and the magnetic stirrer is started at a speed just below that causing cavitation. The two platinum electrodes, 150- by 2.5-mm rods, are occasionally burnished by rubbing them with an agate pestle. The amalgamated-gold cathode is a gold sheet 60 by 55 by 1 mm joined to a platinum rod 150 by 2.5 mm by placing about 10 mm of the rod flat against the top part of the sheet in the center of the largest dimension and gold-soldering it to the gold sheet. The electrode is then immersed in molten potassium pyrosulfate for a few minutes, cooled, and washed well with water and acetone. When dry, it is amalgamated by immersing in doubly distilled mercury until ready for use. Prior to use the amalgamated cathode is electrolyzed in sulfuric acid (5+95) for about 15 min. This is followed by burnishing with hardened filter paper. The electrodes are then immediately immersed in the sample solution with the current turned on. The power is supplied from a Fisher electroanalyzer, which has a 6000-μf electrolytic condenser across the terminals to reduce the a-c ripple voltage. The two anodes are immersed about 1 cm in the solution. The voltage is adjusted at 4.5 to 5 volts, with a current reading of 1 amp. The solution is electrolyzed until the color turns red-brown by transmitted light and nearly opaque by reflected light. (This is for samples containing about 5 to 10 g of uranium.) The operation for this size sample may take nearly 2 hr. With the current on, the cover is lifted, and the cover, the electrodes, and the walls of the beaker are washed down with 1 vol. % sulfuric acid. The electrodes are then removed, and the electroanalyzer is turned off.

(14) *Reduction to U(III).* As indicated in Sec. 1–3.2(a)(1), when sulfuric acid solutions are passed through a Jones reductor, most of the uranium is reduced to U(IV) and a small fraction is reduced to U(III). If all the uranium could be reduced to U(III), this would give an added valence change. Kennedy [253] found that U(VI) could be reduced completely to U(III) in a 1*M* hydrochloric or 1*M* perchloric acid medium when the uranium concentration was 0.01*M* or less. The U(III) solution is caught in an Fe(III) solution in the usual fashion employed with unstable reduced solutions. A 5 wt. % mercury and 95 wt. % zinc amalgam prepared from the elements and contained in a 250-ml buret was used. The solution was run through the reductor at a rate of 50 ml/min followed by 200 ml of acid wash. The solution was caught in a 0.05*M* ferric sulfate solution and titrated with permanganate after the addition of 10 ml of phosphoric acid per 250 ml of solution. Experiments showed unexpected stability of U(III) in 1*M* hydrochloric acid. After one week in a sealed flask, one-half of the U(III) had been oxidized by the hydrogen ion.

(b) *Oxidation of U(III) to U(IV).* Varying amounts of U(III) are formed in certain reduction processes, chiefly with those employing a zinc-amalgam reductor. Several methods can be employed for the oxidation of this U(III) to U(IV) before final titration with a standard oxidant. The one most usually employed is air oxidation although oxidizing agents have been employed with a potentiometric end point.

Aeration. Trivalent uranium is rapidly oxidized by aeration to quadrivalent uranium, which is quite air stable, in cool acid solutions that do not have impurities that might cause catalytic oxidation [Sec. 1–3.2(c)].

The rate of aeration is not critical, but oxidation is slow if the solution is not agitated either by a rapid stream of air bubbles or by stirring.

The addition to uranium of 10 wt. % of nickel, cobalt, manganese, aluminum, zinc, or magnesium, 1 wt. % calcium, or 20 wt. % sodium does not interfere with its aeration.[317]

The U(III) may also oxidize to U(IV) by hydrogen-ion reduction in a nitrogen atmosphere.

Borton [302] has used a Sargent-Malmstadt automatic titrator, which measures the second derivative in a potentiometric titration, with a stirrer revolving at 2100 rpm for introduction of air into a reduced uranium solution to oxidize the U(III) to U(IV). When the inflection point is reached, the stirrer is automatically turned off. In very precise work there are indications [318] that traces of U(IV) are air oxidized by aeration to U(VI).

Procedure. The reduced uranium solution, which contains at least 4 vol. % of sulfuric acid and is free of molybdenum, copper, or other interfering substances, is aerated at 20 to 25°C with a rapid stream of fine bubbles of washed air for 15 min or until 5 min after the characteristic green color of quadrivalent uranium appears.

(c) *Stability of U(IV) Solutions.* Since most of the volumetric methods in use at the present time depend on the oxidation of U(IV) to U(VI) with an oxidant, the question of stability of the U(IV) to air oxidation is important, especially with those procedures in which excess U(III) is oxidized to U(IV) by a current of air.

Pure U(IV) solutions are relatively stable to air oxidation at room temperature, but hot (60 to 80°) U(IV) solutions are air oxidized at an appreciable rate.[64, 319] When 0.65 g of uranium was reduced in a Jones reductor in the usual manner in an initial sulfuric acid concentration of 5 ml per 100 ml of solution, no evidence of U(VI) was found after 15 min of aeration at room temperature.[319] Lundell and Knowles [64] found no oxidation to U(VI) after a 4-hr exposure to air using 0.25 g of uranium. Kolthoff and Lingane [320] reported that very dilute solutions of quadrivalent uranium (0.001*N*) in 5 per cent sulfuric acid appeared to be stable in air for at least 30 min. After air had been passed through this solution for 1 hr, 1 per cent of the uranium was oxidized to the hexavalent state. Pepkowitz [256] reported that on a microscale the reduced state was very susceptible to air oxidation. When air was blown through a solution containing 1 mg of uranium and when the potential of the system was followed electrometrically, there was a continuous rise in potential until the U(VI) state was reached. At no time did the oxidation stop at the U(IV) state. However, microquantities of uranium have been determined by titration in air after the solutions had been passed through a micro Jones reductor and aerated briefly. Errors were less than ±0.6 per cent [257] for 0.5 mg and ±2 per cent [254] for 0.1 mg of uranium. Kennedy and Kaufman,[237] using 0.3 to 1.5 mg of uranium, followed the usual Jones reductor procedure and aerated for 5 min. Their results were comparable to those obtained on larger samples of uranium.

Molybdenum seriously interferes with aeration. In solutions containing 0.4 g of uranium and 0.25 to 90 mg of molybdenum per 100 ml, molybdenum acts as a catalyst and causes the oxidation of uranium to go beyond the quadrivalent state during aeration; but, if the molybdenum concentration is over 90 mg per 100 ml, complete oxidation of the molybdenum from the trivalent to the quadrivalent state by aeration is difficult, and high results may be obtained for uranium.[321] Martin and McCoy [322] found that molybdenum and vanadium caused catalytic oxidation of U(IV), Nichols [323, 324] reported that the autooxidation of U(IV) chloride is markedly accelerated by traces of

cupric ion, whereas Heaney and Rodden [325] found the same effect with U(IV) sulfate solution. Although copper is precipitated in the Jones reductor, it does not all stay in the amalgam; some is washed through with the reduced solution. It rapidly redissolves and causes the air oxidation of uranium to go beyond the quadrivalent state. Later work in France [326] also indicated that Cu(II) as well as Mo(VI) ions caused catalytic atmospheric oxidation of U(IV) solutions when the usual volumetric procedure for uranium was employed. Later Sill and Peterson [277] confirmed the above findings. Ferric chloride has a very slight accelerating effect, but other chlorides, such as chromic, uranyl, or cobaltous, have negligible effects. Bricker and Sweetser [293] showed that Fe(II) induced air oxidation of U(IV). This effect was quite dependent on acid concentration. Paley [168] indicated that the catalytic effect of molybdenum and copper was more pronounced in sunlight or ultraviolet light. In view of the above, it is especially desirable to remove such interfering elements before reducing the solution. Although copper will plate out on a reductor, it is advisable to remove it by a sulfide precipitation.

(d) *Titration of U(IV).* The titration of U(IV) to U(VI) can be made with many oxidants using either a potentiometer or an indicator to determine the end point. The oxidants chiefly used are ceric sulfate and potassium dichromate. The choice between these two appears to be a matter of preference although potassium dichromate does have the advantage of being obtainable in a pure form from which a standard solution can be readily prepared. However, the effect of the indicator is much more marked with potassium dichromate than with ceric sulfate.

Potassium permanganate is, at present, rarely used for uranium determinations. Titration with ferric sulfate at elevated temperatures is used to a considerable extent for routine work.

In most instances it is desirable to standardize the oxidizing solution against compounds of known uranium composition. The material that has been used to the greatest extent is U_3O_8, No. 950, from the National Bureau of Standards, which, when ignited at 900°C for 1 hr, contains 99.94 per cent U_3O_8. Another material that has been used is U_3O_8 prepared from a purified uranyl oxalate by igniting at 900°C for 2 hr. The material obtained indicates a U_3O_8 content of 99.99 per cent. In all instances when material other than uranium containing a normal isotopic composition is involved, corrections for the atomic weight of uranium are necessary. For this an isotopic assay is necessary.

(1) *Titration With Potassium Dichromate.* The use of potassium dichromate for the titration of reduced uranium solutions has been quite widespread. Both potentiometric and visual indicator methods have been used. In the indicator method it is necessary to add a ferric

salt before titration; thus, the titration is essentially that of the ferrous salt formed by reduction of the ferric ion by the U(IV) solution.[320, 328] Phosphoric acid is used to form stable ferric complexes, which result in a lower potential during the titration. It also serves to decolorize the ferric ion. Diphenylamine sulfonic acid as indicator gives more soluble oxidation products and a more pronounced color change than diphenylamine.[329] One disturbing factor in the dichromate titration using diphenylamine sulfonate as indicator is that the uranium titer of the dichromate solution, when a constant titration blank is used, varies with the amount of uranium present. This is shown graphically in Fig. 1.27.

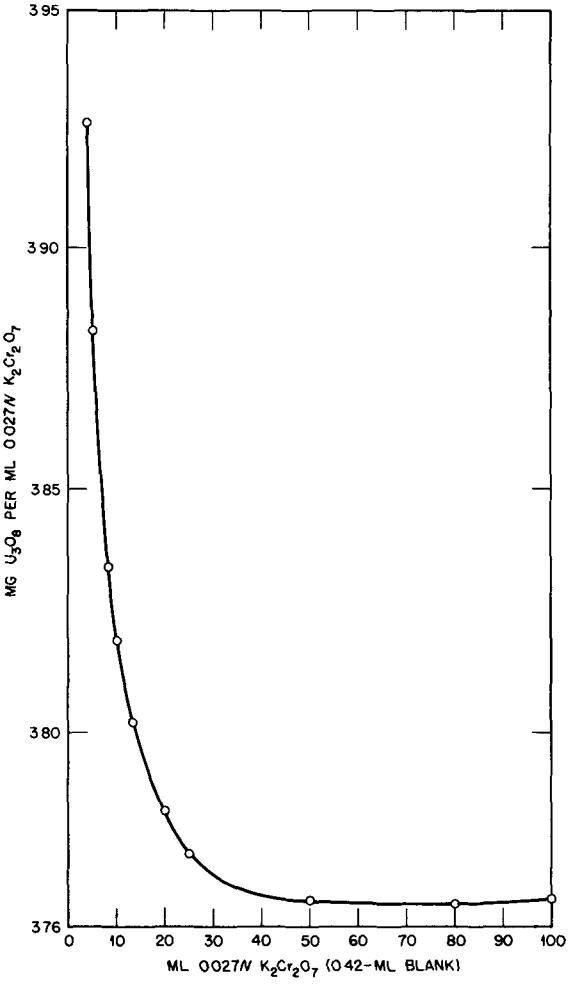


Fig. 1.27—Variation of uranium titer of a dichromate solution with volume of titrant.

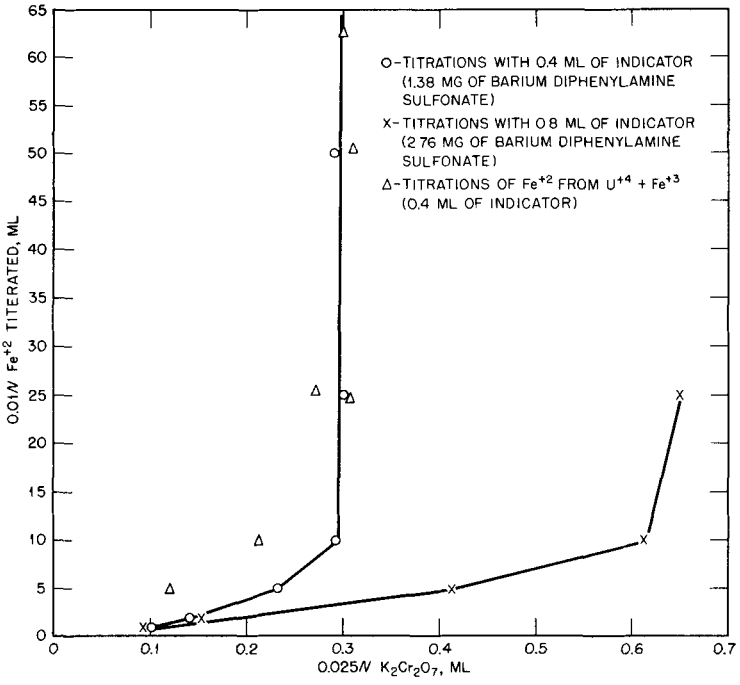


Fig. 1.28—Difference between potentiometric method and indicator method.

Since no such effect is noted when a potentiometric titration is made, this variation in titer must be connected with the indicator. The action of the indicator is usually described as an irreversible oxidation of the diphenylamine to diphenylbenzidine. After the addition of a certain amount of the oxidant, a part of the diphenylbenzidine can be further oxidized before all the amine is converted. The reaction only occurs in the presence of ferrous ion that is being oxidized by a strong oxidant.

Normally, the indicator blank is considered to be the amount of oxidant used to oxidize the indicator. Work at the New Brunswick Laboratory indicates, however, that the same amount of dichromate is not being consumed by the indicator in every case but that the amount is dependent on the amount of ferrous ion being titrated. This information was obtained from experiments in which the potentiometric titrations of ferrous ion were compared with those obtained using the diphenylamine sulfonate indicator. The amount of indicator used was 0.4 ml of 0.01*M* indicator in one set of experiments and 0.8 ml in another. The differences between the potentiometric titration and the indicator titration are shown graphically in Fig. 1.28.

The amount in excess used with the indicator appears to level off at about 0.3 ml of 0.025*N* dichromate for the oxidation of iron above 10 ml of 0.01*N* ferrous ion when 0.4 ml of indicator is used and at 0.65 ml of 0.025*N* dichromate when 0.8 ml of 0.01*M* indicator is used. Since 0.16 ml of the dichromate is needed to oxidize 0.4 ml of the indicator to the diphenylbenzidine form, the above work indicates that the oxidation of the ferrous ion and the indicator are progressing simultaneously, at least when low amounts of ferrous ion are concerned.

It has been the practice to standardize the dichromate solution against standard U_3O_8. Usually it is desirable to use a weight of standard U_3O_8 such that the volume of oxidant will be the same as that which will be used in the titration of the sample.

The titration is very sensitive to nitrate ions; no end point is detected when more than a few tenths of a gram of nitric acid is present.

Under carefully duplicated conditions an experienced analyst can obtain an accuracy of 0.1 to 0.2 per cent with the visual method.[270, 330] A precision of 1 part in 5,000 to 10,000 can be obtained by potentiometric-titration procedures that have been developed for high-precision work. In one procedure [318] a weighed amount of solid National Bureau of Standards potassium dichromate is added, and the titration is completed with 0.01 potassium dichromate using calomel and platinum electrodes. In other procedures a slight excess of solid dichromate is weighed and added to the U(IV) solution. The excess dichromate is titrated with 0.01*N* ferrous sulfate using calomel and gold electrodes [331] or calomel and platinum electrodes.[332]

Procedure (Visual). The reduced uranium solution, U(IV), which is in a sulfuric acid (5 + 95) solution and which has a volume of about 300 ml, is treated with 20 ml of a freshly prepared solution of ferric chloride (4 per cent). The solution is stirred, and 15 ml of a phosphoric–sulfuric acid mixture containing 350 ml of 85 per cent phosphoric acid and 150 ml of sulfuric acid is added. The solution is stirred, and 8 drops (0.4 ml) of a 0.01*M* solution of the sodium salt of diphenylamine sulfonic acid are added. The solution is titrated with a 0.03*N* potassium dichromate solution, with constant stirring, until the pure green color changes toward a gray-green. The dichromate is then added dropwise until the first tinge of purple or violet-blue appears. The uranium titer for the dichromate solution is determined by carrying known amounts of uranium through the procedure. When a volume of 40 to 100 ml of 0.03*N* dichromate is used, an indicator titration-blank correction is made by titrating approximately 0.19 g of uranium and then titrating double this amount of uranium. The titration blank is then taken as twice the volume used for the first titration minus the volume used for the second titration. The volume of dichromate is corrected for this blank both in the standard and in the unknown. When less than 40 ml of 0.03*N* dichromate is used, the uranium titer should be obtained by

titrating essentially the same amount of standard uranium as is to be titrated in the unknown sample without applying a blank correction.

Procedure (Potentiometric).[318] A 10-g sample of pure uranium oxide is dissolved in 30 ml of $HClO_4$, and the solution is diluted to 150 ml. The uranium is reduced by passing the solution through a Jones reductor at the rate of 25 ml/min and washing the reductor with three 25-ml portions of 2*N* sulfuric acid and three 25-ml portions of water. The solution, which after reduction contains uranium in the trivalent and tetravalent states only, is kept under nitrogen and titrated potentiometrically to the U^{+4} end point, using tungsten and platinum electrodes. Two solutions of potassium dichromate are used in this titration: a 0.1*N* solution is added until nearly all the U^{+3} is oxidized, and the titration is then completed with a 0.01*N* solution. After the U^{+4} end point has been reached, a quantity of solid National Bureau of Standards potassium dichromate, calculated to oxidize approximately 99 per cent of the U^{+4} to U^{+6}, is added. The oxidation is completed by titrating to the U^{+6} end point with a 0.01*N* solution of potassium dichromate, using platinum and calomel electrodes.

Procedure (Potentiometric).[331] After reduction of the hexavalent uranium electrolytically to the trivalent and tetravalent states by the second procedure given in Sec. 1–3.2(a)(13), a calomel and gold-amalgam electrode pair is immersed in the solution. While the solution is being stirred by the magnetic stirrer, the potential, which is generally between +600 and +700 mv at the start, will slowly decrease to about 300 mv. At this point a sudden decrease to −100 mv occurring in 1 to 2 min signifies the trivalent–tetravalent end point. The amalgam electrode is quickly replaced by a gold electrode. Solid National Bureau of Standards dichromate, 2 to 3 mg in excess, is then added.

After about 15 min the excess dichromate is titrated with 0.01*N* ferrous ammonium sulfate. The end point is indicated by a sudden break from about −720 mv to about −560 mv.

(2) *Titration With Ceric Sulfate.* Ceric sulfate has been used to a considerable extent for the titration of uranium, chiefly by employing the indicator ferrous 1,10-phenanthroline sulfate (ferroin) although some potentiometric methods have been reported. Practically no titrations are made in hot solutions. In the presence of either phosphoric acid [272] or ferric salts,[320] titrations can be made at room temperature. The end point with ceric sulfate may be overshot unless care is taken; two methods have been employed to minimize this effect. For titrating small amounts of uranium [277] with ferroin as an indicator, a small amount of phosphoric acid (2 to 3 drops) is added initially, and the solution is titrated with ceric sulfate to a color change. This occurs prior to the true end point. Then 2 ml of phosphoric acid is added, causing the original color to form, and the titration is completed using small increments of ceric sulfate.

In the case in which large amounts of uranium are being titrated, the presence of phosphoric acid is undesirable because uranous phosphate precipitates. In this case, after the indicator has been added,

the titration is made with ceric sulfate until a green color appears. Then a ferric sulfate solution is added to bring back the original color, and the titration is completed by the dropwise addition of ceric sulfate.

In both methods given above, the overshooting of the end point is avoided. With large amounts of uranium (0.1 to 0.3 g), a precision of 1 part in 1,000 can be obtained.

The titration with ceric sulfate can also be carried out by adding 0.1 to 0.5 ml in excess and then back-titrating with ferrous ion.

Automatic potentiometric titrations of uranium for 10 to 100 μg in *M* sulfuric acid have been made on pure uranium solutions.[333] Microliter amounts of ceric sulfate are automatically delivered, and the volumes are recorded on the chart of a recording potentiometer.

Although the indicator-blank correction with ceric sulfate is not as troublesome as with the dichromate titration, it is still preferable to standardize the ceric sulfate with U_3O_8. A blank is usually run, especially when low amounts of uranium are to be titrated. This blank does not change with the amount of uranium being titrated.

A spectrophotometric end point has been used [293] for the titration of U(IV) with ceric sulfate. Uranous, uranyl, and cerous ions do not absorb at 350 mμ, but ceric sulfate absorbs strongly.

Procedure (Visual: For Large Amounts of Uranium).[334] Thirty-five milliliters of sulfuric acid (1+1) and 3 drops of 0.025*M* ferroin solution are added to the aerated sample. With the standardized ceric sulfate solution in a calibrated and certified buret, a titration is made rapidly until the sample solution changes to a green color. Ten milliliters of 20 per cent (wt./vol.) ferric sulfate solution is added, and the titration is continued immediately with the standardized ceric sulfate solution (0.08*N*) until the maximum change in color intensity occurs. The partially titrated sample should not be allowed to stand. A buret correction and a temperature correction to 25°C are made to the total volume of ceric sulfate solution consumed.

Procedure (Visual: For Small Amounts of Uranium).[334] The blank determinations on the reductor column (lead) are carried out by passing 80 ml of a solution containing 20 ml of hydrochloric acid through a column at the rate of about 100 ml/min. The column is washed with 80 ml of *N* hydrochloric acid, added in small portions to obtain maximum washing efficiency. The solution is transferred to a titration flask, using *N* hydrochloric acid for washing purposes. Then 2 ml of phosphoric acid (sp. gr. 1.75) and 1 ml of 0.001*N* ferroin are added, and a titration is made with 0.02*N* ceric solution to the discharge of the indicator color. The uranium solution in a hydrochloric acid solution (1+4) is passed through the reductor (lead), using 80 ml of *N* hydrochloric acid, which is added in small portions, to wash the beaker and the reductor column. The solutions are transferred to a titration flask, using *N* hydrochloric acid for washing purposes. After the addition of 1 ml of 0.001*N* ferroin solution and 1 drop of phosphoric acid (sp. gr. 1.75), a rapid titration is made with the standard ceric solution

until the indicator color just fades. Then 2 ml of phosphoric acid is added, and the titration is continued slowly to the end point. This volume of titrant is then corrected for the blank value, and the uranium content is calculated.

(3) *Titration With Ferric Solution.* The titration of U(IV) solution with a ferric salt has certain advantages over some other oxidants. The main one is that iron salts do not interfere. A potentiometric titration with platinum and calomel electrodes is the usual practice after reduction in a Jones reductor.

Since the titration is usually made at 90°C and under an atmosphere of carbon dioxide, the method does have certain drawbacks; however, for routine determinations it has proved useful.[335, 339]

The most accurate and precise procedure is the ferric sulfate potentiometric titration in 4 to 6 per cent sulfuric acid at 90 to 95°C under an atmosphere of carbon dioxide.[336, 337] The accuracy and precision are ±0.1 per cent in routine analysis. The accuracy is similar in 3 to 10 vol. % perchloric acid [338] but a little lower with 0.1*N* ferric chloride in hydrochloric acid solutions; [257, 271] the optimum hydrochloric acid concentration is 15 to 30 vol. %. Chlorides appear to interfere with the ready establishment of an equilibrium electrode potential.[270] Nitrates, phosphates, and fluorides should be absent.[338] Copper,[305] tungsten, molybdenum, and vanadium [257] interfere seriously. The interference of vanadium is stoichiometric and can be corrected for. Small amounts of tin produce a slight positive error.[305] Very large amounts of zinc or chromium tend to reduce the sensitivity of the platinum indicator electrode during titration.[304] Large amounts of iron or cadmium [304] and moderate amounts of chromium, manganese, nickel, aluminum, or lead do not interfere although large amounts of iron do have a depressing effect on the size of the U (IV)/(VI) break.[270] The U (III)/(IV) system frequently yields an unsatisfactory end point. More consistent end points are obtained by replacing the U (III)/(IV) system with the Cr (II)/(III) or the Ti (III)/(IV) system.[270] The U (III)/(IV) system yields an end point at 0.5 volt. When Ti(IV) is added, the Ti (III)/(IV) system replaces the U (III)/(IV) system and yields a very satisfactory and reproducible end point at 0.1 volt. The amount of titrant consumed between the Ti (III)/(IV) and the U (IV)/(VI) end points corresponds to the U (IV)/(VI) titer. However, in the presence of titanium the U (IV)/(VI) end point is more difficult to observe because the potentials appear to be very slowly established. The addition of Cr(III) and the resulting substitution of the Cr (II)/(III) system, which gives an end point at 0.4 volt, yield sharp end points and readily established potentials throughout the titration.

The present practice [334] is to reduce the U(VI) with Cr(II) formed by passing a chrome alum solution through a Jones reductor. The excess Cr(II) and U(III) are titrated potentiometrically at 90°C under a carbon dioxide atmosphere with a 0.1*N* ferric sulfate solution using gold and calomel electrodes. The difference in volume of the titrant used between this end point and the U(IV) end point is the volume used for the uranium alone. For the automatic potentiometric titration of milligram amounts of uranium with ferric sulfate, a syringe type buret driven by a mechanism connected with a Brown recorder [340] is used. A relative standard deviation of 0.1 per cent has been obtained with this procedure.

For aluminum–uranium alloys the sample can be dissolved in hydrochloric acid and hydrogen peroxide, and the uranium can be reduced to U(IV), which is then titrated potentiometrically with a ferric chloride solution.[341] Although the potentiometric break is much smaller than it is in a sulfate medium, satisfactory results can be obtained [342] when a polarized-electrode system [343] is used.

Procedure (*Modified, Oak Ridge National Laboratory*). A sample solution containing 75 to 100 mg of uranium is transferred to a 200-ml beaker, and 5 ml of sulfuric acid is added. The solution is fumed to dryness on a hot plate. (In the presence of aluminum such as is obtained with aluminum–uranium alloys, infrared lamps are preferred to a hot plate.) The residue is cooled and is dissolved in 100 ml of 7.5 per cent sulfuric acid. The solution is brought to the boiling point on a hot plate. The hot solution is then transferred to a magnetic stirring apparatus having an aluminum heating jacket set at 100 to 115°C and a cover with openings for both the gold and calomel electrodes (high temperature) as well as for carbon dioxide gas and a buret. The carbon dioxide flow is adjusted to 2 bubbles per second. A Jones reductor is washed with 7.5 per cent sulfuric acid. Then 8 ml of a 10 per cent chrome potassium alum is added to the reductor, followed by 15 ml of 7.5 per cent sulfuric acid. The reduced chromous solution is allowed to descend to the base of the reductor, and then the stopcock is closed. When the sample solution, in the heated beaker containing a stirring bar, has begun to boil, the beaker with the cover is placed under the Jones reductor. The previously heated gold and calomel electrodes are placed in position through the cover and are connected to the potentiometer. The chromous solution is added from the reductor until the potentiometer indicates the presence of excess Cr(II). The temperature of the solution is kept at 90±5°C, and the solution is titrated with 0.1*N* ferric sulfate, with the tip of the buret under the solution and with the carbon dioxide flowing. The solution is titrated to the first end point. The volume is recorded, and the solution is then titrated to the second end point. The difference in volume of the 0.1*N* ferric sulfate is that used for the U(IV).

Procedure (*Westinghouse*).[342] Polarized platinum electrodes are used in a chloride solution replacing the temperature-dependent calomel electrode. The uranium is reduced with a Jones reductor, aerated to U(IV), and titrated potentiometrically.

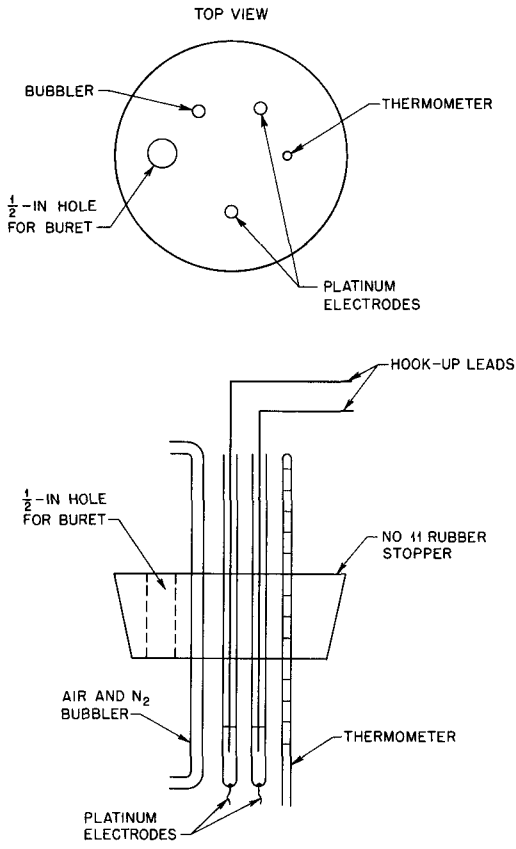


Fig. 1.29—Detail of electrode assembly.[342]

A sample of uranium–aluminum alloy containing 0.1 to 0.3 g of uranium is treated in a 250-ml beaker with 150 ml of water and 15 ml of hydrochloric acid. The solution is heated until the sample has dissolved; then 1 ml of 30 per cent hydrogen peroxide is added, and the solution is heated until entirely clear. The solution is cooled and passed through a Jones reductor at the rate of 15 to 30 ml/min. The beaker is washed with three 30-ml portions of hydrochloric acid (5+95). the washing being used to remove the uranium from the reductor. Each wash solution is allowed to drain to the top level of the amalgam each time. Finally the column is washed well with three 30-ml portions of water. The volume is adjusted to 300 ml with water, and the electrode assembly (30-gauge platinum wire in 6-mm-ID soft-glass tubing, Fig. 1.29) containing the electrodes, bubbler, and thermometer is placed in the flask (Fig. 1.30). The solution is aerated for 8 min. The flask is transferred to a combination hot plate and magnetic stirrer. Nitrogen is passed through the solution at the same time, increasing the temperature to 90±1°C. The electrode system is then connected to a vacuum-tube voltmeter. With the nitrogen flowing the solution is titrated with 0.05*N* ferric chloride. After an initial emf

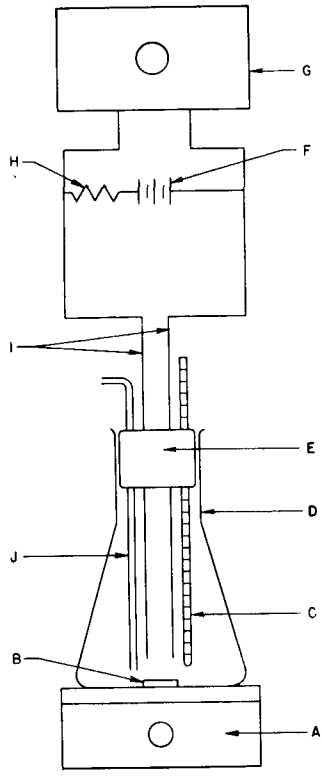


Fig. 1.30—Titration assembly.[342] A, combination magnetic stirrer and hot-plate. B, magnetic stirring bar. C, 0 to 100°C thermometer. D, 500-ml wide-mouth Erlenmeyer flask. E, No. 11 rubber stopper. F, 45-volt battery. G, vacuum-tube voltmeter. H, 60-megohm carbon resistor. I, platinum electrodes. J, gas-inlet tube.

drop of about 100 mv, the voltage remains constant up to the end point, where a change of about 180 mv takes place.

(4) *Titration With Potassium Permanganate.* Potassium permanganate is the classical reagent employed for the titration of U(IV) solutions. Although rarely used at present, potassium permanganate has been used either without an indicator or with one such as ferroin;[263, 344, 345] the end point can also be determined by potentiometric methods.[270] Uranium (50 to 500 mg) has been determined with an accuracy of 0.1 per cent with this reagent.[346]

(5) *Titration With Vanadate.* Potassium vanadate salts have been used[168, 347] as titrants with phenylanthranilic acid as an indicator for the titration of U(IV). These procedures are based on the work of Sirokomskii.[348]

In the work reported by Paley,[168] ammonium vanadate is dissolved in sulfuric acid and phenylanthranilic acid is used as an indicator.

The titration is performed in a sulfuric acid solution (1+2), and distinct color changes are reported when 0.0004*N* ammonium vanadate is used in 20 ml of solution containing 1 to 2 drops of the 0.2 per cent indicator solution. In addition to being applicable to small amounts of uranium, the presence of quadrivalent vanadium has no adverse effect on titration. Direct titration with sodium vanadate, employing diphenylbenzidine as indicator, was not satisfactory.[349]

(6) *Miscellaneous Titration Methods.* Various other titrants have been used under certain conditions although they are rarely used at present. Among these are potassium bromate,[67] phosphate,[350] and sodium hydroxide.[63] The 8-hydroxyquinolate can also be titrated with a bromate–bromine solution.[64]

(7) *Potentiometric Titration* (see Chap. 15, "Electrometric Methods"). Several procedures call for the potentiometric determination of the U (III)/(IV) end point. The oxidation to quadrivalent uranium can be accomplished by aeration in a cold solution [313, 351] or by titration with an oxidizing agent either in a hot solution in a carbon dioxide atmosphere [346, 352] or in a cold solution.[318]

In titrations the precise end point of the U (III)/(IV) change is difficult to determine. It can be found if a 0.1*N* oxidizing reagent is used, but, if the titrating increments are decreased by using a more dilute reagent, the drifts in potential become more and more dominant until they completely obscure the end point.[353] Work by Voss and Greene,[318] however, indicates that satisfactory titrations can be performed with platinum–tungsten electrodes. The solution is kept under nitrogen and titrated potentiometrically to the U(IV) end point.

Work at New Brunswick Laboratory [331] showed that following the above procedure the potentiometric U (III)/(IV) end point did not agree with the spectrophotometric disappearance of U (III) as measured at 313 mμ. The spectrophotometric end point appeared earlier than the potentiometric one. In titrations at approximately 80°C, the interval between the two potential breaks corresponds stoichiometrically to the quantity of uranium present, but at room temperature the interval is somewhat too short. The first potential break probably corresponds not to the disappearance of trivalent uranium but to the disappearance of the adsorbed hydrogen layer on the platinum electrode. These correspond at high temperatures (80°C) when hydrogen is rapidly oxidized by the titrant; but at low temperatures oxidation is slower, and there is a time interval before the electrode responds to the disappearance of trivalent uranium.[354] In one modification [270] trivalent uranium is oxidized to quadrivalent uranium by the addition of chromic sulfate, and the Cr (II)/(III) break is used in place of the U (III)/(IV) break.

1–3.3 Spectrophotometric Methods

The determination of uranium by spectrophotometric means has been employed for many years and is of increasing interest, as is shown by the many recent journal articles published on these methods. The number of these articles and the variety of reagents employed are so large that only those reagents dealing directly with analysis will be considered. The literature up to 1945 has been covered [355] and several review articles have been published.[76, 278, 356]

The methods employed are based on the radiant-energy absorption of (1) uranous or uranyl ions in aqueous or nonaqueous solutions, (2) inorganic compounds or complexes of uranium in aqueous and nonaqueous solutions, and (3) organic compounds or complexes of uranium in aqueous or nonaqueous solutions.

The sensitivity of the methods to uranium varies considerably and in many instances the selection of the method to be employed will be guided by this factor. Table 1.6 gives the molar absorbancy indices of the more commonly used reagents.

Table 1.6—MOLAR ABSORBANCY INDICES FOR URANIUM

Reagent	Molar absorbancy index
Peroxide	900–1, 200
Diethyldithiocarbamate	4, 050
Thiocyanate, aqueous	3, 770
Thiocyanate, aqueous acetone	3, 900
Thiocyanate, butyl cellusolve	5, 500
Oxine	3, 000–6, 500
Thoronol	16, 400
Dibenzoylmethane	19, 000
Arsenazo	22, 900
1-(2-Pyridylazo)-2-naphthol	23, 000

Most of the reagents listed in the table are subject to interference by a variety of anions and cations. In many cases a previous separation from these interferences is necessary, but in some instances the effect of these interferences can be circumvented.

The recent development of differential spectrophotometric methods of analysis enables uranium determinations with a precision approaching that obtained with volumetric methods of analysis. These methods also allow the determination of larger concentrations of uranium than is possible with the usual spectrophotometric methods where the solvent alone is used as the reference solution.

(a) *Direct Determination of Uranium Ions in Aqueous and Nonaqueous Solvents.* The determination of uranium by a spectrophotometric measurement of the solution without the addition of a color-forming reagent is made usually with rather concentrated uranium solutions. Since the various valence states of uranium exhibit a characteristic absorption spectra from which bands that do not overlap can be selected, the method has proven quite useful in determining the various oxidation states as well as total uranium in mixtures. Various anions have been employed including nitrate,[357-360] phosphate,[361-363] sulfate,[364] perchlorate,[365, 366] oxyfluoride,[367] chloride,[368, 369] fluoride,[361] and acetate.[361] Although in several instances analyses have been made directly on aqueous solutions, in others separations have been made by solvent extraction to remove interfering ions. The spectrophotometric measurements can then be made on the organic solvent directly without stripping the uranium from the solvent.

The absorption spectra of uranium solutions are characterized by narrow, and in most instances, sharply defined bands. The absorption spectra varies with the valence state of the uranium ion and has been used to determine the amount of one valence state in the presence of another. Since U(III) and U(VI) will not exist in a single solution, the effect of one of these absorption bands on the other does not have to be considered. The absorption spectra in the 400- to 1000-mμ range of the various valence states in a chloride solution are given in Fig. 1.31. An extension of this work for a perchloric acid solution is given in

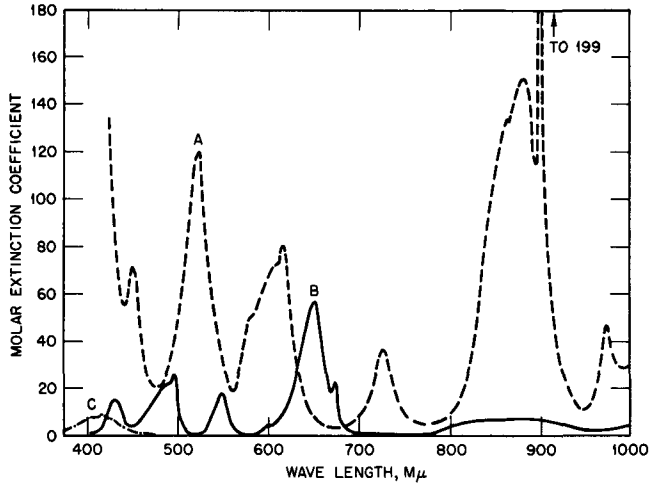


Fig. 1.31—Absorption spectra of uranium[355] (0.01*M* uranium solution in 1*M* HCl). Curve A, U(III); curve B, U(IV); curve C, U(VI). Measurements were made with a Beckman spectrophotometer using 1.75-cm cells.

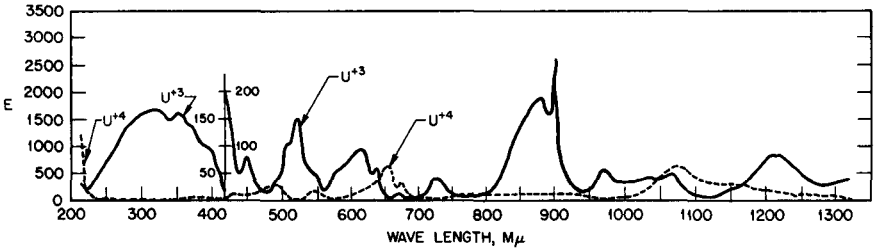


Fig. 1.32—Absorptions spectra of uranium salts in perchloric acid.[499]

Fig. 1.32. As can be noted there are certain wave lengths suitable for use in analysis. Although from Fig. 1.31 it would appear that the band at 410 mμ is the only one available for U(VI), Callahan [369] has shown that a band at 250 mμ can be used with a chloride solution. There will be a certain contribution by U(IV) at the 410-mμ wave length. In Fig. 1.31, the wave lengths at 520 and 750 mμ would appear to be useful for determining U(III); however, the strong diffuse band at about 300 mμ (Fig. 1.32) is more sensitive and is quite useful for determining traces of U(III). The band at 630 mμ has been used for the determination of U(IV); however, in the presence of U(III) there may be some interferences, as shown in Fig. 1.31. Corrections can be made, by measuring the U(III) at 750 mμ.

The absorption band from one valence state will vary somewhat in width and wave length depending on the anion concentration and temperature. For a U(VI) solution the band will be between 390 and 450 mμ for the one most often used; for a U(IV) solution it will be in the region of 630 and 660 mμ. Occasional use is made of other absorption bands [369] such as the one at 246 mμ for microgram quantities of U(VI).

Determination of U(VI). In certain plant streams the composition does not vary to a great extent and continuous analyses of process streams have been made on radioactive solutions with a single-beam filter photometer using the light absorption of the uranyl ion [370] at 418 mμ and with dual-cell filter photometers for the analysis of aqueous and organic plant streams.[371]

Interfering elements will show their greatest effect when the absorption at 250 mμ is used since this region has been shown to be a general absorption region of considerable sensitivity for many inorganic materials in hydrochloric acid and other solvents.[372] When use is made of other regions, such as wave lengths of 410 and 630 mμ, the interference is chiefly by colored ions although ions that form complexes can interfere. Some use has been made of these bands for the analysis of materials containing certain selected inter-

ferences;[361, 365] in general, however, a separation of interfering elements is desirable. This separation may be by solvent extraction of the nitrate using tributyl phosphate[358] or by a methyl isobutyl ketone extraction of tetrapropylammonium uranyl nitrate from an acid-deficient aluminum nitrate solution[373] followed by a direct spectrophotometric measurement on the organic extract. An extraction of the uranium into ethyl acetate using aluminum nitrate as a salting agent has also been used prior to the determination in a chloride solution.[369] In another separation procedure[368] the uranium is selectively absorbed from a sulfate solution at pH 2 by Dowex 2 and eluted with dilute hydrochloric acid; the absorbancy measurements are then made at 390 mμ. In all instances attention to detail is necessary and conditions must be kept constant since, as indicated above, results are affected by many variables.

Procedure (Solvent Extraction From Acid-deficient Solution.)[373] After separating interfering elements [see procedure given in Sec. 1–2.4 (c)], transfer the organic phase with a pipet to a 1-cm absorption cell and determine the absorbancy at 452 mμ against a blank of 1*N* nitric acid run through the procedure. A concentration-absorbancy curve is prepared from known amounts of uranium carried through the procedure.

(b) *Inorganic Compounds or Complexes of Uranium.* Among the various inorganic compounds that are used for the spectrophotometric determination of uranium, alkaline peroxide, carbonate, and thiocyanate are the most common. Alkaline peroxide has been used extensively but certain organic reagents are now being used more frequently owing to their increased sensitivity. Ferro-cyanide is used rarely at present.

(1) *Peroxide.* The use of peroxide in a sodium carbonate solution as a means of determining uranium was first proposed by Hackl.[374] The effect of changes in concentration of carbonate[375, 376] and the effect of bicarbonate[377, 378] have been noted. Rodden and coworkers[379, 380] recommended the use of sodium hydroxide in place of the carbonate as giving more reproducible results and eliminating the effects of vanadium. A complete discussion of the work on the alkaline peroxide method is given by Rodden and Warf.[381] Little change in procedures has been noted in the past few years although many applications of this method have been made.[162, 164, 382–385]

For reproducible results with the hydrogen peroxide–sodium hydroxide system, the conditions are not critical and the color is particularly stable.

The method has certain disadvantages. Since a strongly alkaline solution is used, certain elements precipitate. In addition, certain colored compounds with other elements are formed. This is partic-

ularly noticeable with chromium. Vanadium causes interference that can be removed by heating in a strongly alkaline solution;[380] molybdenum can also interfere under certain conditions. Tartrate is sometimes used to mask vanadium. Because of interferences the method has been applied chiefly after a separation such as by solvent extraction or by one of the other methods discussed in Sec. 1–2. This need for separation of itself is not a drawback to the use of the method since essentially all spectrophotometric methods require prior separation of the uranium, but the method does have low sensitivity compared to some others employing organic reagents. The acid peroxide method[381] has been rarely used.

Procedure. The solution containing 1 to 25 mg of U_3O_8, after being purified by an appropriate method, is evaporated to dryness on a steam bath. The sides of the beaker are washed with 15 ml of nitric acid (1+1), and 1 ml of perchloric acid is added followed by 3 ml of sulfuric acid. After a few glass beads have been added, the beaker is covered with a Speedivap watch glass and heated until fumes of sulfur trioxide are evolved. The sulfuric acid is allowed to reflux halfway up the sides of the beaker before it is removed from the hot plate. (This treatment is necessary to remove organic material that could interfere in the spectrophotometric determination.) After the solution has been cooled and diluted with water, it is neutralized with a sodium hydroxide solution (1+1). After neutralization 5 ml of sodium hydroxide (1+1) is added, and the solution is diluted to 100 ml. To this solution is added 0.5 g of sodium peroxide; then the solution is stirred and filtered through a dry, double, No. 40 Whatman filter paper into a 125-ml Erlenmeyer flask. The solution is placed in a cell of a spectrophotometer, and the absorbancy is read at 425 mμ against a cell containing distilled water. An absorbancy-concentration curve is obtained by running known amounts of uranium through the above procedure, and the uranium concentration is read from this curve.

(2) *Sodium Carbonate.* Uranyl compounds, when dissolved in a sodium carbonate solution, form a characteristic yellow color that can be used for the determination of uranium. This method has been used[386] with absorbancy measurements in the ultraviolet at somewhat below 320 mμ. As would be expected, nitrate ion interferes.

(3) *Thiocyanate.* Thiocyanate ion reacts with uranyl ion in acid solution to form a yellow-colored complex that absorbs in the ultraviolet. This property is the basis of an analytical method.[387–390]

Since the reagent itself absorbs strongly below 340 mμ, the more satisfactory wave length of 365 to 375 mμ is used. The method is applicable from 0.2 to about 4 mg of uranium per 100 milliliters.[391] An automatic analyzer for process streams based on the above method[392] has been made.

Like many other spectrophotometric reagents for uranium, thiocyanate is not specific, and there are numerous interferences (see Refs.

168, 387, 389, 391, 393, and 394). The interference of ferric ion can be eliminated by reducing it to the ferrous state. Stannous chloride has been used for this reduction, but ascorbic acid [395] is more satisfactory since stannous chloride causes increasing interference as the thiocyanate ages.[391] In addition, stannous chloride reduces vanadium to V(III), which with thiocyanate has a strong absorption band. Ascorbic acid, however, reduces vanadium to V(IV), which does not give this strong band in the ultraviolet. The chief interferences come from the cations of molybdenum, vanadium, titanium, cobalt, lead, niobium, and some of the platinum metals, and certain anions as acids in high concentration, notably nitric acid, hydrochloric acid, and sulfuric acid, react with the thiocyanate reagent.

Many modifications of the method have been made with the purpose of removing interfering ions. In the work by Crouthamel and Johnson,[396] the use of thiocyanate in an acetone medium eliminates the interference of many anions and also increases the sensitivity of the method. Cations, however, interfere more seriously than in the aqueous solution.

As is usually the case in nonspecific reagents for uranium, the trend has been to the separation of the uranium by a solvent-extraction procedure prior to the spectrophotometric determination. These solvent-extraction procedures include the use of ether,[397, 398] ethyl-acetate,[158, 160] tributyl phosphate (TBP),[176] TBP from an ethylenediaminetetraacetic acid (EDTA) solution,[394] dibutoxytetraethylene glycol,[399] and methyl ethyl ketone.[168] Although the above separation procedures have overcome many interferences, in some instances there are certain drawbacks. With the TBP separation [176] anions such as fluoride, phosphate, and sulfate inhibit the extraction, and the color is not particularly stable. When methyl ethyl ketone [168] is used, small amounts of titanium, vanadium, bismuth, and molybdenum are extracted and interfere. In the ethyl acetate separation, vanadium extracts and causes interference. The color is also unstable and must be read within 10 min.

Of the various methods proposed, the one employing a methyl isobutyl ketone extraction from a solution containing aluminum nitrate as a salting agent appears to be the most satisfactory.[169] The extract is treated with a solution of ammonium thiocyanate in a butyl–Cellosolve–water solvent. The yellow uranium thiocyanate complex forms immediately, and the color is stable for 48 hr. The optimum range of uranium concentration (1-cm cells) is from 0.4 to 2 mg of U_3O_8. Titanium is the only interference found, and this interference can be eliminated by tartaric acid if not more than 5 mg of titanium is present. This method does have the drawback of requiring the use of only 3 ml of the aqueous solution to avoid excess amounts of

aluminum nitrate. The method is therefore applicable chiefly to solutions that are rather concentrated in uranium. The use of longer absorption cells increases the sensitivity of the method by a factor of 5 to 10.

Procedure.[169] Aqueous samples are diluted to a concentration of 0.2 to 2.0 g of U_3O_8 per liter if absorbancy measurements are to be made at 375 mμ, or they are analyzed as received if the absorbancy measurements are to be made at 420 mμ. Organic samples, such as those from solvent-extraction studies, are best treated by stripping the uranium into an aqueous carbonate solution before proceeding with any dilution. Ore and concentrate samples are decomposed by any suitable method and diluted to a convenient volume after neutralizing any large amount of caustic or acids.

An aliquot of the sample (not more than 3 ml) is transferred into a 40-ml screw-capped (aluminum lined) vial (4.25 in. long and 1 in. in diameter). If the sample is strongly acid or alkaline or is in a concentrated buffer solution, especially carbonate–bicarbonate, the pH is adjusted to 0 to 3 by the dropwise addition of nitric acid or concentrated sodium hydroxide. Approximately 15 ml of the appropriate aluminum nitrate reagent is added. [For the preparation of such a reagent, five hundred milliliters of distilled water and 1880 g of reagent-grade aluminum nitrate nonahydrate (uranium free) are added to a 4-liter beaker. The cool solution is treated with 200 ml of ammonium hydroxide (1+1), which is added slowly with stirring until the precipitate dissolves. After the solution has cooled to room temperature, it is diluted to 2 liters. When titanium is present, the salting agent is made as above; however, before it is diluted to volume, 60 g of reagent-grade tartaric acid is added followed by 60 ml of the ammonium hydroxide (1+1), and the mixture is stirred to ensure dissolution.] To the vial is added exactly 20 ml of methyl isobutyl ketone. The vial is capped and shaken for 2 min. The organic and the aqueous phases are completely separated by centrifugation. Ten milliliters of the organic phase is transferred by pipet into another vial and 15 ml of the chromogenic reagent is added [prepared by dissolving 46 g of reagent-grade ammonium thiocyanate and 2 g of reagent-grade ascorbic acid in a solution of 11 parts of butyl–Cellosolve (ethyleneglycol monobutyl ether) and 4 parts of water to a final volume of 150 ml]. The vial is capped, and the solution is well mixed. A reagent blank is prepared in the same manner as the samples. The absorbancy is measured against the reagent blank at 375 mμ or, if the absorbancy is greater than 1.0, at 420 mμ. Known amounts of uranium are run through the same procedure, and an absorbancy-concentration curve is obtained from which the uranium concentration of the unknown can be determined.

(c) *Organic Compounds or Complexes of Uranium.* (1) *8-Hydroxyquinoline (Oxine) (8-Quinolinol).* The orange color obtained with organic solvent solutions of uranyl compounds and oxine has been used for the determination of uranium. The sensitivity under certain conditions is greater than with thiocyanate but less than with dibenzoylmethane (see Refs. 179, 203, 204, 354, 400–403). Beer's law is followed. As would be expected with this reagent, the number of inter-

fering elements is quite numerous, and, except in limited circumstances,[401, 402] a preliminary separation is necessary. The absorption spectrum of the colored uranium compound is not sharp,[204] and a variety of wave lengths has been used, ranging from 400 to 500 mμ. Below 400 mμ the reagent begins to absorb strongly. The most common solvent used is chloroform. The pH of the solution being extracted affects the amount extracted markedly. The pH range is narrow [179, 204] and is about 7 to 8. The color is stable for 16 hr, but certain grades of oxine in chloroform are affected by the illumination from fluorescent lights. The use of ammonium carbonate [183] to remove uranium from a portion of the extract prior to the spectrophotometric determination is quite novel and useful. In this way impurities that are extracted can be blanked out since the extract containing the uranium is measured against the extract from which the uranium has been removed.

Procedure.[188] To 70 ml of a slightly acid solution containing from 40 to 800 μg of uranium is added 3 ml of a 1 per cent oxine solution (1 g of oxine and 3 ml of 12*N* sulfuric acid diluted to 100 ml). The pH is adjusted to between 8.5 and 9.0 with ammonium hydroxide (made from gaseous ammonia). The solution is transferred to a separatory funnel and diluted to 100 ml; it is then extracted with 20.0 ml of chloroform (washed with *N* sulfuric acid, 2*N* ammonium hydroxide, and water; the chloroform is then distilled over anhydrous calcium chloride). After the phases have separated, half the extract is poured into an Erlenmeyer flask containing 1 g of anhydrous sodium sulfate to remove water droplets. The other half of the extract is transferred to another separatory funnel and is shaken with 20 ml of 0.2*M* ammonium carbonate (purified by adjusting to pH 8.5 with ammonium chloride, shaking several times with a 1 per cent (wt./vol.) oxine in chloroform solution and finally filtering). The difference in the absorbancy between the two extracts is measured at 380 mμ. Standard uranium solutions are run through the same procedure so that an absorbancy-concentration curve can be constructed.

The following procedure, which is used for the determination of uranium in thorium metal, with slight modification has been used for monazite, phosphate rock, carnotite, and bismuth metal.[179]

Procedure (*Uranium in Thorium Metal*). For samples of thorium containing less than 40 ppm of uranium, a 15-g sample in a 400-ml beaker is dissolved with 100 ml of nitric acid and 5 ml of dilute hydrofluoric acid (5+95). The beaker is placed on a steam bath until the sample has dissolved; then the contents of the beaker are evaporated to dryness on a hot plate. Heating is continued until the residue becomes powdery. The residue is ignited in a muffle furnace at 400°C for 30 min. After the residue has cooled, 50 ml of hydrochloric acid and 5 ml of dilute hydrofluoric acid (5+95) are added. The mixture is then boiled until the oxide has dissolved. The solution is transferred, while still warm, to a 250-ml short-stemmed separatory funnel, and 25 ml of tributyl phosphate (TBP) and 25 ml methyl isobutyl ketone are added. The contents are shaken vigorously for 30 sec. The lower aqueous phase

is discarded, the organic phase is washed with five 50-ml portions of 7*N* hydrochloric acid, and the washings are discarded. The organic phase is washed with four additional 50-ml portions of 4.7*N* nitric acid, and the washings are discarded. The uranium is removed from the organic phase by extracting successively with 20-, 15-, and 15-ml portions of 25 per cent ammonium acetate solution (made by diluting 369 ml of glacial acetic acid with 1000 ml of water, neutralizing with 430 ml of ammonium hydroxide, and, after cooling, adjusting the pH of the solution to 7.6 with ammonium hydroxide, and diluting to 2 liters). The ammonium acetate washes are collected in a 150-ml beaker, and the pH of the solution is adjusted to 7.6 with ammonium hydroxide and/or dilute nitric acid. The solution is transferred to a 250-ml separatory funnel with no more than 15 ml of water. The solution is extracted with 25 ml of a 1 per cent oxine–chloroform solution. The chloroform phase is filtered through a folded 12.5-cm Whatman No. 41 filter paper placed in the mouth of a dry 150-ml beaker. The absorbancy of the chloroform solution is measured at 500 mμ in 5-cm cells against a reference solution blank prepared as above. The uranium concentration is obtained from absorbancy-concentration curves prepared by carrying 100, 300, and 500 μg of uranium through the procedure.

(2) *Dibenzoylmethane.* Yoe, Will, and Black[404] recommended dibenzoylmethane (1,3-diphenyl-1,3-propanedione) as a colorimetric reagent for uranium as being five to six times more sensitive than thiocyanate. The bright-yellow color, that is formed at an optimum pH of 6.5 to 8.5 in an ethyl alcohol–water medium is stable, obeys Beer's law, and has a maximum absorbance at 395 mμ. Since many ions interfere, an ether extraction of the uranium from a nitrate solution was recommended.

Přibil and Jelínek[405] extracted the uranium with ethyl acetate containing dibenzoylmethane from an aqueous solution and measured the color in the combined extracts directly. They recommended ethylenediaminetetraacetic acid (EDTA) as a complexing agent for the elimination of certain interferences. Anions that form complexes with uranium, such as oxalates, tartrates, citrates, carbonates, and phosphates, have to be absent. Eberle and Lerner[179] used a 70 per cent tributyl phosphate–30 per cent ethyl acetate extraction from 5*N* nitric acid to separate the uranium from a large variety of materials. After the organic phase has been washed with 5*N* nitric acid, the organic extract is neutralized with ammonia, and the color is developed. Thorium and zirconium also extract to a certain extent and interfere in the color development. The interference of zirconium is avoided by developing the color in the presence of calcium–EDTA, and the thorium interference is removed by separating the uranium in a 7.5*M* hydrochloric acid medium. Adams and Maeck[406] used dibenzoylmethane for the analysis of low-grade geologic specimens after separating the uranium by an ethyl acetate extraction of the nitrate.

Blanquet,[407] in a rather thorough study, developed a method in which an aqueous pyridine medium in the presence of EDTA and tartaric acid is used with dibenzoylmethane. Absorbancy measurements are made at 415 mμ. The color was found to be quite temperature dependent. A variation of 1°C in the temperature gave a relative error of 0.7 per cent. In the medium employed the ratio of uranium to dibenzoylmethane was found to be 1:1 in comparison to the ratio of 2:1 obtained by Yoe in an alcohol–water medium. It was found that a preliminary separation with sodium carbonate, prior to the color development with the above-mentioned mixture, was such that pitchblende, autunite, thorianite, columbite, uranothorianite, tantalite, and carnotite, containing from 0.05 to 25 per cent uranium, could be analyzed satisfactorily. It is interesting to note that Blanquet found that the entrainment of uranium by oxides or carbonates, which are precipitated with sodium carbonate, is insignificant. The main disadvantage to the method is the objectionable odor of the pyridine, especially for routine work.

Francois [408] combined the methods of Blanquet [407] and Eberle and Lerner [179] and determined uranium by separating it from contaminants by a single extraction with a 10 per cent (vol./vol.) solution of tributyl phosphate in isooctane from an aqueous phase containing 500 g of aluminum nitrate nonahydrate per liter. The yellow uranyl dibenzoylmethane complex is formed by direct addition of the extract to an acetone–water solution of dibenzoylmethane and pyridine. The absorbancy is measured at 410 mμ. Thorium is the only common cation that interferes. Pyrophosphate, tartrate, citrate, peroxide, and thiocyanate, because of their complexing action with uranyl ion, interfere and must be absent. The color has also been developed directly [193] after extraction of the uranium by tri-*n*-octyl-phosphine oxide in cychlohexane [see Sec. 1–2.4(e)]. Similarly the color has been developed after extraction of the uranium with hexone [409] [see Sec. 1–2.4(c)]. The separation from uranium can also be accomplished by in ion exchange prior to color development in 80 per cent alcohol.[138]

Procedure (Carbonate Precipitation: Pyridine Method).[407] A weighed amount, 250 mg, of the ground mineral sample is transferred to a 50-ml pyrex beaker. After the addition of 1 ml of sulfuric acid, the mixture is heated to dryness on a hot-sand bath. The beaker is then heated over a Meker burner until the sulfuric acid that has condensed on the sides has volatilized. An additional 0.5 ml of sulfuric acid is added, and the heating to dryness is repeated. After 2 g of potassium bisulfate has been added, the beaker is heated over a Meker burner until the bisulfate has been converted to pyrosulfate. To the cooled melt are added 5 ml of a 5 per cent alcohol solution and 5 ml of an iron solution containing 300 ml of a 47 per cent ferric chloride solution, 15 ml of phosphoric acid, 500 ml of perchloric acid, and water to make 2000 ml. The solution is

heated until the pyrosulfate cake disintegrates. To this solution is added cautiously 25 ml of a sodium carbonate solution containing 150 g per liter. (The ferric precipitate should persist after the addition of less than two-thirds of the carbonate solution. The pH is then in the neighborhood of 10.) The solution is then heated to near the boiling point for about 15 min to flocculate the ferric precipitate. The contents of the beaker are then transferred to a 50-ml volumetric flask. The walls of the beaker are washed with water, and the ferric precipitate is removed with a rubber policeman. After the mixture has cooled, the volume is made up to 50 ml with water. The solution is filtered on a dry filter paper, and the first 5 to 10 ml of filtrate is discarded. Five milliliters of the filtrate is then transferred to a 25-ml volumetric flask, and 1 $\pm$0.05 ml of a tartaric acid solution containing 500 g per liter is added, after which the flask is carefully shaken The flask is made up to volume with the color-developing solution, consisting of 2 g of dibenzoylmethane, 12.5 g of EDTA, 500 ml of colorless pyridine, and water to make 1000 ml. After the solution has been allowed to stand for half an hour to stabilize the temperature and to develop the color, the absorbancy is read at 415 mμ in a cuvette (1 to 5 cm) against a blank run with all reagents. The amount of uranium is read from a curve made from a solution of 250 mg of U_3O_8 dissolved in 10 ml of perchloric acid and made up to 1 liter which is carried through the above procedure. For larger amounts of uranium, a smaller aliquot of the filtered solution is taken.

Procedure (TBP-Pyridine Method).[408] A volume of aqueous sample not exceeding 5 ml and containing between 0.05 and 0.50 μg of uranyl ion is pipetted into a 60-ml separatory funnel. The volume is adjusted to 5 ml with water. Any Ce(IV) present is reduced by adding 1 to 3 drops of 5 per cent (wt./vol.) sodium sulfite solution. One drop of *m*-cresol purple indicator is added, and then, by dropwise addition of ammonium hydroxide or nitric acid, the pH is adjusted to the yellow form of the indicator or until metal ions just begin to precipitate. If titanium or zirconium precipitates during the pH adjustment, 50 mg of sodium fluoride is added to complex these cations. If thorium is present, a drop of glacial acetic acid is added at this point.

Eight milliliters of the aluminum nitrate salting reagent is now added [900 g of $Al(NO_3)_3 \cdot 9H_2O$ in water to make 1 liter] followed by 3.0 ml (by pipet) of TBP extractant (1 volume of TBP plus 10 volumes of isooctane). The funnel is stoppered and shaken for 30 sec. After the phases have separated, the aqueous phase is discarded. With a dry pipet 2.0 ml of the organic phase is transferred to a 25-ml volumetric flask. The volumetric flask is filled to the mark with the chromogenic reagent (17.5 ml of 1 per cent (wt./vol.) acetone solution of dibenzoylmethane, 809 ml of acetone, 43.5 ml of pyridine, and water to make 1 liter). After 1 hr. the absorbancy is measured at 410 mμ against a blank carried through the procedure. If thorium is present, 1 ml of pyridine is added, followed by swirling, before the chromogenic reagent is added.

(3) *Diethyldithiocarbamate.* The spectrophotometric determination of uranium with diethyldithiocarbamate has been known for quite some time [410] but until recently has had limited use owing to the large number of interferring elements. In most instances the com-

plex is extracted with chloroform,[411, 412] in which solvent the color does not change for 6 hr, whereas, with ethyl acetate or water, the color starts to change at once.[168] The range of pH for the formation and extraction of the complex into chloroform is rather limited. The maximum extraction occurs [411] from an aqueous solution at a pH of 7 to 8. At lower and higher pH values, the extraction is considerably curtailed. Although the absorption spectrum of the complex with uranium extends from 350 to about 500 mμ, the reagent itself absorbs strongly below 390 mμ so that the greatest difference in absorption occurs at 400 to 420 mμ. The chloroform extract obeys Beer's law. The presence of ethylenediaminetetraacetic acid (EDTA) does not influence the extraction, but phosphate and carbonate interfere.[413] Since many other ions are extracted,[411, 413] it is generally necessary to use a preliminary separation. The method has been used for the analysis of bismuth-base alloys,[412] and the procedure is given in Sec. 1–2.4(i).

(4) *Arsenazo.* Arsenazo is evidently one of the most sensitive colorimetric reagents for uranium that has been investigated in detail.[168] Paley mentioned the use of arsenazo [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid] by Soviet investigators as being of high sensitivity and suitable for the spectrophotometric determination of uranium. A blue color is produced with uranyl ions at an optimum pH of 4.5 to 4.9. Kuznetsov [414] described the use of this reagent and showed that U(IV) gives a violet color in mineral acid medium; he applied [415] the method to the analyses of low-grade minerals. Fritz and Johnson-Richard [196] made a detailed study of this reagent for quantitative work. A pH of 7 to 8 was found to be best for color development. A 1:1 complex is formed. Many ions cause interferences especially thorium and the rare earths. Since Fe(III), Zr(IV), and several divalent ions also interfere, several complexing agents were tried as masking agents. Ethylenediaminetetraacetic acid (EDTA) was found to be the most widely applicable. Recoveries better than 98 per cent were achieved in a direct determination of uranium using EDTA to complex ions of Al^{+3}, Ba^{+2}, Bi^{+3}, Ca^{+2}, Cd^{+2}, Cu^{+2}, Dy^{+3}, Fe^{+3}, Hg^{+2}, Mg^{+2}, Mn^{+2}, Ni^{+2}, Pb^{+2}, Sc^{+3}, Sr^{+2}, Ti^{+4}, VO^{+2}, VO_3^-, Y^{+3}, Zn^{+2}, and Zr^{+4}. The amount of EDTA used is critical, and only a slight excess can be permitted since higher than 0.005 millimole of EDTA per 50 ml gives low uranium values. Other masking agents that are useful are tartrate for molybdenum(VI), tungsten(VI), and titanium(IV), sulfosalicylate for aluminum, and thioglycerol for antimony, bismuth, and copper. Moderate excess of these masking agents does not affect the uranium results. Phosphate interferes seriously, but nitrate, chloride, perchlorate, or acetate at 0.2*M* and fluoride, oxalate, or sulfate at 0.01*M*

do not interfere. Although direct colorimetric determinations can be made with the use of masking agents, a preliminary separation of uranium, especially from thorium, is desirable. Holcomb and Yoe [416] also made a detailed study of the reagent for use in the determination of uranium. The findings of Fritz and Johnson-Richard [196] were essentially confirmed. No substantial effect of temperature on the color was found. An ether extraction for the separation of interferences was performed. Diethyldithiocarbamate can also be used for this purpose in conjunction with EDTA to prevent extraction of several other metal diethyldithiocarbamates. The procedure employing extraction of the diethyldithiocarbamate complex is given in Sec. 1–2.4(i). The following procedure is for a sample or aliquot containing 5 to 500 μg of uranium, which contains only interferences that are complexed by EDTA. The dilution and cell size can be adjusted to handle smaller or larger amounts of uranium.

Procedure.[196] If the sample is highly acidic, the pH is adjusted to approximately 2 to 3 with sodium or ammonium hydroxide. Sufficient 0.01*M* EDTA (disodium or diammonium ethylenediaminetetraacetate) is added to complex foreign metal ions that react with EDTA. Not more than 0.5 ml excess of 0.01*M* EDTA should be added. If the amount of foreign metal ions present is negligible, 0.5 ml of 0.01*M* EDTA is added. Two milliliters of 0.001*M* arsenazo solution is now added. (Commercial arsenazo is purified by slowly dropping a saturated aqueous solution of arsenazo into an equal volume of hydrochloric acid. The orange precipitate is filtered off and washed with acetonitrile and dried at 110°C for 1 to 2 hr.) To the solution is added 5 ml of triethanolamine buffer (equal volumes of 1*M* triethanolamine and 0.5*N* nitric acid), and the resulting solution is diluted to approximately 40 ml. The pH of the solution is adjusted to 7.5 with dilute nitric acid or ammonium hydroxide, and the solution is transferred to a 50-ml volumetric flask and made to volume. The color is measured against a reagent blank at 595 mμ in a 1-cm cell. The concentration is obtained from a calibration curve made with known amounts of uranium carried through the same procedure. If aluminum is present, it is advisable to heat the solution to boiling after adding the EDTA. If Mo(VI), W(VI), or Ti(IV) is present, 1 ml of 0.1*M* tartaric acid is added to the acidic sample before continuing with the rest of the procedure.

(5) *Thoronol* [*(1-o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid*]. Thoronol is found in the literature under a variety of common names such as Toron, thorin, thoron, and thoronol. It reacts with U(IV) to give a red complex with maximum absorption of about 540 mμ. Paley [168] mentioned the use of this reagent as a sensitive color reagent permitting the determination of as little as 10^{-8} g of uranium per milliliter. A list of interfering elements was given. Foreman, Riley, and Smith [417] made an extended study of this reagent for the determination of uranium. It was found that aqueous–acetone solutions of the complex were stable. The complex was found to contain 2

690–457 O—64——9

molecules of thoronol to 1 of uranium. The pH of the solution for color formation was not critical; a final acidity of up to 0.2*N* hydrochloric acid can be used for full color development. The color of the aqueous solution of the complex was found to be unstable; however, in an 80 per cent acetone–aqueous mixture, the maximum sensitivity of color formation and stability was obtained. The sensitivity is about the same as that of dibenzoylmethane. Iron, chromium, vanadium, zirconium, copper, mercury, manganese, cerium, and particularly molybdenum and thorium interfere. Phosphate, nitrate, and sulfate also can be present in only small amounts. As in the case of many other spectrophotometric methods for the determination of uranium, a preliminary separation is advisable. This can be done by extracting the uranium with a chloroform solution of diethyldithiocarbamate from an ethylenediaminetetraacetic acid (EDTA)[417] solution. Iron(III), bismuth, and copper are removed by a prior extraction of their cupferrates into chloroform. The method was used for the determination of uranium in bismuth-base alloys by first removing the bismuth in an ion-exchange column. After the uranium has been reduced by means of a lead reductor, the color is developed with thoronol.

Procedure.[417] One milliliter of a hydrochloric acid solution containing 5 to 30 μg of U(VI) is diluted to 5 ml with 1*M* hydrochloric acid. (Up to 1*M* nitric acid can be tolerated at this stage although the following interfering ions should be lower than indicated: sulfate, 2.5*M*; oxalate, 1.2*M*; aluminum, 0.3*M*; copper(II) 0.05*M*; cerium(III), 0.02*M*; fluoride, 0.5*M*; phosphate, 0.2*M*; iron(III), maganese(II), nickel(II), and cobalt(II), 0.01*M*; tin(II) and strontium, 0.005*M*; and mercury (II), thorium and lanthanum, 0.003*M*. To this solution is added 2 ml of a 5 per cent aqueous cupferron solution and 15 ml of chloroform. After being shaken for 1 min the solution is allowed to settle, and the organic layer is drawn off and discarded. An additional 2 ml of cupferron solution and 15 ml of chloroform are added, and the extraction is repeated. To the separated aqueous phase is added 1 drop of phenolphthalein solution; then 20 ml of a saturated solution of EDTA is added. The solution is made just alkaline with sodium hydroxide solution and then is buffered to about pH 6 by adding 2 ml of 20 per cent sodium acetate solution and 0.5 ml of 20 per cent acetic acid. To this solution is added 5 ml of a 5 per cent aqueous sodium diethyldithiocarbamate solution and then 20 ml of 0.3*M* calcium nitrate solution. (If appreciable quantities of oxalate are present, magnesium nitrate must be used to bind the excess EDTA.) The solution is readjusted to pH 6 if necessary.

The aqueous phase is extracted with three 15-ml portions of chloroform. The chloroform extracts are combined and washed once with water containing 1 ml of 5 per cent sodium diethyldithiocarbamate solution buffered with acetate to pH 6 and made up to 0.05*M* in calcium ethylene diaminetetraacetate. The chloroform phase is extracted with two 5-ml portions of a 10 per cent ammonium carbonate solution, and the extracts are combined and evaporated to dryness in a silica dish.

The residue is ignited over a Bunsen burner for 30 sec, cooled, and dissolved in 2 ml of hydrochloric acid; then the solution is evaporated to dryness.

The residue is dissolved in 1 ml of 3*N* hydrochloric acid and is transferred, along with an additional 1 ml of water used for washing the dish, to a 10-ml flask containing 15 g of freshly cleaned lead shot (cleaned with hydrochloric acid, then with 3*N* hydrochloric acid, and stored in 3*N* hydrochloric acid). The contents of the flask are shaken for 1 min, and the solution is transferred, together with about 1 ml of water washings, to a 25-ml volumetric flask. To this flask are added 20 ml of acetone and 1 ml of 0.5 per cent aqueous thoronol solution (the commercial product is recrystallized from dilute acetic acid, washed, dried at 110°C for 15 min, dissolved, and made to volume with water). The absorbancy of the solution is measured at 540 mμ in 5-cm cells against a blank prepared by carrying a solution with no uranium through the procedure. An absorbancy-concentration curve is made by carrying known amounts of uranium through the procedure.

(6) *1-(2-Pyridylazo)-2-naphthol* (PAN). One of the most sensitive and seemingly quite versatile reagents for the spectrophotometric determination of uranium is that reported by Cheng,[219] who used PAN in *o*-dichlorobenzene for both the separation and determination of uranium. The compound reacts with many polyvalent metals, but in the presence of EDTA and cyanide the interferences are effectively complexed. The color formed is intense, with a maximum absorption at 570 mμ. The dye itself is very highly colored, but it has a broad absorption band below 550 mμ; therefore filter photometers may not be too satisfactory for measurement of the color. A complex of 2:1 between the dye and uranyl ion is formed under the conditions studied. There is some competition between the EDTA and the dye for uranium when large amounts of free EDTA are present; for 0.1 millimole of iron, thorium, and zinc, 0.5 millimole of EDTA is sufficient. The pH effect is quite marked, the maximum absorbancy being obtained at pH 10. The absorbancy drops markedly on both sides of this pH. Copper(II), nickel(II), mercury(II), zinc(II), iron(III), zirconium(IV), and thorium(IV) did not interfere when complexed by either potassium cyanide and/or EDTA. Chloride, bromide, iodide, sulfate, nitrate, carbonate, thiosulfate, acetate, sulfite, and fluoride anions did not interfere. Hydrogen peroxide inhibited the color formation, as did phosphate ion, which caused precipitation of uranyl phosphate. The time of standing before extraction was found to be important, maximum color being developed in 10 min. The method has also been used [184] following a tributyl phosphate extraction.

Procedure.[219] An aliquot of the slightly acid or neutral solution, containing 2 to 100 μg of uranium, is mixed with 1 ml of a pH 10 buffer solution (60 g of NH_4Cl is dissolved in 200 ml of water, 570 ml of NH_4OH is added, and the solution is diluted to 1 liter with water). The solution

is diluted to 20 ml, and 1 ml of a 1 per cent potassium cyanide solution is added. The pH is adjusted to 10 if necessary, and 2 ml of 0.1 per cent PAN solution in methanol is added. After the solution has stood for 10 to 15 min, exactly 10 ml of *o*-dichlorobenzene is added, and the mixture is shaken vigorously for 30 to 60 sec. The dichlorobenzene extract is centrifuged, and the absorbancy is measured at 570 mμ against the reagent blank. Known amounts of uranium are run through the procedure to obtain an absorbancy-concentration curve.

(7) *Benzohydroxamic Acid.* Overholser and Grimes [418] proposed the use of benzohydroxamic acid for the quantitative analysis of uranium and vanadium. The solvent used was water. A rather thorough examination of the effects of pH, reagent and buffer concentration, temperature, and diverse ions was made. Meloan, Holkeboer, and Brandt [218] repeated much of the above work but also found that the color could be extracted into 1-hexanol. They studied interferences, reagent stabilities, and the effect of pH on the extraction. The ratio of uranium to benzohydroxamic acid varied with pH. The effect of the pH on the extraction was quite marked, being at a maximum at pH 6.2. The age of the 1-hexanol was found to be important, freshly distilled 1-hexanol being desirable. The color of the 1-hexanol extracted complex was quite stable in comparison to the color developed in an aqueous medium. The compounds that caused interferences were strong oxidizing and reducing agents. Aluminum, tin(IV), zirconium(IV), and titanium(IV) also caused interference in much the same way as did these elements in the work of Overholser and Grimes. It was found that an increase in the concentration of reagent reduced certain interferences such as thorium, molybdenum and tungsten. Cerium(IV), when reduced by the reagent to Ce(III), also caused no interference.

Procedure.[218] To a solution containing not more than 5×10^{-5} mole of U(VI) is added 10 ml of 0.1*M* benzohydroxamic acid. The solution is diluted to 50 to 100 ml with water, and the pH is adjusted to 6.2± 0.1 with 0.3*M* sodium hydroxide. The solution is extracted with 25-ml portions of 1-hexanol. If the layers do not separate in 5 min, the mixture is centrifuged. The absorbancy is measured at 380 mμ against a 1-hexanol blank. An absorbancy-concentration curve is run on known uranium solutions in the same manner.

(8) *Other Organic Reagents.* There have been many other methods used at one time or another for the spectrophotometric determination of uranium. These have been considered by Rodden and Warf.[355] Among the various reagents proposed are ferrocyanide,[227, 419, 420] which forms a colloidal solution obeying Beer's law only under specific conditions;[421] 1-ascorbic acid;[85, 422, 423] chromotropic acid;[89, 424-426] salicylates;[98, 427] sodium alizarin sulfonate;[100] 2-acetoacetylpyridine;[428, 429] certain β-diketones;[430, 431] isatin β-oxime;[432] morin;[433-435] and thioglycollic acid.[159, 161, 436, 437]

(d) *Uranium by Differential Spectrophotometry.* In the differential spectrophotometric method of analysis, the sample is measured against a known amount of uranium that is somewhat lower in concentration than the sample in question instead of against a solution containing all reagents except the uranium or, in some cases, against a pure solvent.

The theory of differential spectrophotometry has been discussed in a number of papers.[438-441] This technique has been applied by Rodden [356] to the determination of uranium using peroxide, and Crouthamel and Hubbard [442] have used it with thiocyanate. A study of this method was made by Bacon and Milner,[443] who determined uranium in a sulfate medium. The effects of variables were studied, and it was found that the control of temperature was important. The effect of acidity, slit width, and cell size and the wave-length variations of the spectrophotometer were also studied. Although maximum absorption of the uranium in 4*M* sulfuric acid occurred at 412 and 422 mμ, interference by niobium and molybdenum resulted in the use of the 430-mμ band. The accuracy of the determination compared favorably with volumetric and gravimetric procedures, but the necessity of using calibrated volumetric equipment and thermostatically controlled baths prompted the authors to suggest that the method is best suited to laboratories having to determine uranium continuously since the time taken to set up apparatus and calibrate equipment is then spent advantageously.

Studies of the effects of impurities in a sulfate medium have been made,[444] and this method has been used for the determination of uranium in binary alloys of uranium and niobium [445, 446] and in uranium alloys containing zirconium, molybdenum, and titanium.[445] Steele [366] used a differential spectrophotometric method in a perchloric acid medium for the analysis of uranium in plant products. He showed that chromium, vanadium, nickel, and cobalt as well as sulfate and phosphate interfered. It would appear that without prior separation of interfering elements the direct differential method has certain drawbacks.

1–3.4 Fluorometric Methods

For the determination of trace amounts of uranium, there are at present no methods that are more sensitive than the fluorometric ones. However, some of the newer spectrophotometric methods are approaching the sensitivity obtained with the fluorometric ones. Unfortunately, since the rather wide use of these fluorometric methods began, variations in techniques and equipment have been such that one is hard pressed to make a reasonable selection of a satisfactory method. Indicative of this are the values for the coefficients of variation reported that range from 0.7 to 20 per cent.

The fluorescent properties of uranium when exposed to ultraviolet light were first pointed out by Stokes [447] and by Becquerel.[448] Nichols and Slattery [449] found that the fluorescence was intensified by fusion with solids such as borax and sodium fluoride. Early work on liquids and solids has been reviewed by Pringsheim.[450] Hernegger and Karlik [451] were the first to develop this fluorescent property into a quantitative analytical method. The early analytical work has been described by Price [452] and Rodden and Warf.[453]

In certain instances sulfuric and phosphoric acid solutions have been used in place of the fused disks. The solution technique has great potential value since the fusion, which has been a source of error and requires considerable attention to detail, is eliminated.

Uranyl salts fluoresce with a characteristic yellow-green light when excited by ultraviolet light. The visible fluorescence is a maximum in the region of 555 mμ, and the most efficient excitation region is about 365 mμ. Jacobs [454] made a study of various fluxing agents. Of the solid materials (fluxes) studied, sodium fluoride produces the greatest intensification. The analytical procedure most widely used consists of fusing the uranium in a fixed amount of sodium fluoride, sodium fluoride with 2 per cent lithium fluoride, or sodium fluoride–sodium carbonate–potassium carbonate in a metal dish and then measuring the total fluorescence of the flux when excited by ultraviolet light.

Nichols and Slattery [449] tentatively suggested uranium hexafluoride as the compound that excited the fluorescence. Evans [455] collected uranium hexafluoride on sodium fluoride–potassium carbonate beads, but the mixture had to be fused before maximum fluorescene could be obtained. In all probability, judging from chemical evidence, the uranium that is fused in sodium fluoride is present as uranyl ion. Solution of the phosphor in water, followed by evaporation to dryness under an Infraradiator, destroys fluorescence. Refusion of the phosphor is necessary to restore the original intensity of fluorescence.

There are a great many ions that can interfere with the fluorescence method of analysis. Any ion or mixture of ions in the fluorescent disk or bead which causes the apparent content, as obtained by comparison with disks or beads of known uranium content, to be less than the actual uranium content is known as the "quencher," and the degree of quenching is designated as "Q." The quenching of fluorescence by impurities present in the sodium fluoride–uranium phosphor was described by Papish and Hoag.[456]

The symbol ϕ represents a relative efficiency and can be defined as the ratio of the fluorescence found in any one sample to the fluorescence produced by an equal amount of uranium in the absence of quenching

ions. When no quenching occurs ϕ is 1; when there is 100 per cent quenching, ϕ is 0. The relation between Q and ϕ is: $Q=100\ (1-\phi)$.

Quenching is constant in many cases when the concentration of quencher in the flux in constant, even though the uranium concentration varies by a factor of several thousand. The critical factor in the quenching phenomenon is the concentration of the quencher in the flux and not the ratio of quencher to uranium.

Since solutions of uranium show fluorescence, but not so strongly as in fused beads or disks, it is highly improbable that quenching is due to a change in the state of the uranium ion by an interfering element. Price, Ferretti, and Schwartz [457] and Kinderman and Newton [458] have derived mathematical explanations of theoretical quenching phenomena.

Elements that are the most commonly encountered contaminants in solutions and solids are iron, chromium, copper, calcium, and silicon. Elements and ions that present more specific interferences but that are not so common and normally are not present in such high concentration as the previous five are molybdenum, cerium, niobium, vanadium, zinc, nickel, tin, aluminum, rubidium, magnesium, titanium, sulfate, chloride, and phosphate.

Investgiations have been made in regard to the quantity of ions other than uranium which act as quenchers. A summary of tolerances and effects of addition of foreign ions above allowable limits [409, 459–461] is presented in Table 1.7.

Some of the substances tested, particularly molybdenum, strontium, magnesium, nickel, and lead, showed variable quenching; [459] the results given are for the maximum quenching found.

Whether or not sufficient interfering elements are present to result in quenching of the emitted fluorescent light, can be determined by the "spiking" (addition) or the "internal-standard" technique. The basis of the spiking technique is that the same proportion of added uranium would be quenched as the uranium that is present in the original sample. This procedure can be applied to any individual fused disk or bead by making the initial reading and repeating the fusion and reading after a known amount of uranium has been added. If the difference between the second and first reading is equal to the amount of uranium added, no quenching has occurred.

Where large quantities of foreign ions that reduce or enhance the fluorescence of uranium are present the internal-standard method is sometimes used. In this method a known amount of uranium is added to the sample melt, and the calculation is made on the basis that the fluorescence is a linear function of the uranium content. Aluminum in any great quantity interferes with the internal-standard method by preventing the uranium from being evenly distributed

Table 1.7—EMPIRICAL QUENCHING DATA OBTAINED BY FUSING 2.5 G OF FLUX (2.5 PER CENT KF AND 97.5 PER CENT $NaKCO_3$) WITH 1.0 μG OF URANIUM FOLLOWED BY ADDITION OF THE QUENCHER IN SOLUTION AND BY RE-FUSION OF THE DISK

Quenching ion	Amount of ion, mg			
	$\phi=1.0$	$\phi=0.9$	$\phi=0.75$	$\phi=0.5$
Ag		0. 001		0. 5
Al	*50			
Au		0. 005	0. 02	0. 15
B as H_3BO_3	1	1 5	2 5	3. 5
Ba	0. 5	5. 0	>50	
Be	1			
Br	*1, 000			
Ca	0. 1	1. 0		15. 0
Ce		0. 02		0. 2
Cl	*250			
ClO_4		0. 5		1. 5
Co		0. 001		0. 01
Cr(III) or (VI)		0. 001		0. 01
Cu		0. 01		0. 05
Fe(II) or (III)		0. 003		0. 06
Hg†	0. 005			
Li‡	1	2	3. 5	6
Mg§		0. 05		0. 65
Mn(II) or (VII)		0. 002		0. 01
Mo as molybdate§	0. 5	1. 0	>100	
NH_4	Volatilized			
NO_3		0. 3		1. 8
Ni§		0. 001		0. 1
PO_4	1	>50		
Pb§		0. 002		0. 1
Pt		0. 005		0. 1
SiO_2 as Na_2SiO_3	0. 1	1		13
Sm		0. 15		0. 8
SO_4	*350			
Sn(II)		0. 05	0. 5	2
Si§	0. 1	1	>50	
Sn(IV)		0. 05	10	
Th		0. 015		0. 15
Ti in H_2SO_4¶		0. 05		0. 5
W	0 02	0. 5	100	
Zn		0. 028		0. 15
Zr	1			
V as vanadate	*30			

*Maximum tested.
†All but a trace is vaporized during fusion.
‡Quenching complete ($\phi=0$) at approximately 7.5 mg unless more fluoride is added.
§Variable quenching.
¶Greenish fluorescence when more than 0.2 mg of titanium is present.

in the pellet; the uranium is almost totally concentrated in the bottom of the pellet when samples containing any great amount of aluminum are processed. Of the various ions used, aluminum was the only one that has been found to interfere with the method although others not tested may be found to interfere.

If quenching occurs, the safe procedure is to remove all substances not known to be harmless by a method that has been examined and proved satisfactory for the type of sample concerned. Usually the methods of separation are based on solvent extraction.

Another method of overcoming the quenching of emitted fluorescent light by interfering ions is the "dilution" technique. The dilution technique is based on the premise that ϕ approaches 1 as the concentration of quencher is decreased. It is possible to reduce quenching to a negligible factor by using a sufficiently small aliquot for analysis and by using the same amount of flux. Phosphors made from solutions containing quenching ions and uranium show less quenching as the solutions are progressively diluted, as indicated in Fig. 1.33. Application of the "dilution" technique is limited to so-

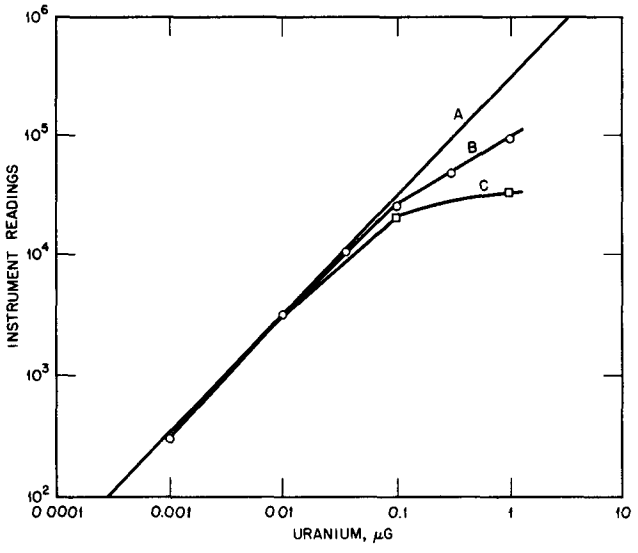


Fig. 1.33—Variation of fluorescence with dilution.[453] Curve A, uranium with no quencher. Curve B, uranium plus mixed quencher. Uranium was added to mixed quencher to have a final ratio of 72 of quencher to 1 of uranium. This solution was progressively diluted, and a portion was added to the sodium fluoride flux. Curve C, uranium plus iron. Uranium was added to a ferric nitrate solution to yield an iron-to-uranium ratio of 1000 to 1. Progressively diluted samples of the solution were used as in curve B. Two hundred milligrams of NaF was used as flux.

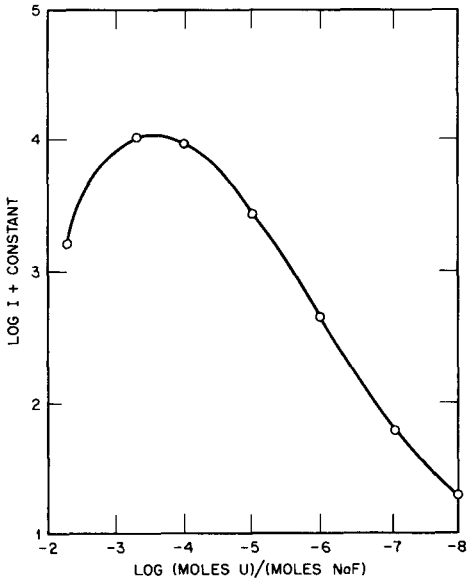


Fig. 1.34—Variation of fluorescence intensity vs. the ratio of uranium to sodium fluoride.[453] Phototube IP21 was used to measure the light intensities. Corrections were made for the light because of the blank. Twenty milligrams of NaF bead was used as flux.

lutions in which quenchers are not present in ratios exceeding 1000 : 1 (quencher to uranium) and for which an instrument of sufficient sensitivity is employed.

In addition to interfering ions that cause quenching of emitted fluorescent light, a high ratio of uranium to sodium fluoride can quench fluorescent light, [449, 462] as shown in Fig. 1.34. The intensity of fluorescent light varies in a linear manner with the uranium content until the fused pellet contains about $10^{-3.5}$ mole of uranium per mole of sodium fluoride.[451] Essentially the same relationship has been found when the sodium fluoride–sodium carbonate–potassium carbonate flux was used.[463]

A few elements that interfere with the fluorescence analysis do not quench but rather enhance emitted fluorescent light. Niobium [456] and tantalum show some fluorescent properties if fused with sodium fluoride. Five hundred micrograms of niobium gave the same fluoresence as 0.3 μg of uranium, and 50 μg of tantalum gave the same fluoresence as 0.6 μg of uranium.[461] This fluorescence may have been caused by a trace of uranium in the niobium or tantalum. Neodymium, nibium, and tantalum fere examined by Price, Ferretti and Schwartz,[457] who concluded that no known element interfered with the determination according to their procedure.

Salts of beryllium are reported to fluoresce,[464] but, when 1 mg of beryllium was treated in a manner similar to uranium, no measurable fluorescence was found.

The minimum quantity of uranium detectable by the fluorescence method of analysis is 10^{-11} g of uranium in a phosphor made with a flux of 200 mg of pure sodium fluoride.[457] The accuracy in such concentrations is extremely poor owing partially to the fluorescence caused by impurities in the flux.

Of the various fluxes indicated above which can be used for forming pellets in the fluorometric analysis of uranium, the ones using sodium fluoride are employed to the practical exclusion of all others. These fluoride fluxes can consist of sodium fluoride alone, sodium fluoride containing a small percentage of lithium fluoride, or a sodium carbonate–potassium carbonate fusion mixture containing sodium fluoride. Each of the three mentioned fluxes have been used extensively. All have certain advantages and disadvantages that are intimately tied in with the flux chosen.

Fusion of the flux and uranium mixture for the high sodium fluoride fluxes is accomplished by melting the mixture in a platinum dish with a resistance furnace, a gas burner, a gas-fired stove, or an induction heater. With the lower melting high carbonate fluxes, fusion is generally accomplished with a low-temperature muffle or a burner in either a platinum or a gold dish.

Although there are many methods of melt preparation, reproducible results can be obtained only when the fusion process is carefully controlled.

Various methods of fusion, including muffle, tube furnace, burner, and induction heating have been studied in detail and found capable of producing acceptable results.[454, 467] However, the methods are not interchangeable, and best results are obtained when one controlled method of fusion is used.

The composition of the atmosphere to which the flux is exposed while molten greatly affects the reproducibility. Pure sodium fluoride–uranium melts fused in carbon dioxide are nonfluorescent. Fusion in an inert atmosphere such as nitrogen, helium, or argon produces normal fluorescence. High sodium fluoride fluxes attack platinum when fused in high oxygen (greater than 90 vol. %) atmosphere. Ordinary air-atmosphere fusions produce normal fluorescence and are best suited for normal laboratory use. The flux should remain molten long enough to allow the uranium to be uniformly distributed in the flux and yet keep dish corrosion to a minimum. Quenching by dissolved platinum is a major source of error. As a consequence, fusions are generally carried out only slightly above the melting point of the flux (m.p. + 50°C). The duration of the fusion depends upon the tempera-

ture of fusion. High-temperature fusion times range from 30 sec to 3 min, whereas low-temperature fusion times range in duration from 3 to 40 min.

Various types of melt crystals with correspondingly different fluorescent properties are produced by different methods of cooling the molten flux. Rapid cooling of the pure sodium fluoride fluxes usually produces a fractured crystal, whereas annealing or slow cooling produces a more-uniform surface and more-transparent crystals. Lithium fluoride–sodium fluoride (1 to 3 per cent lithium fluoride) and high carbonate fluxes are not as subject to this phenomenon as are the pure sodium fluoride fluxes. With a consistent cooling method, reproducible results have been achieved for a wide variety of fluxes and cooling methods.

When the uranium fluorescence is measured in a bright fusion dish, dish reflectivity must be controlled. Variations in the amount of light reflected by the bright fusion dish cause significant variations in the amount of uranium fluorescence measured. The problem of dish reflectivity has been resolved by many workers through the use of a "knock-out" melt. The melt (sodium fluoride with greater than 90 wt. % sodium–potassium carbonate or burner-fused 2 per cent lithium fluoride in sodium fluoride) is tapped out of the fusion dish and transferred to a dish of uniform brightness in which the fluorescence of all the melts is measured.

Minor variations in uranium fluorescence are caused by variations in flux weight and thickness. Flux weights and thicknesses in common use range, respectively, from 0.3 to 3.0 g and from 0.015 to 0.09 in. Thickness of flux is usually controlled by controlling the flux weight and fixing the dish size. Good reproducibility is obtained by controlling the flux weight to ± 25 per cent.

Both the high carbonate and the high fluoride fused fluxes increase in fluorescence upon standing in moist air. The absorption of water vapor produces a faint luminescence in the fused flux itself; apparently water vapor acts as an activating impurity. This phenomenon is called "blank rise." It is quite pronounced in the high sodium–potassium carbonate fluxes and necessitates the use of desiccators or the immediate measurement of fluorescence after fusion. The same effect is measurable in the high sodium fluoride fluxes but is generally only important in very low level work.

The two types of fluorometers used are the reflection type and the less frequently used transmission type. With the reflection fluorometer the fluorescence of the melt is measured from the same melt surface that is irradiated with ultraviolet light. With the transmission fluorometer the ultraviolet irradiation is made on one side and the fluorescence measurement is made on the other. Reflection

fluorometry employs an opaque melt holder; transmission fluorometry requires a transparent melt and a transparent melt holder. Both systems employ a mercury lamp as the ultraviolet source, filters to isolate the ultraviolet and fluorescence regions, and phototubes to measure the visible fluorescence.

(a) *Fluxes and Fusion Methods.* In an attempt to clear up some of the misunderstandings on the fluorometric determination, the choice of flux and methods of fusion will be discussed first, followed by a discussion of instrumental methods for measuring the fluorescence.

(1) *Sodium Fluoride Flux.* Much of the earlier work employed sodium fluoride as a flux.[452, 465] Although high sensitivity is obtained, the method of fusion, the atmosphere in which the fusion is made, and the high melting point (about 1000°C) of the flux have been the source of some problems. The amount of flux used is generally between 0.3 and 0.5 g, which weight must be fairly constant, and the flux is usually dispensed from a pellet-forming device. Owing to the high temperature of the fusion, it is necessary to use a platinum dish. Because the button is not readily removed from the dish, the fluorescence of each button must be measured in the fusion dish. As a result the reflectivity of the dish affects the amounts of light reaching the detection system. This reflection varies markedly from dish to dish and constitutes an important source of error. The principal source of this variation is the presence of brown stains on the fusion dish, presumably formed by the high-temperature reaction among the flux, the dish, and the atmosphere. Certain impurities in the flux mixture may also react with the platinum dish causing subsequent problems. It is generally necessary to clean the dishes after each use and, when necessary, to polish each dish by a tedious detailed procedure.

The conditions for fusion of the sodium fluoride pellet have been the subject of several articles.[466–468] The precision of the results appears to be affected by the fusion factor more than by instrument variables.[467] A variety of methods for fusion of the fluoride pellet has been described, including muffle or tube furnaces, induction heaters, and gas burners. Steele and Taverner[76] found that when the fusion is made in an electric furnace, regardless of the temperature and time of heating and the rapidity with which they are cooled, the fusions emerge from the furnace with a brown discoloration and with half the fluorescence of flame-heated fusions. The fluorescence, moreover, is not reproducible. It has been shown that the discoloration is due to dissolved platinum and the low fluorescence is due to the strong quenching by the platinum. Excess oxygen present during fusion in an electrical furnace may cause the platinum to dissolve in the melt.[465] This attack does not occur as readily in flame fusion, where, it is presumed, the oxidizing conditions are less severe. The use of gas

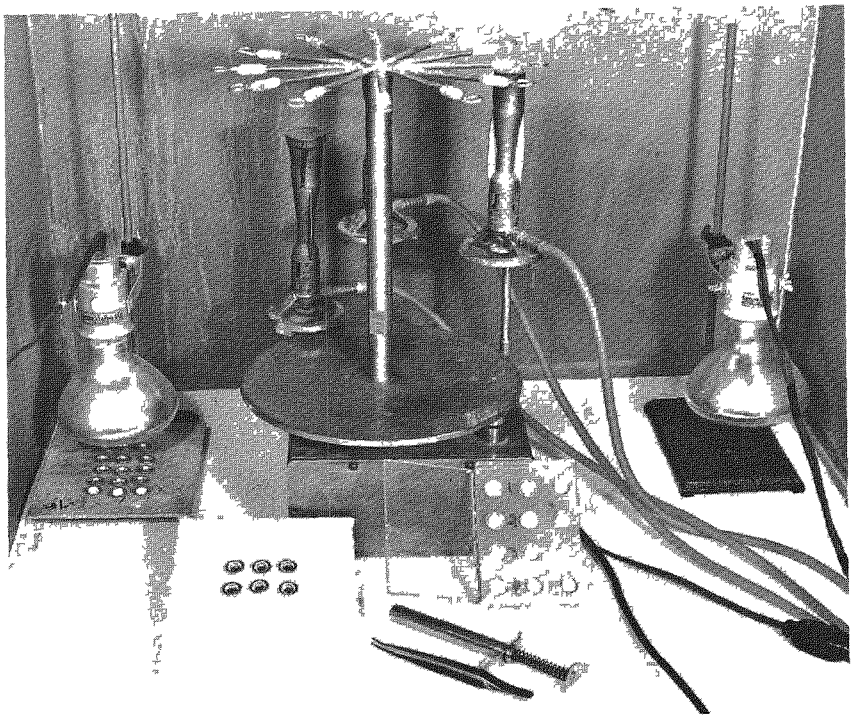


Fig 1 35—Oak Ridge National Laboratory fusion device.

burners seems to be more satisfactory. These are essentially of two types: (1) a modified Fletcher burner,[469] and (2) a multiple fusion device that has been used extensively at Oak Ridge National Laboratory (Fig. 1.35).[470] Unfortunately the latter device is not available commercially. A somewhat similar device has been described recently.[471] When fusions are made with the fusion device, the settings of the first two burners (close to holder in Fig. 1.35) are such that the temperature of the platinum dishes supported above them is approximately 1000°C. The third burner is adjusted to a lower position such that the temperature of the dish above it is 800°C. All temperature measurements are made with an optical pyrometer. The fusion period, which is automatically controlled by the device, is 1.5 min.

(2) *Sodium Fluoride–Lithium Fluoride Flux.* As the result of a considerable amount of experience in the fluorometric determination of uranium, Centanni, Ross, and DeSesa [469] proposed the use of a mixed fluoride flux containing 98 wt. % sodium fluoride and 2 per cent lithium fluoride. The advantages of this mixed flux over sodium fluoride alone are such that the use of sodium fluoride alone does not appear to be warranted.

A temperature of 850 to 900°C was found to be adequate for the fusion of the mixed fluoride flux. The resultant button can be removed readily from its dish; thus the fluorescence of each button can be measured in the same holder, and variations in reflectivity are eliminated. The necessity for carefully controlled cleaning and polishing of the fusion dishes is also eliminated. The dishes are simply washed in water and reused. After several months of use, the dish should be polished, however, to preserve the platinum. The analytical precision afforded by the mixed flux was found to be much superior to any known flux. The relative variability (coefficient of variation) of the method employing the mixed fluoride flux was reported to be 0.7 per cent compared to 4.7 per cent when sodium fluoride was used. The method includes a separation procedure since it appears that the elimination of quenchers is more satisfactory than the use of dilution and spiking techniques.

An aliquot of a liquid sample or of a solution of a solid sample is diluted and acidified so that the diluted sample contains approximately 0.01 mg of U_3O_8 per milliliter in a 5 per cent nitric acid solution. One milliliter of the diluted sample is salted with saturated aluminum nitrate solution, and the uranium is extracted into 10 ml of ethyl acetate. Aliquots of 0.1 ml are removed and transferred onto pellets of a 2 per cent lithium–fluoride–98 per cent sodium fluoride flux in platinum dishes. The pellets are dried, fused, and allowed to cool; they form buttons which slide easily from the dish. The fluorescence of the fluoride button is measured in a Galvanek–Morrison fluorometer. For details of the equipment and the procedure employed, reference should be made to the original article.[469]

(3) *Sodium Fluoride–Sodium–Potassium Carbonate Flux.* The high carbonate fluxes generally contain about 1 to 10 percent of sodium fluoride, the rest consisting of sodium–potassium carbonate. Like the other fluxes described, these have certain advantages and disadvantages. The amount of flux used is generally 2 to 3 g, which is considerably larger than that used with the sodium fluoride fluxes. The fused pellet is readily removed from the fusion dish, which may be platinum or gold, and the fluorescence is measured on the pellet alone. The fusion dish plays no part in the measurement of the fluorescence intensity of the button. The transmission type fluorometer can be used with the high carbonate fluxes.[475] Although objections have been given [469] to the use of high carbonate fluxes on the basis of fluctuation between daily flux batches prepared from the same reagent lots, this variation has not been observed at the New Brunswick Laboratory. The high carbonate flux does appear to be somewhat more hygroscopic than the sodium fluoride fluxes, but this has been a problem only on very humid days.

As with the sodium fluoride fluxes, it is preferable to remove interfering elements prior to fusion so that the interference effects are alleviated. For the procedure described it does not appear to be necessary to use the precautions employed with the sodium fluoride fluxes in so far as air conditioning and air filtering are concerned. Normal laboratory environment has been satisfactory for analysis. For the laboratory engaged in only a few fluorometric analyses at a time, the high carbonate fluxes do have the advantage of not requiring special burners for fusion of the pellets.

The following procedure[145] has been used for approximately 10 years, and over this time has given an average standard deviation of about 5 per cent. Interferences from foreign ions, such as iron, chromium, manganese, and copper which inhibit the fluorescence are eliminated by extraction of the uranyl nitrate with ethyl acetate. The method has been used in the 0.001 to 1 per cent uranium range. Lower concentrations of uranium require a preliminary concentration. A blank is analyzed simultaneously with the samples so that a correction can be made for the amount of uranium in the reagents.

Special Reagents. 1. *Aluminum Nitrate.* The aluminum nitrate should be analyzed for uranium before use since some analytical grades of aluminum nitrate have been found to contain objectionable amounts of uranium.

2. *Aluminum Nitrate Solution.* The aluminum nitrate solution should contain 20 mg of aluminum per milliliter. It is made by dissolving 277 g of aluminum nitrate nonahydrate in 1 liter of water.

3. *Magnesium Nitrate Hexahydrate.* The magnesium nitrate hexahydrate should be low in uranium.

4. *Sodium Fluoride.* The sodium fluoride should be low in uranium. Some analytical grades of sodium fluoride have been found to contain

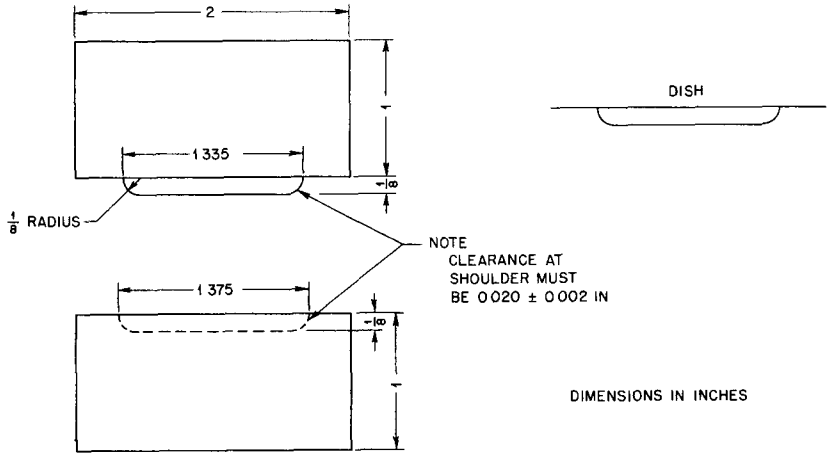


Fig. 1.36—Die for forming gold dishes.

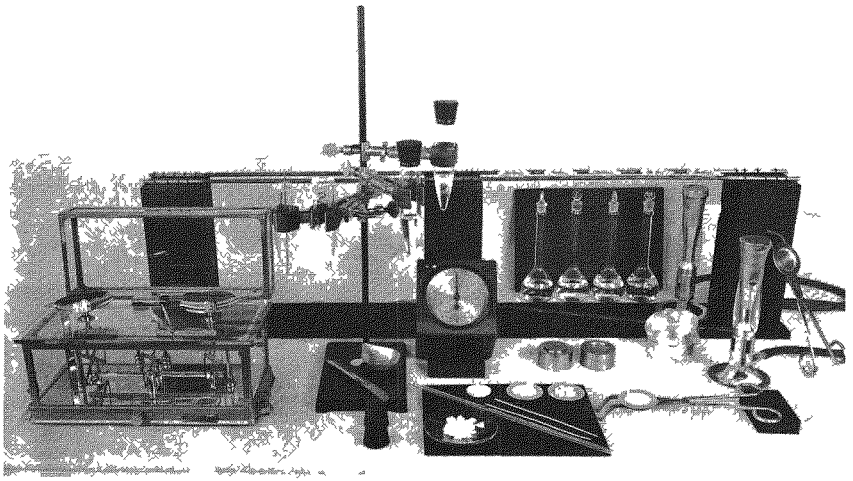


Fig 1 37—Fluorometric apparatus

objectionable amounts of uranium Baker and Adamson analytical reagent has been found satisfactory.

5. *Sodium Carbonate–Potassium Carbonate Fusion Mixture* This should be a mixture in the ratio of 1 : 2

6 *Prepared Flux.* Twenty-four grams of sodium potassium carbonate fusion mixture (low uranium) and 6 g of sodium fluoride are weighed into a 100-ml platinum dish and thoroughly mixed The mixture is fused over a Meker burner When a clear homogeneous melt results, the dish is quickly floated in a shallow pan of cold water. The melt is transferred to a clean mortar, broken up into small pieces, and kept in an oven at 110°C until used.

Special Apparatus. 1. *Gold Dishes.* The gold dishes are made from gold disks 2 in. in diameter and 0 020 in. thick. These disks are formed into dishes with the dies shown in Fig 1.36 After each use the gold dishes are straightened in the dies and cleaned in molten potassium pyrosulfate. They are kept under nitric acid between analyses and washed with distilled water just prior to use.

2. *Gold-dish rack.* This rack, which holds the gold dishes, is shown in Fig. 1 37. It is made from Nichrome rods on a wood base.

3. *Fluorometer.* A Galvanek–Morrison fluorometer or its equivalent is used.

Procedure: Fluorimetric Determination of Uranium With High Carbonate Flux. A sufficient quantity of the finely ground sample estimated to contain 100 to 600 μg of U_3O_8 is weighed into a 250-ml beaker. After the sample has been wet with water, 20 ml of nitric acid (1+1) is added, the beaker is covered, and the mixture is placed on a hot plate and boiled. The solution is filtered through Whatman No. 40 filter paper, and the filter paper is washed thoroughly with hot water. The filtrate and washings are reserved. The filter paper and residue are ignited in a platinum crucible until the filter paper has been destroyed. After the crucible has cooled, 2 ml of sulfuric acid and 10 to 15 ml of hydrofluoric acid are added, and the solution is evaporated to fumes and then

to dryness on a hot plate. Sufficient sodium potassium carbonate fusion mixture (no fluoride) is added to the crucible, and the resultant mixture is fused over a blast burner. After the melt has been cooled, it is dissolved in the acid filtrate that was reserved. The volume is reduced to about 75 ml and, after cooling, is transferred to a 100-ml volumetric flask and made to volume.

Twenty-milliliter aliquots of the blank, standard solutions (see calculation), and the sample are measured into 50-ml graduated centrifuge tubes (shown in Fig. 1.37), and 1 ml of the aluminum nitrate solution is added to each tube. Ammonium hydroxide is then added slowly with stirring, to precipitate the R_2O_3 group. The tube and contents are then centrifuged for 5 min at 2000 rpm. The liquid portion is decanted and discarded. The precipitate is dissolved in 2 ml of nitric acid, and the solution is diluted to 20 ml with water. A reprecipitation of the R_2O_3 group is made with ammonium hydroxide as described, and the solution is again centrifuged. After the supernatant has been discarded, the precipitate is dissolved in 1 ml of nitric acid (1+1). Eight grams of magnesium nitrate hexahydrate are weighed on a torsion balance and then added to the centrifuge tube. The volume is adjusted to almost 10 ml, and 5 ml of ethyl acetate is added from a buret. The tube is closed with a rubber stopper and shaken vigorously for 2 min. The solution is then centrifuged at 2000 rpm.

Gold dishes, one for each solution, are placed on the rack, heated with a Meker burner, and then cooled. One milliliter of the ethyl acetate layer is pipetted from the centrifuge tube and transferred to a gold dish. The solution is ignited immediately with a lighted taper to avoid creeping. After all the solutions have been transferred to the gold dishes, the dishes are heated over a Meker burner to destroy organic matter.

After being weighed on the torsion balance, 2.5 g of the prepared flux is transferred to each gold dish. With the aid of crucible tongs made of Nichrome, the flux is fused in the gold dish for exactly 2 min over a Meker burner. During the fusion the molten flux is rotated around the rim of the dish. The tongs holding the gold dish with the fused flux are placed in such a position that the gold dish rests in a level position (Fig. 1.37), and the melt is allowed to solidify undisturbed. When cool the disk is removed from the dish. The intensity of fluorescence of each sample is then measured with a Galvanek–Morrison fluorometer.

The amount of U_3O_8 is determined from a curve prepared by running a series of 20-ml aliquots of solutions containing 5, 10, 20, 100, 200, 500, 700, and 1000 μg per 100 ml. From the measured intensity of fluorescence, expressed in units of microamperes, a standard curve is obtained by plotting microamperes against concentration. The microampere reading of the sample is compared with this standard curve. The results are corrected for the uranium content of the reagent blanks. Every day three standards that bracket the uranium content of the samples that are being analyzed should be run.

(b) *Fluorometers.* The fluorescence of the uranium pellet is measured in various types of fluorometers. All fluorometers in general use employ a source of ultraviolet light that is filtered to remove

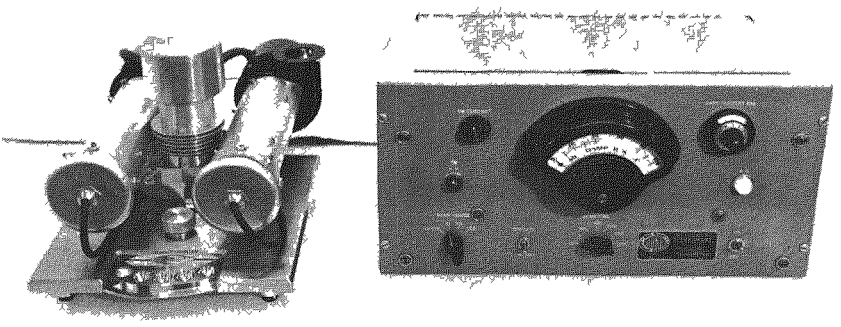


Fig. 1.38—Oak Ridge National Laboratory fluorometer.[492]

the visible light. Corning filters No. 5860, 5874, and 5875 are satisfactory for this purpose. The fluorescent light emitted from the pellet passes through a yellow filter (Corning No. 3486 or 3484) and a blue filter (Corning No. 9780). These filters are necessary to remove reflected ultraviolet and extraneous visible light from the pellet. The fluorescent light falls on a photocell, and the signal is amplified and read on a meter. Many types of fluorometers embodying the above principles have been made.

The fluorometers of Price,[476] Neuman,[477, 478] and Coleman [479] were used for many years but have gradually fallen into disuse. Other models are those described by Pickle,[480] Rider,[481] Kaufman, Castillo, and Koskela,[482] May and Fletcher,[483] DiGiovanni, Graveson, and Dwork,[484] Lynch and Baumgardner,[485] Milligan and Watts,[486] and Byrne.[487] A fluorometer was designed by Fletcher, May, and Anderson,[488] for use with high carbonate fluxes in which the ultraviolet light passes through the fused pellet. Various modifications of this instrument have been made.[489-491] The above instruments are custom made and are not available commercially.

Of the fluorometers that were developed for the analysis of uranium and that are, or were, available commercially the ones of Kelley, Hemphill, and Collier,[492] Galvanek and Morrison,[473] and the Hilger and Watts, Ltd. model described by Davey and Florida [174] have been used to the greatest extent.

(1) *Oak Ridge National Laboratory Model.* The Oak Ridge National Laboratory model [492] consists of two units, the optical unit and the electronic unit, each housed separately, as shown in Fig. 1.38. The constant-voltage transformer for the instrument and the ballast transformers, one for each of the two mercury-arc lamps, are not shown in the illustration.

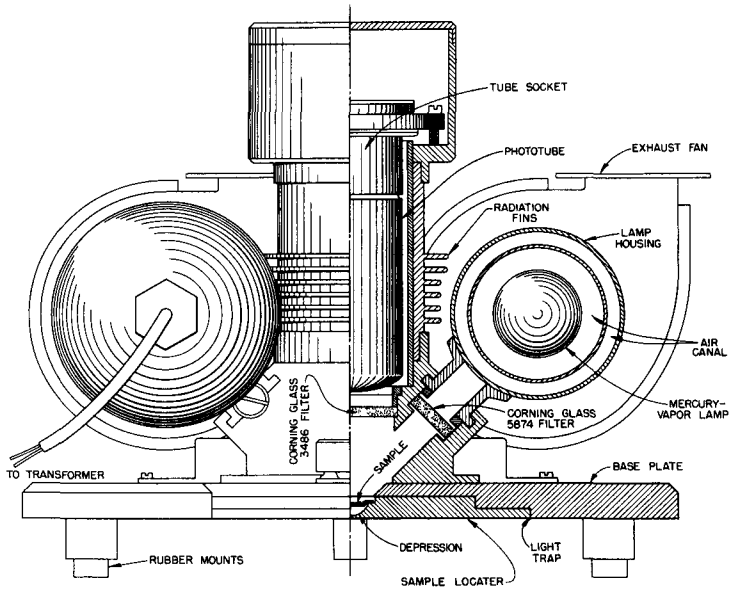


Fig. 1.39—Diagram of the optical system of the model Q–1165 fluorophotometer.[492]

The optical unit contains an ultraviolet-light source, cooling blowers, optical filters, a photomultiplier tube for measuring the intensity of the fluorescent light, a sample carrier, and appropriate shields and housings. The geometry of these components has been simplified, as shown in Fig. 1.39, to obviate the necessity of lenses or reflectors. This arrangement improves the efficiency of the light system and makes the alignment of the parts less critical. The distance between each ultraviolet lamp and the sample phosphor is $3\frac{13}{16}$ in.; the distance between the phototube window and the sample phosphor is $1\frac{9}{16}$ in. The proximity of the components is made possible by the efficient removal of heat from the ultraviolet lamps by the blower system; thus excessive heating of the photomultiplier tube, with consequent change in the sensitivity and dark current, is avoided.

The ultraviolet-light source consists of two General Electric type A–H4 mercury-vapor lamps, each operated from a General Electric 89G182 ballast transformer. The use of two lamps makes the illumination of the sample more nearly uniform, greatly reducing the effect of sample orientation.

The tube housing has external radiating fins, which, together with the lamp blowers, maintain the temperature of the optical unit very close to ambient temperature.

The photomultiplier tube is mounted vertically in an aluminum housing located between the two lamp housings and directly above

the sample position. The fluorescent light strikes the photosensitive surface of the electron-multiplier tube, a type 6199 tube with an end-window construction and ten stages of electron multiplication. The photocathode emits an electron current, the amplitude of which is directly proportional to the intensity of the incident light; this current is amplified by the ten stages of electron multiplication and fed into the electronic unit.

The sample carrier is a circular stainless-steel plate mounted on a spring-loaded pivot bearing in the base of the optical unit. Near the circumference of the top of the carrier are depressions designed to accommodate as many as 24 phosphor-sample plates. The sample is rotated into position under the photomultiplier tube for reading, and an indexing system identifies the sample position being measured. The labyrinth design of the sample wheel reduces leakage of extraneous light to a low level; therefore the high voltage to the photomultiplier tube need not be interrupted while samples are being changed. Samples are held in position under the photomultiplier tube by a spring-loaded roller that snaps into a groove on the underside of the sample wheel when the positioning is correct. This positive method of positioning reduces the possibility of error and is a decided advantage in operation.

(2) *Galvanek and Morrison Model.* The Galvanek–Morrison [473] fluorometer was developed after years of experience in the field of fluorometric analysis. It was designed primarily to provide an instrument of sufficient precision, simplicity, and flexibility to meet the requirements of control and research laboratories engaged in the analysis of solid and liquid samples containing uranium.

Because of the ultraviolet source chosen (4-watt 360 Blacklight–Blue fluorescent lamps), it was possible to produce an instrument of simplified construction (no lens or cooling systems).

A microammeter used in conjunction with a vacuum-tube voltmeter circuit measures the detector output. A keyboard arrangement of decade-resistance switches, used in conjunction with the meter to change levels of sensitivity, enhances both speed and ease of operation. In addition, automatic features incorporated into the design ensure precision of results if the instrument is operated properly.

The multiplier phototubes used were the RCA 1P21 or the 931A. The compressed geometry of this fluorometer permits operation of the detector at much lower voltages. This lessens the fatigue effect inherent in this type of detector and, consequently, helps to increase the precision of the instrument.

A well regulated power supply (necessary for proper operation of multiplier phototubes) of the Cascode Regulator type was designed to supply power to the detecting and measuring circuits.

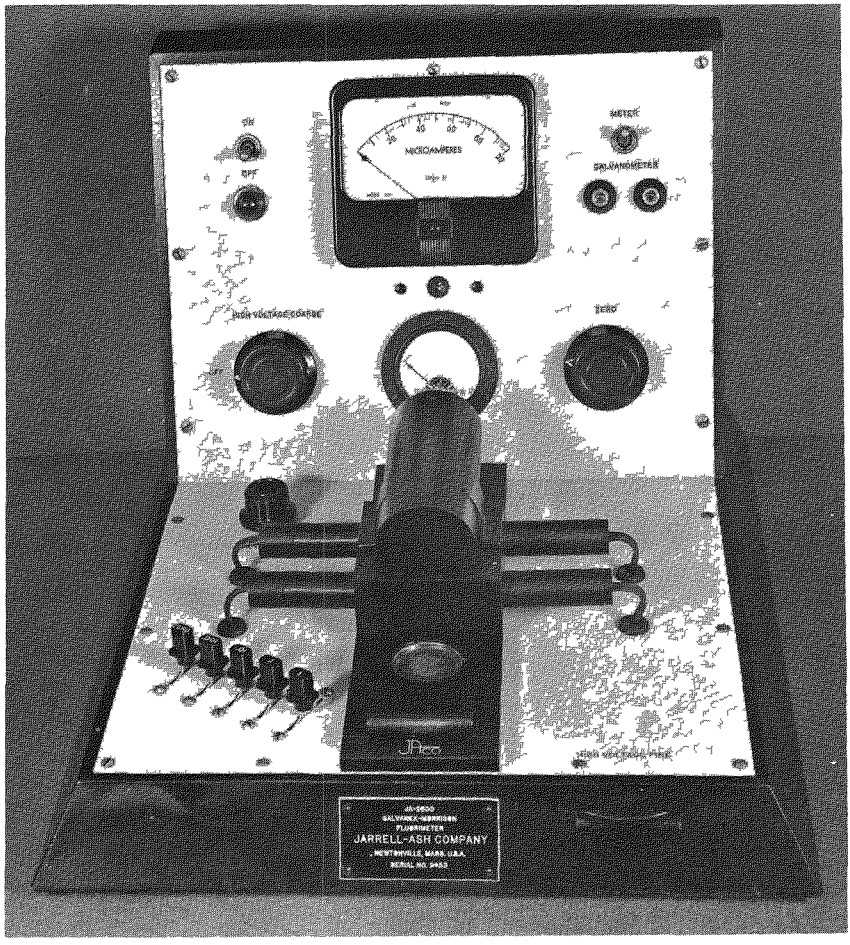
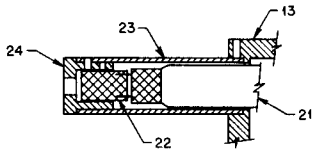


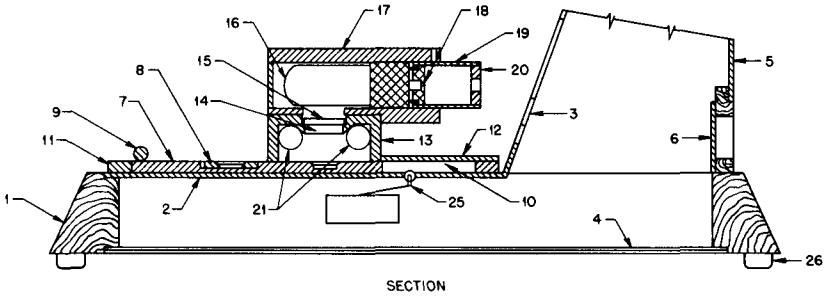
Fig 1 40—Galvanek–Morrison fluorometer [473]

Statistical analysis of results obtained with the instrument on known standard samples, with the sodium fluoride method, shows an average standard deviation of less than 3 per cent and an average accuracy of within less than 2 per cent over the range of 4- to 2000-mμg of U_3O_8 (4×10^{-9} to 2×10^{-6} g of U_3O_8). Average standard deviation and accuracy at the 0.4 mμg level (4×10^{-10} g of U_3O_8) were 5.4 per cent and 2 per cent, respectively.

A photograph of the instrument is shown in Fig. 1.40, and a sectional view of the console is shown in Fig. 1.41.



SECTION
FLUORESCENT-TUBE-HOLDER ASSEMBLY



SECTION
FLUOROMETER ASSEMBLY

Fig. 1.41—Sectional view of console.[473]

1, base
2, base plate
3, meter panel
4, bottom cover panel
5, back cover panel
6, socket-mount plate
7, slide bar
8, slide-bar insert
9, slide-bar handle
10, slide-bar guide rail
11, slide-bar stop
12, slide-bar cover
13, fluorescence chamber
14, yellow filter
15, blue filter
16, phototube
17, phototube holder
18, phototube socket
19, phototube-socket mount
20, phototube-socket inspection cap
21, fluorescent tube
22, fluorescent-tube socket
23, fluorescent-tube holder
24, fluorescent-tube holder cap
25, microswitch
26, rubber foot

The instrument is available from the Jarrell-Ash Company, Newtonville, Mass., or the Engineering Equipment Co., Boynton Beach, Fla.

(c) *Fluorescence in Solution.* The fluorescence of certain solutions of uranium has been known for many years. Solutions of uranyl sulfate show little fluorescence at room temperature, but, when they are cooled to −180°, they produce a strong band fluorescence. Fluorescence observed in sulfuric acid solutions was quenched by the addition of traces of hydrochloric acid or alcohol. Novak[493] used the fluorescence in sulfuric acid for the detection of uranium. Uranyl sodium phosphate in phosphoric acid solution showed somewhat

similar properties. In syrupy phosphoric acid, which on cooling to −185°C became a glass, fairly strong fluorescence was observed.[450] This fluorescence of a phosphoric acid solution of uranium was employed for the semiquantitative determination of uranium in plutonium nitrate solutions.[494] The nitrate solution (containing about 10 μg of uranium) was evaporated to dryness, treated with a few drops of phosphoric acid, and heated again. After it had cooled, the solution was made up to volume (1 ml) with organic-free phosphoric acid. The vials, which were cooled in a dry-ice–methanol bath, were irradiated with ultraviolet light from a mercury arc which had passed through a copper sulfate solution and Corning filter 986. The estimation was made with a hand spectroscope by comparison to standard uranium solutions treated in the same manner. Sill and Peterson [495] used fluorescence for the detection of uranium in 5 per cent phosphoric acid solution. The effects of many elements were investigated. It was found necessary to make preliminary separations before final fluorescence examination. The sensitivity obtained was 0.5 μg of uranium per milliliter of phosphoric acid solution.

The advantages of a method employing liquids for the fluorometric determination of uranium compared to the fusion method can be seen from the difficulties described previously for the fusion method. With this in mind Davydov, Dobrolubskaya, and Nemodruk [496] investigated the quantitative determination of uranium in phosphoric acid solutions by irradiation with ultraviolet light. They found that phosphoric acid was more satisfactory than sulfuric acid since the intensity of the fluorescence was greater with phosphoric acid and phosphoric acid alone did not show fluorescence as did sulfuric acid. Furthermore, phosphoric acid solutions absorbed less ultraviolet light than did sulfuric acid. The effects of various salts were studied as

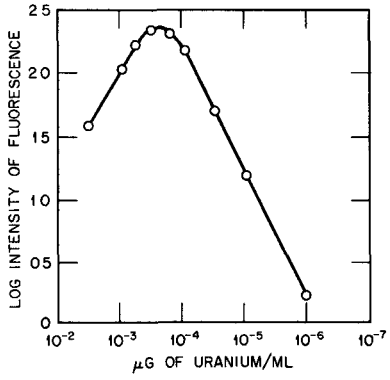


Fig. 1.42—Variation of intensity of fluorescence with uranium concentration in 5 per cent phosphoric acid. (From Davydov, Dobrolubskaya, and Nemdruk, *Zhurnal Analiticheskoĭ Khimii*, Ref. 496.)

well as those of traces of certain reducing and oxidizing substances and organic materials. Glycerin, ethyl alcohol, hydrazine, hydroxylamine, and hydrogen peroxide decreased the intensity of fluorescence. As shown in Fig. 1.42, the intensity of fluorescence rises and then falls with increase in uranium concentration, a phenomenon similar to that found when sodium fluoride fluxes are used. The quartz cuvettes used were 5 cm between working faces, and with these the useful range was found to be about 10^{-6} to 10^{-4} g of uranium per milliliter of solution. An ultraviolet bactericidal lamp BUV–15 with filter UFS–1 was used for excitation, and the intensity of fluorescence was measured with a Pulfrich photometer. A photoelectric photometer was also used for measurement of the fluorescence. With this instrument quartz test tubes of 1.5 cm diameter were used.

As was indicated in earlier work the intensity of fluorescence increased with an increase in temperature. A temperature of 20°C was used throughout the investigation. The intensity of fluorescence increased with increases in phosphoric acid concentration up to 5 per cent and from there to 10 per cent remained constant. A 5 per cent solution was used in the standard procedure.

As was reported by Sill and Peterson,[495] the authors found that many elements caused quenching. A solvent extraction procedure employing 20 per cent tributylphosphate (TBP) in carbon tetrachloride salted with calcium nitrate was used for separation of the interfering elements. It was found that commercial TBP had to be purified by treating 100 ml of the TBP in 400 ml of carbon tetrachloride with 750 ml of 1 per cent sodium hydroxide solution. After the solution has been shaken vigorously, the organic layer is allowed to settle and is then removed; the organic layer is then shaken with two 750-ml portions of water. Activated charcoal (5 g) is added, and the solution, after being shaken, is filtered through folded filter paper. The filtered TBP solution is again washed with two 750-ml portions of water and then filtered as above. Since ethylenediaminetetraacetic acid (EDTA) was used for complexing certain elements prior to extraction, tests were made with various commercial preparations. It was found necessary to purify the EDTA, according to Blaedel and Knight,[497] since some of the commercial preparations showed a blue fluorescence when extracted with TBP.

The uranium is reextracted from the TBP–CCl_4 with 5 per cent phosphoric acid. The intensity of fluorescence of this reextracted phosphoric solution was not as great as when the same amount of uranium was added to 5 per cent phosphoric acid even though better than 99.9 per cent of the uranium was originally extracted with TBP–CCl_4. Boiling the 5 per cent phosphoric acid reextract increased the fluorescence significantly owing to the elimination of car-

bon tetrachloride. Because of this loss of fluorescence intensity on reextraction, it was found necessary to carry standards of known amounts of uranium through the entire procedure.

The following procedure was used on synthetic samples with various quenchers to determine uranium of the magnitude of 1 μg of uranium per milliliter or less with a precision of 10 per cent. The time of analysis did not exceed 25 min.

Procedure.[496] To 25 ml of a nitrate solution in a separatory funnel, which has had the pH adjusted to 2.5 to 3.0 by the use of nitric acid or sodium hydroxide, is added 0.25 to 0.5 g of purified EDTA (weight used depends on the concentration of the interfering elements). Then 12.5 ml of a 20 per cent solution of TBP in CCl_4, prepared as described above, is added, and the mixture is vigorously shaken for 2 min. The separated organic phase is filtered through a folded filter paper. To the aqueous phase remaining in the separatory funnel, is added 12 ml of a TBP solution in CCl_4, and the extraction is repeated. Both extracted fractions are transferred to a separatory funnel, 12.5 ml of a 5 per cent solution of phosphoric acid is added, and the mixture is shaken vigorously for 2 min. After the layers have settled, the lower organic layer is drained into another separatory funnel, and the remaining aqueous layer is run off into a quartz beaker of 60 to 75 ml capacity. To the organic phase is added an additional 12.5 ml of 5 per cent phosphoric acid, and after the mixture has been shaken and the organic phase has settled, the aqueous phase is added to the first aqueous phase in the quartz beaker. After being boiled for 10 min, this aqueous phase is cooled and transferred to a 25-ml volumetric flask and diluted with water to the mark. The intensity of the fluorescence is measured, and the results are obtained by comparison with known amounts of uranium run through the same procedure.

1–3.5 Isotopic Composition

Since the beginning of the atomic energy program, the isotopic composition of uranium has been of considerable importance, and much time and money have been spent on the development of various methods for its determination. The power output of a reactor depends largely on the U^{235} content of the fuel. The cost of the nuclear fuel, as well as the critical concentration in the core, necessitates an analytical method for the determination of U^{235} that is accurate and economical. There are many methods that can be used, and the cost per analysis varies widely with the method employed. As would be expected the more-precise methods are, in general, the most expensive ones.

A list of the methods currently used for the isotopic analysis of uranium[498] is given in Table 1.8. An estimated cost for the instruments employed, as well as the precision usually obtained with each method, is also given. The methods are described under the various chapters dealing with the techniques involved.

Table 1.8—CURRENT METHODS FOR THE ISOTOPIC ANALYSIS OF U^{235}

Method	Relative precision, %	Estimated cost of equipment	Chapter and Section
Mass spectrometry (gas)	±0.02 to ±0.05	$60,000	Chap. 13, Sec. 13–1.
Mass spectrometry (surface emission).	±0.05 to ±0.5	$80,000	Chap. 13, Sec. 13–2.
Neutron activation (Ra-Be source).	±0.2 to ±1	$25,000	Chap. 14, Sec. 14–5.1(c).
Gamma-ray spectrometry	±0.2 to ±2	$3,000 to $4,000.	Chap. 14, Sec. 14.5–1(a).
Emission spectrometry	±0.5 to ±7	$10,000 to $40,000.	Chap. 12, Sec. 12–1.13(c).

(a) *Mass Spectrometry (Gas).* Mass spectrometers employing uranium hexafluoride as a gas are capable of high precision. All ranges of U^{235} concentration can be determined. The gas type instrument, however, is affected by "memory," and the results obtained are biased depending on the sample that was previously run in the instrument. When a variety of U^{235} concentrations is to be analyzed, this property can cause considerable trouble when only one instrument is available. In routine work one spectrometer is generally used for a certain limited concentration range.

(b) *Mass Spectrometry (Surface Emission).* A mass spectrometer employing a surface-emission source can be used for all concentrations of U^{235}. Although the precision obtained with a surface-emission type instrument is not so good as with the gas type instrument, the lack of memory has certain advantages. When a variety of different U^{235} concentrations is to be determined, a single surface-emission instrument is more versatile than a gas type instrument since the entire isotopic range can be covered.

(c) *Neutron Activation.* The determination of U^{235} by neutron activation, although generally necessitating a chemical purification, is quite versatile. Runs can be made on U^{235} concentrations ranging from 0.4 to 93 per cent. All measurements are made against standards; the series issued by the National Bureau of Standards is used for this purpose. The precision of the method is not so good as that obtained with mass spectrometers, but the cost per analysis is lower, except in the gas type instruments where uranium hexafluoride samples are run from the cascades. The major portion of the installation cost is for the radium–beryllium neutron source and the shielding that is necessary with this type source. Some use has been made of reactors for irradiation purposes.

(d) *Gamma-ray Spectrometry.* The use of a gamma-ray spectrometer for the U^{235} determinations has certain advantages. The cost of the instrument needed is considerably lower than other instruments used for isotopic analyses, and in certain instances no chemical separations are necessary. With material of unknown origin, it is generally desirable to purify the uranium by some type of solvent extraction, such as the extraction of the nitrate with diethyl ether. Concentration ranges from 0.4 to 93 per cent U^{235} have been analyzed. Other isotopes of uranium cannot be determined with this method.

(e) *Emission Spectroscopy.* The emission spectrograph can be used for the determination of the U^{235} content when the accuracy and precision of the analysis are not of prime importance. It can be quite useful when the approximate concentration only is required. The method is generally used for U^{235} in the high concentration range or in the low concentration range. It is rarely used for intermediate U^{235} concentrations. The precision obtained with the emission type spectrograph is not so good as that obtained with certain other methods. In addition, the presence of U^{236}, which is becoming more common in samples in which the U^{235} is in high concentration, has caused some problems. The cost of the instrument may vary widely, depending on whether or not photomultiplier tubes are used to measure the intensity of the lines obtained. In most instances the spectrograph can be used for other work besides U^{235} isotopic analysis. A single instrument can be used for the analysis of a wide variety of U^{235} isotopic compositions.

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CHAPTER 2

PLUTONIUM

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2–1 GENERAL INFORMATION

2–1.1 Discovery and Production

Plutonium was the second of the transuranium actinide elements to be "discovered."[1] Unlike elements that appear more or less abundantly in nature, each of the transuranium actinides was discovered as a direct result of attempts to produce heavier nuclides. Undoubtedly the most striking property of these elements is their ability to undergo fission when bombarded with high-energy neutrons. Plutonium shows the more unique property of being fissionable by either thermal (slow) or high-energy (fast) neutrons. It is partly because of this property that plutonium is destined to play an important role in nuclear reactors of the future.

The original discovery of plutonium by Seaborg, McMillan, Kennedy, and Wahl[1] came as the result of the bombardment of uranium with deuterons. The new nuclear species, for which evidence was obtained by observation of its radioactive properties, was postulated as being formed by the nuclear reactions shown in Eqs. 2.1 and 2.2.

$$_{92}U^{238} + {}_{1}H^{2} \rightarrow {}_{93}Np^{238} + 2{}_{0}n^{1} \tag{2.1}$$

$$_{93}Np^{238} \xrightarrow[\text{decay}]{\beta^-} {}_{94}Pu^{238} \text{ } (\alpha \text{ emitter, 90-year half life}) \tag{2.2}$$

Plutonium-239, the second isotope of plutonium to be discovered, was first produced and identified by Kennedy, Seaborg, Segre, and Wahl.[2] These investigators bombarded uranium, in the form of uranyl nitrate solution, with cyclotron-produced neutrons. Again, the new nuclear species was identified from its radioactive properties; it was postulated as having been produced according to the nuclear reactions shown in Eqs. 2.3, 2.4, and 2.5.

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} \text{ (a } \beta^- \text{ emitter, 23.5-min half life)} \tag{2.3}$$

$$_{92}U^{239} \xrightarrow[\text{decay}]{\beta^-} {}_{93}Np^{239} \text{ (a } \beta^- \text{ emitter, 2.33-day half life)} \tag{2.4}$$

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$$_{93}Np^{239} \xrightarrow[\text{decay}]{\beta^-} {}_{94}Pu^{239} \text{ (an } \alpha\text{-emitter, } 2.436\times10^4 \text{ year half life)} \quad (2.5)$$

Plutonium-239 has been found [3-6] in Canadian pitchblende and Colorado carnotite, although in exceedingly small quantities. Its origin has been postulated [7] to be as follows:

$$_{92}U^{238}({}_0n^1,\gamma){}_{92}U^{239} \xrightarrow[\text{decay}]{\beta^-} {}_{93}Np^{239} \xrightarrow[\text{decay}]{\beta^-} {}_{94}Pu^{239} \quad (2.6)$$

Ratios were calculated for the weight of Pu^{239} to the weight of ore and were found to be in the range $<1\times10^{-14}$ to 7×10^{-12}. Ratios were calculated for the weight of Pu^{239} to the weight of U^{238} and were found [4, 5] to be between 1.5×10^{-11} and $<0.4\times10^{-12}$. It is thus clear that there is essentially no likelihood of the existence in nature of commercially useful deposits of plutonium. Plutonium is produced in nuclear reactors that are frequently called "production reactors." Usually normal uranium, or uranium slightly enriched in the 235 isotope, is used as the nuclear fuel. Neutrons produced by the fissioning of U^{235}, as indicated by Eq. 2.7,

$$_{92}U^{235} + {}_0n^1 \rightarrow 2.5n + \text{FP} + 200 \text{ Mev} \quad (2.7)$$

are captured by U^{238}, and Pu^{239} is produced as indicated by Eq. 2.6.

Graphite or heavy water is normally used as the neutron moderator, largely because the capture cross section of U^{238} is larger for thermal neutrons than for fast neutrons, and thus greater neutron efficiency is achieved for the production of plutonium. If one of the neutrons resulting from the fissioning of each atom of U^{235}, as indicated in Eq. 2.7, were absorbed by a U^{238} isotope, as indicated in Eq. 2.6, with the eventual formation of an atom of Pu^{239}, it is clear that in the operation of a plutonium-production reactor the U^{235} burned up would be replaced by an equal number of atoms of Pu^{239}. As can be seen from Eqs. 2.6 and 2.7, the production of the Pu^{239} isotope is always accompanied by the formation of fission-product elements and a significant amount of energy. In production reactors the energy is wasted. Fission-product elements present formidable problems in the chemical processes for separation and purification of the plutonium. The fission-product elements of greatest concern are listed in Table 2.1 which is taken, in part, from a paper published by Steinberg and Glendenin.[8]

Of particular interest in the commercial production of plutonium is the variation in its isotopic composition. This arises when the 239 isotope captures a neutron, thus forming an unstable nucleus that loses energy in the form of gamma radiation, thereby giving rise to the

Table 2.1—FISSION PRODUCTS ENCOUNTERED IN CHEMICAL PROCESSING OF IRRADIATED URANIUM FOR PLUTONIUM[8, 9]

(Following 10-day Cooling)

Fission product	Fission yield, %	Half life	Nature of radio-activity	Absolute curies/g of U^{235} fissioned (10-day cooling)
Ru^{103}	3. 7	39. 8d	β	39. 0
			γ	37. 1
Ru^{106}–Rh^{106}	0. 4	1y	β	6. 23
			γ	1. 45
Zr^{95}–Nb^{95}	6. 77	63d	β	112. 4
			γ	213. 1
Nb^{95}	6. 77	35d	β	107. 2
			γ	107. 2
Ce^{141}	5. 7	33. 1d	β	69. 7
			γ	69. 7
Ce^{144}–Pr^{144}	5. 8	282d	β	124. 6
			γ	3. 8
Kr^{85}	0. 381	10. 27y	β	0. 47
Sr^{89}	4. 8	53d	β	81. 0
Sr^{90}–Y^{90}	6. 1	28y	β	7. 96
Y^{91}	6. 24	61d	β	116. 3
Te^{129m}–Te^{129}	1. 0	33. 5d	β	16. 7
			γ	50. 1
Cs^{137}–Ba^{137}	5. 9	33y	β	2. 21
			γ	2. 10
Ba^{140}	6. 4	12. 8d	β	79. 5
			γ	23. 9
La^{140}	6. 4	40d	β	84. 3
			γ	140. 32
Pr^{143}	5. 4	13. 7d	β	62. 0
Nd^{147}	2. 6	11. 3d	β	29. 53
			γ	12. 8
Pm^{147}	2. 6	2. 6y	β	12. 2
All other fission-product elements	----------	----------	β	463
			γ	27. 8
Total	----------	----------	β	998
			γ	688

Pu^{240} isotope. In addition, neutron capture by the 240 isotope and successive neutron capture by each succeeding isotope results in several higher isotopes being formed by (n, γ) reactions according to Eq. 2.8

$$_{94}Pu^{239}(n,\gamma)_{94}Pu^{240}(n,\gamma)_{94}Pu^{241}(n,\gamma)_{94}Pu^{242}(n,\gamma) \ldots \quad (2.8)$$

The rates of formation of these higher isotopes is a complicated function of the neutron spectrum existing in the reactor. The percentages of these higher isotopes increase with the total exposure to the neutron flux, and, as would be expected, the heavier the isotope, the smaller the amount produced. Because the 239 isotope is the most desirable as far as plutonium reactor fuel is concerned, it is clear that isotopic composition is of primary importance in the design and performance of plutonium fuel elements.

2–1.2 Role of Plutonium in Reactors

The production of plutonium in production reactors has already been discussed and the accompanying nuclear reactions have been described in Eqs. 2.6 and 2.7. Although the source of the neutrons is different, it is interesting to note these are the same nuclear reactions that were postulated as producing the first man-made plutonium (Eqs. 2.3, 2.4 and 2.5). In addition, these are thought to be responsible for the natural origin of plutonium in uranium minerals (Eq. 2.6).

Similar nuclear reactions occur in all cases when U^{235} is the fissionable material, whether in normal or slightly enriched uranium, both in production and power reactors. Furthermore, well-designed power reactors using normal or slightly enriched uranium as fuel will produce a weight of plutonium approximately equal to the weight of U^{235} consumed, or fissioned.

Up to the present time (1963), most power reactors have employed slightly enriched uranium as a fuel. However, a few experimental reactors have been operated with plutonium or plutonium-alloy cores. In this "preliminary" work, a binary alloy of plutonium with aluminum or iron, ternary alloys with uranium and molybdenum or uranium and fission-product elements, and mixtures of plutonium dioxide and uranium dioxide have been proposed and partially tested. Binary alloys of plutonium with cerium, cobalt, nickel, and osmium and ternary alloys with cerium and cobalt also have been seriously considered. An incomplete listing is given in Table 2.2.

As far as uranium-fuel reactors are concerned, the analytical problems involving plutonium consist primarily of its determination in the spent fuels. Because of the monetary value of plutonium, it is normally recovered from the spent-fuel dissolver solutions. For this reason, closely associated with recovery processes is the assay of the purified plutonium as metal, oxide, or salt. The determination of impurities is also required.

Obviously, when plutonium-rich reactor fuels come into use, the associated analytical problems will be expanded tremendously and will include the determination of plutonium in fabricated and ex-

Table 2.2—PROPOSED PLUTONIUM FUEL MATERIALS

Alloys	Ceramics	Cermets
Pu–Al	PuO_2	PuO_2
Al–Pu	PuO_2–UO_2	PuO_2–Mo
Th–Pu	PuO_2–MgO	PuO_2–UO_2–SS†
Zr–Pu	PuO_2–ZrO_2	PuC–Fe, Mo, Nb, Ta, W, Th
U–Pu–Fs*	PuC	PuC–Zircalloy–2
U–Mo–Pu	PuC–UC	PuO_2–Al_2O_3
U–Pu–Nb	PuN	
Pu–Fe	Pu_2Si_3	
	$PuSi_2$	

*Fs denotes fission product elements.
†SS denotes stainless steel.

pended fuels and in plant and process streams, as well as its measurement in the fertile material and also in the purified state.

2–1.3 Hazards and Techniques in Handling

The physiological and toxicological properties of plutonium have been studied in great detail in a variety of biological systems, including dogs,[10–14] mice,[15–16] rats,[17–18] and man,[19–20] and probably need not be discussed here. The radiological hazards of plutonium lie in the fact that it is an energetic alpha emitter (except Pu^{241}), and, when absorbed into the body, it is primarily a bone seeker. The alpha particles, because of their relatively large mass, exhibit strong ionizing power and impair the proper functioning of the bone marrow. This pernicious physiological behavior is prolonged because the biological half life of plutonium is about 200 years.[20] In fact, chronic alpha irradiation of the skeleton over many years may produce bone cancer and such nonmalignant bone changes as necrosis and osteoporosis, which cause spontaneous fractures and other clinical manifestations of radiation damage.

Fortunately there is no evidence that plutonium is absorbed through the normal unbroken skin. It may, however, enter the body through contamination of freshly produced wounds; it may be inhaled as small insoluble particles or droplets; or it may enter the body from the gastrointestinal tract. Body retention from the latter is normally quite low, probably not over 0.1 per cent. If inhaled, as much as 75 per cent may deposit on the lung surfaces, where it produces local irradiation exposure, and about 10 per cent may be absorbed from the lung into the blood and subsequently deposited in the skeleton. Because of the high lung deposition and absorption rate, inhalation is potentially the most dangerous route of exposure.

690–457 O—64——12

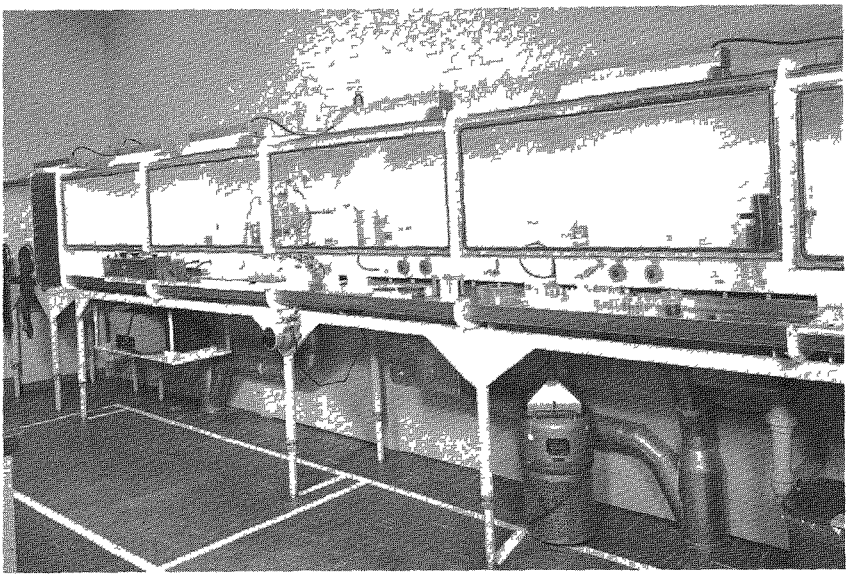


Fig. 2.1—Dry box assemblage, open-front type.

Once plutonium has been absorbed into the biological system, the most dependable and widely used evidence that absorption has occurred is the appearance of plutonium in the urine. Its presence is determined by radiochemical measurements. Biological data for the more common isotopes of plutonium are listed in Table 2.3.

The highly toxic and intensely radioactive nature of plutonium requires that special equipment and handling facilities be used in the analytical laboratory to adequately protect workers. The external

Table 2.3—BIOLOGICAL DATA FOR SOME ISOTOPES OF PLUTONIUM [21]

Isotope	MPC_{air}*	MPC_w†	Body burden,‡ μc	Gram/curie	Biological halflife, 10^4 days
Pu^{238}	4. 4	3.3×10^{5}	0. 044	5.9×10^{-2}	7. 3
Pu^{239}	3. 9	3.0×10^{5}	0. 044	1. 62	7. 3
Pu^{240}	3. 9	3.0×10^{5}	0. 044	4. 41	7. 3
Pu^{241} + daughters	2.1×10^{2}	1.5×10^{7}	0. 93	8.86×10^{-3}	7. 3
Pu^{242}	4. 1	3.0×10^{5}	0. 046	2.56×10^{2}	7. 3

*MPC_{air}=maximum permissible concentration in air, disintegration/min/meter^3, based on an exposure of 40 hr per week.

†MPC_w=maximum permissible concentration in water, disintegrations/min/liter, based on continuous exposure.

‡The critical organ for each isotope is the bone



Fig 2 2—Dry box assemblage with glove ports, gloves removed

radiation hazard is not great from reactor-produced plutonium because the isotopes encountered are alpha emitters, with the exception of Pu^{241}, which is a beta emitter. The soft gamma radiation accompanying the alpha radiation is not hazardous from the quantities of plutonium normally encountered in the analytical laboratory. Thus heavy shielding against penetrating radiation is not required.

However, for the handling of low-level beta and gamma radiation and high-intensity alpha radiation, special enclosures called "dry boxes" or "glove boxes" are used. For the routine handling of plutonium, it is advantageous to assemble the dry boxes in such a manner that assembly-line type operations can be carried out. For example, the sample to be analyzed is placed in the assemblage at one end, and all subsequent analytical operations to be made on that sample are performed without its being removed from the dry boxes.

Generally speaking, analytical work on plutonium-containing solutions may be performed in open-front dry boxes, as illustrated in Fig. 2.1, or in glove boxes with the rubber gloves removed, as illustrated in Fig. 2.2. In all cases where analyses are being performed on plutonium samples in the solid, dry state, it is essential to use glove boxes with the rubber gloves in place, as illustrated in Fig. 2.3. In well-designed boxes, it is possible to carry out all types of analytical

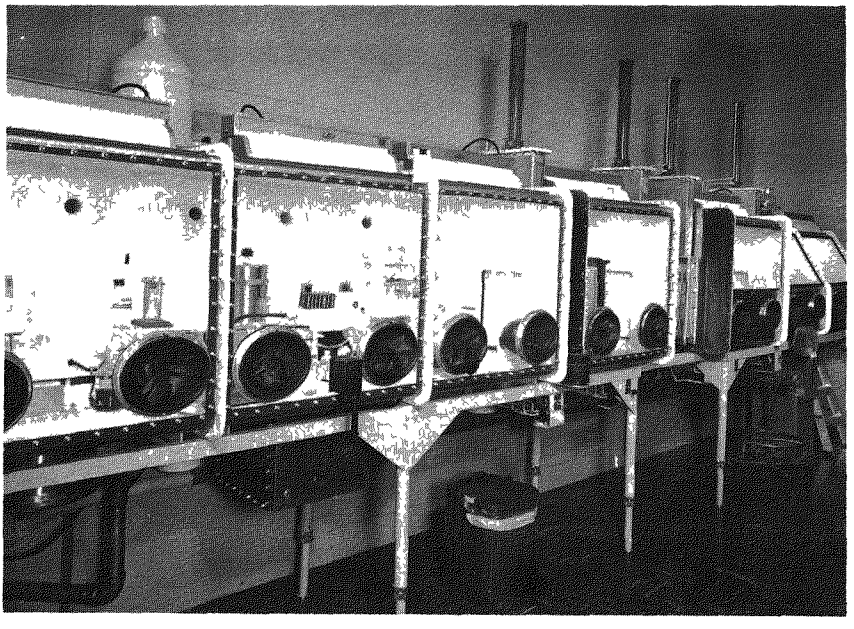


Fig. 2.3—Dry boxes with gloves.

operations, although sometimes it may be necessary to design equipment especially for dry-box use. Figure 2.4 shows a dry box designed for chemical microscopy operations. More-detailed information of the various problems encountered in planning analytical laboratories for the handling of plutonium can be found elsewhere.[22, 23]

2–1.4 Criticality Problems

Normally, critical masses of plutonium would not be encountered in the analytical laboratory. As a matter of fact, it is the responsibility of the analytical chemist to make certain that plutonium-containing analytical residues are removed daily. If this policy is adhered to, it is extremely unlikely that anything approaching a critical mass would accumulate in a laboratory as a result of one day's work. However, it is perhaps important that the nature of the problem be discussed briefly.

The number of neutrons produced by the splitting of a nucleus (following absorption of a neutron) is, on the average, between two and three. Whether or not a chain reaction will be propagated depends on the availability of sufficient numbers of neutrons, via the fission-capture route, to perpetuate the fission reaction. To offset this, the neutrons produced by the splitting of a nucleus may escape or undergo nonfission capture by the fissionable material or by the impurities therein. The relative number of neutrons that will escape from any particular quantity of fissionable material will depend on

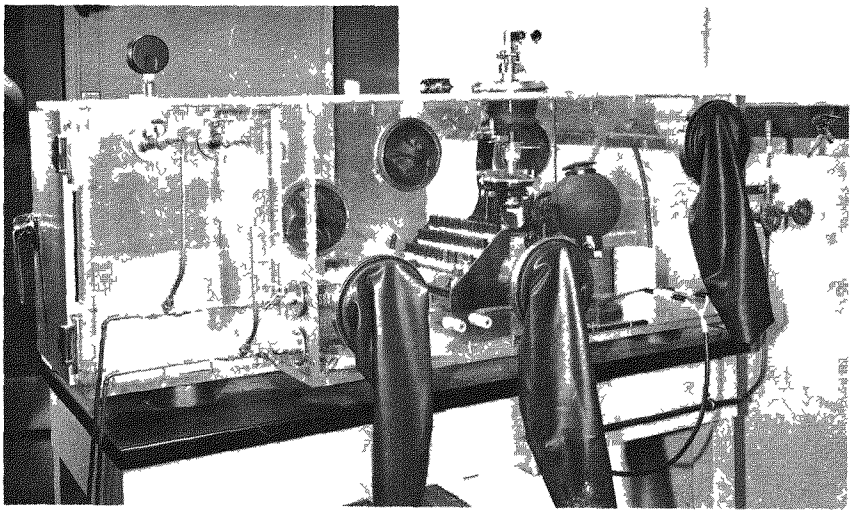


Fig. 2.4—Dry box of special design for chemical microscopy.

the surface-to-volume ratio of the particular configuration in which the fissionable material is contained. Thus the escape of neutrons from a quantity of fissionable material is a surface effect, whereas fission capture occurs throughout the volume occupied by the fissionable material and is, therefore, a volume effect. In addition, the greater the amount of fissionable material in a unit volume, the greater is the possibility of a chain reaction. Other factors, such as external materials that reflect neutrons back into the volume occupied by the fissionable material and the presence of neutron absorbers, influence the conditions under which a chain reaction will occur.

The critical mass of a fissionable material is that mass, under a given set of conditions, for which the production of free neutrons by fission is just equal to their loss by escape and by nonfission capture.

In actual practice, it is always necessary to prevent a chain reaction by exercising rigid control over three factors: (1) the total mass of fissionable material, (2) its concentration, and (3) the geometrical configuration in which the fissionable material is confined. This is best accomplished by specifying the conditions under which the fissionable material is handled and stored. The following restrictions, or parameters, have been recommended [24] for Pu^{239}:

Mass, g	Volume, liters	Cylinder diameter, cm	Slab thickness, cm	Concentration, g/liter
≤509	≤5.0	≤13.7	≤4.8	≤7.8

The above figures for mass and volume assume spherical geometry, for which these parameters are minimal. It is also assumed that the volume is completely surrounded by an effectively infinite water reflector. The cylinder diameter shown is such that nuclear safety is imposed by the diameter alone. This means that the cylinder may be of any length containing any mass at any chemical concentration and may be surrounded by a hydrogenous reflector. This is sometimes known as an "ever-safe" container.

Slab-like volumes of aqueous solutions, if the thickness is no greater than that shown above, will be subcritical even when surrounded by an effectively infinite water reflector.

Aqueous solutions having concentrations below the value shown will not be critical no matter what the total volume.

Any one of the above limitations, mass. volume, container dimensions, or concentration, will prohibit a chain reaction regardless of other conditions. It is assumed, however, that only ordinary materials such as concrete, stainless steel, ordinary water, and other normal materials of construction are present and also that the plutonium has a density of less than 1 g/cm^3 in a homogeneous solution sufficiently dilute to thermalize the neutrons.

There is no safety factor in the above numbers, and it is recommended [24] that a factor of 2 be applied to protect against analytical and sampling errors.

For the above reasons it is clear that careful record keeping and mass control is necessary in analytical laboratories handling fissionable materials. Good housekeeping practices are of considerable importance in the mass-control problem.

2–2 GENERAL CHEMISTRY OF PLUTONIUM

2–2.1 Physical Properties

The metal has a silvery white lustre and is somewhat brittle when pure. It melts at the surprisingly low temperature of 639 ± 0.5°C. It is known to exist in six different allotropic modifications, as described by Jette.[25] A considerable body of information exists concerning physical properties such as crystal structures and densities of the various allotropic phases.[26] Other properties such as linear expansion, electrical resistivity, and magnetic properties have been reviewed by Jette.[25] A detailed discussion of physical properties is beyond the scope of this chapter.

A considerable body of information regarding the intermetallic compounds of plutonium also exists and has been reported by Coffinberry and Waldron.[26] Included are X-ray diffraction and crystal

structure data for the following binary compounds: $PuAg_3$, Pu_3Al, $PuAl_2$, $PuAl_3$, $PuAl_4$, PuAs, $PuBe_{13}$, $PuBi_2$, PuC, Pu_2C_3, Pu_6Co, Pu_2Co, $PuCo_2$, Pu_2Co_{17}, Pu_6Fe, $PuFe_2$, Pu_2Ge_3, $PuGe_2$, $PuGe_3$, $PuH_{2.0}$, $PuH_{2.7}$, PuH_3, $PuHg_3$, $PuHg_4$, Pu_3In, Pu_2Mg, $PuMg_2$, $PuMn_2$, $PuNi_2$, $PuNi_5$, Pu_2Ni_{17}, PuO, Pu_2O_3 to Pu_4O_9, PuO_2, $PuOs_2$, PuP, $PuPb_3$, PuSi, Pu_2Si_3 or β-$PuSi_2$, α-$PuSi_2$, $PuSn_3$, PuTe, Pu_2Th, Pu_3U, and PuU.

2–2.2 Chemical Properties

Plutonium is a chemically reactive metal.[27, 28] At somewhat elevated temperatures atmospheric oxidation proceeds rapidly, especially at moderate humidities. At high relative humidities, the metal corrodes rapidly at room temperatures, forming what is probably a mixture of hydride and oxide. The finely divided metal is pyrophoric. Plutonium dioxide, which is usually formed in these cases, is a loosely adhering oxide affording little protection to the metal against further corrosion.

The metal reacts with chlorine, bromine, and iodine at moderate temperatures to form the corresponding trihalide, but fluorine apparently forms a protective coating on the metal. Ammonia reacts with the metal at 1000°C to form the mononitride, and carbon reacts at 1300°C to form the monocarbide. At somewhat higher temperatures, there is evidence of the formation of the sesquicarbide.

The metal reacts with hydrogen at room temperatures to form the dihydride or the trihydride, depending on the amount of hydrogen available. (It has been determined [29] that plutonium and hydrogen form a series of solid solutions whose compositions lie between $PuH_{2.0}$ and $PuH_{2.7}$.)

The metal is readily soluble in hydrochloric, hydrobromic, hydriodic, 72 per cent perchloric, 85 per cent phosphoric, and concentrated trichloracetic acids. Moderately concentrated sulfuric acid dissolves the metal slowly, but nitric acid, in any concentration, produces no action. Water reacts very slowly with the metal at room temperatures. Alkali hydroxides do not perceptibly attack the metal.

(a) *Oxidation States.* The complexity and extent of the chemistry of plutonium are due, in large part, to the several oxidation states exhibited by the element. In addition to the free elemental state, plutonium is known to exist in the (II), (III), (IV), (V), and (VI) oxidation states.[30] The (II) state, unimportant in the analytical chemistry of the element, is exemplified by an oxide and a sulfide. It apparently does not exist in aqueous solution.

The (III) oxidation state is relatively stable in moderately acid solutions, being oxidized rather slowly by air. Many solid com-

pounds of plutonium (III) are known, such as an oxide, all the anhydrous halides, a hydroxide, a nitrate, perchlorate, and sulfate. In aqueous solution Pu(III) exists as Pu^{+3} ion. The (III) oxidation state may be formed by reduction of the (IV) oxidation state with moderate to strong reducing agents such as hydroxylamine, mercurous ion in chloride solution, sulfur dioxide, titanous ion, zinc amalgam, ferrous ion, iodide ion, and stannous ion. In general, the chemical properties of Pu(III) are similar to those of the rare earths, which characteristically exist in the (III) oxidation state.

The (IV) oxidation state is very stable and is obtained on ignition in air of the metal or most plutonium compounds. It may be readily formed by oxidation of the (III) state with strong oxidizing agents such as bromate, dichromate, nitrite, concentrated nitric acid, permanganate, oxygen, and ceric ion. Plutonium tetrafluoride is the only solid anhydrous halide of the (IV) oxidation state which has been definitely identified. All others appear to be thermodynamically unstable and decompose to the trivalent halide and free halogen.[31] Many hydrated compounds of the (IV) oxidation state exist, e.g., halides, iodate, nitrate, oxalate, and sulfate. Unhydrolyzed Pu(IV) ion is believed to exist in aqueous solutions of $0.1M$ hydrogen ion, or greater. It forms complexes with fluoride ion, nitrate ion, oxalate ion, phosphate ion, sulfate ion, and chloride ion in high acid concentrations. In one respect, Pu(IV) solutions are unstable, undergoing partial self-oxidation and -reduction to Pu(III) and Pu(VI). The extent of this disproportionation depends markedly on the acidity and complexing action of the negative ions present. For example, a $2\times10^{-3}M$ solution of Pu(IV) in $0.5M$ hydrochloric acid will disproportionate to the following extent

$$\underset{(27.2\%)}{3Pu^{+4}} + 2H_2O \overset{25°C}{\rightleftharpoons} \underset{(58.4\%)}{2Pu^{+3}} + \underset{(13.6\%)}{PuO_2^{+2}} + 4H^+ \qquad (2.9)$$

and will require about nine days to reach equilibrium.[32] In this case, the rate of disproportionation of Pu(IV) varies directly as the second or third power of its concentration and inversely as the third power of the hydrogen-ion concentration. The hydroxide of Pu(IV) shows no amphoteric properties and is very insoluble. In general, the chemistry of Pu(IV) is very similar to that of Ce(IV) and U(IV).

The (V) oxidation state, although fairly stable in the pH range 2 to 7, is not directly important in the analytical chemistry of the element. Only a few compounds have been prepared in which Pu(V) is present. One of these is believed to contain potassium and hydrox-

Table 2.4—COLORS EXHIBITED BY VARIOUS OXIDATION STATES OF PLUTONIUM

Oxidation state	Color
(III)	Blue to violet.
(IV)	Tan to orange.
(V)	Reddish purple.
(VI)	Yellow to pink.

ide ions. A pentafluoride may also exist. In aqueous solution Pu(V) is believed to exist as PuO_2^+.

The (VI) oxidation state may be formed from the (IV) state by powerful oxidizing agents such as $Ag_2O_2(AgO)$, bromate, dichromate, permanganate, hot dilute nitric acid, and hot 72 per cent perchloric acid. The (VI) oxidation state is quite stable but may be reduced by hydroxylamine, hydrogen peroxide, ferrocyanide, iodide, sulfur dioxide, and by electrolysis. The (VI) oxidation state is well characterized by a number of plutonyl and plutonate salts, which resemble very closely the corresponding uranyl and uranate salts. In aqueous solution Pu(VI) is believed to exist as PuO_2^{+2} ion. Unlike uranyl compounds, plutonyl compounds exhibit no fluorescence.

Frequently, as indicated in Table 2.4, a particular oxidation state may exhibit a characteristic color. However, caution must be exercised in using color as a means of identifying the oxidation state present. This arises primarily from the fact that the color of an individual oxidation state is dependent on the concentration of the oxidation state and also on the concentration and kind of anion present. This latter may influence the color of the solution through formation of a complex ion whose color is different from that of the uncomplexed plutonium ion.

(b) *Oxidation–Reduction Potentials.* The Pu (III)/(IV) and Pu (V)/(VI) couples are reversible, presumably because a one-electron change is involved, requiring no breaking or making of bonds. Hence, these potentials can be measured by cells. The Pu (III)/(VI), (IV)/(V), and (IV)/(VI) couples are not reversible, presumably because of the slowness in making and breaking bonds, and therefore the potentials cannot be determined by direct cell measurements. Plutonium couple potentials have been determined under a variety of conditions.[30, 33, 34] From these data, the following formal potential schemes were obtained by direct cell measurements and disproportionation equilibrium constants.

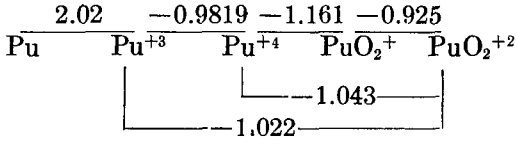
Because these potentials are so close together, it can be predicted that all four oxidation states might be present in stable equilibrium in solution.

The potential of the Pu (III)/(IV) couple has been measured under a variety of conditions,[35] and the values in a few acids are shown in Table 2.5. These differences have been attributed to complex-ion formation with the various anions, this tendency being least in perchloric acid and greatest in sulfuric acid. From the above, it would seem that electrometric methods would afford a ready means for plutonium determination. That this is so will be amply illustrated in Sec. 2–2.5(a).

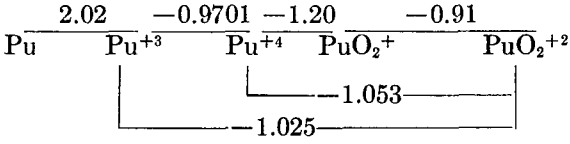
Table 2.5—FORMAL OXIDATION-REDUCTION POTENTIALS OF Pu (III)/(IV) COUPLE[35] AT 25°C

Acid	Potential, volt
1*M* $HClO_4$	−0. 982
1*M* HCl	−0. 9701
0.5*M* HCl	−0. 9704
1*M* HNO_3	−0. 92
1*M* H_2SO_4	−0. 75

In 1*M* $HClO_4$ at 25°C:



In 1*M* HCl at 25° C:



The polarographic behavior of Pu(III) in hydrochloric acid solution containing hydroxylamine as a holding reductant has been investigated by Warren.[36] It was observed that Pu(III) under the conditions mentioned does not produce a polarographic wave within the range 0.0 to −0.9 volt measured against the saturated calomel electrode. It was also found that in the presence of Pu (III) good polarographic waves were obtained for silver, bismuth,

Table 2.6—RADIOACTIVE DISINTEGRATION OF PRINCIPAL PLUTONIUM ISOTOPES AND Am^{241}

Element	Half life, years	Modes of decay and energies of radiation, Mev	Specific activity, disintegrations/min/μg
Pu^{238}	86. 41	α(5.495, 5.452, 5.352)	3. 89 $\times 10^7$
Pu^{239}	2. 436$\times 10^4$	α(5.147, 5.134, 5.096)	1. 372$\times 10^5$
Pu^{240}	6. 580$\times 10^3$	α(5.159, 5.115, 5.014)	5. 06 $\times 10^5$
Pu^{241}	13. 25	β^->99%(0.0205); α(4.91)	2. 53 $\times 10^8$
Am^{241}	457. 7	α(5.482, 5.439 plus others from 5.541 to 5.241) β^- stable.	7. 14 $\times 10^6$
Pu^{242}	3. 79±0. 05$\times 10^5$	α(4.898, 4.854)	8. 73 $\times 10^3$

platinum, uranium, rhodium, copper, tin, antimony, lead, thallium, indium, and cadmium.

(c) *Radioactivity.* Of particular interest to the analytical chemist is the radioactive properties displayed by the element. The significance of this behavior lies in the fact that it affords the most sensitive technique known for the detection of the element and also for determining its isotopes. The radioactive behavior of each isotope is well known; Table 2.6 describes this behavior for the more important isotopes.

Americium-241 is included because it is the daughter of Pu^{241} and is, therefore, always present, except in freshly separated plutonium.

(d) *Insoluble Compounds.* Gravimetric methods for determining plutonium are not in wide use. This is due partly to meager information on the stoichiometry of plutonium compounds and partly to the greater potential hazard in handling the solid dry state. Table 2.7 lists some of the more insoluble compounds and the conditions under which their solubilities were measured.

Although not used to any appreciable extent as weighing forms, some of these insoluble compounds are widely used in coprecipitation procedures for removing small amounts of plutonium from solution. For example, plutonium tetrafluoride is quantitatively carried by lanthanum trifluoride, Pu (III) and (IV) oxalates are quantitatively removed by thorium oxalate, and Pu(IV) phosphate is quantitatively removed by bismuth phosphate. In addition, some insoluble compounds are used to remove the plutonium prior to the determination of some impurity. Examples are precipitation as oxalate prior to the determination of boron, as the iodate prior to the determination of free acid, and as the peroxide prior to the determination of titanium, indium, cadmium, bismuth, and other metals.[37]

Table 2.7—INSOLUBLE PLUTONIUM COMPOUNDS[27]

Compound	Color	Solubility, mg Pu/liter	Conditions of precipitation
PuF_3	Lavender to black.	37	0.5*M* HF—1.0*M* HCl–sat. SO_2.
$Pu(IO_3)_3$	Tan	1. 5	0.017*M* KIO_3—0.17*M* H_2SO_4.
$Pu(PO_4)\cdot 0.5H_2O$	Light purple	20	0.8*M* H_3PO_4—0.1*M* HCl.
$Pu_2(C_2O_4)_3\cdot 9H_2O$	Brilliant green.	6	0.14*M* $H_2C_2O_4$—0.22*M* H^+.
PuF_4	Brown to pink.	"Insoluble"	H^+.
$Pu(IO_3)_4$	Pink	1. 6	0.15*M* KIO_3—1*M* HNO_3.
$PuO_4\cdot xH_2O$	Green	3. 3	3.3*M* H_2O—0.25*M* H_2SO_4—0.5*M* HNO_3.
$Pu(HPO_4)_2\cdot xH_2O$	White	4	0.1*M* H_3PO_4—0.1*M* H_2SO_4.
$Pu(C_2O_4)_2\cdot 6H_2O$	Yellow green	11	0.5*M* $H_2C_2O_4$—1.0*M* HNO_3.
$BiPuH(C_2O_4)_4\cdot 9H_2O$	Pink	90	0.35*M* $C_2O_4^{-2}$—0.1*M* K^+—0.75*M* Bi^{+3}—5*M* HCl.
$NaPuO_2(C_2H_3O_2)_3$	Pink	70	0.6*M* $HC_2H_3O_2$—5.7*M* $NaNO_3$—0.2*M* $NaC_2H_3O_2$.

(e) *Complexes.* (1) *Coordination Complexes.* Early investigations of absorption spectra of solutions of plutonium in various inorganic acids and the discovery of changes in the spectra with ionic strength of the acids were taken as evidence of the existence of coordination complexes. Although much of this information is qualitative in nature, it is certain that the nature of these simple coordination complexes is understood and their relative characteristics are known. For example, the higher the charge on the anion, the stronger the complex formed. In this respect the common anions compare in the following relative manner in their abilities to form complexes with plutonium:

Strong: $CO_3^{-2}, C_2O_4^{-2}, SO_3^{-2}, SO_4^{-2}, C_2H_3O_2^-$
Moderate: F^-, NO_3^-, Cl^-
Weak: Br^-, I^-, ClO_4^-

Also, with plutonium in the (III) or (IV) state of oxidation, the effectiveness of the various anions appears to be

$$SO_4^{-2} > NO_3^- > Cl^- > ClO_4^-$$

For the (VI) oxidation state of plutonium, however, the order is partially reversed,

$$Cl^- > NO_3^- > ClO_4^-$$

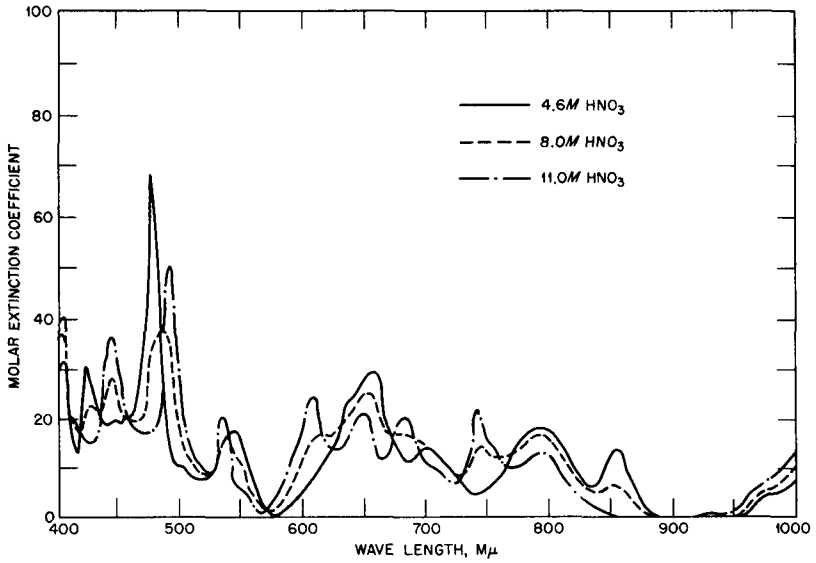


Fig. 2.5—Effect of varying nitric acid concentration on the absorption spectrum of Pu(IV).

As would be expected, the degree of complexing varies with the ionic strength of the anion involved. For example, below a concentration of 4.6*M* nitric acid, it is thought that Pu(IV) forms the complex $Pu(NO_3)^{+3}$, and, with increasing ionic strength of the nitrate ion, higher intermediate complexes are formed until at a nitric acid concentration of 11*M*, the major complex is thought to be $Pu(NO_3)_6^{-2}$.

Additional evidence of the effect of increasing ionic strength of the nitrate ion, and also for other anions, is to be found in the electrical migration behavior of plutonium under various conditions, as shown in Table 2.8.

Table 2.8 also indicates that the various oxidation states of plutonium behave differently in the formation of coordination complexes with various anions. This behavior is amply illustrated [38] in Fig. 2.5, which shows the absorption spectra of Pu(IV) in various concentrations of nitric acid, and also [28] by Fig. 2.6, which shows the absorption spectra of the various states of oxidation of plutonium in perchloric acid.

The formation of coordination complexes with the common anions was of considerable interest to early workers in the field of plutonium chemistry and continues to be of interest to the analytical chemist. Although the molecular extinction coefficients of these complexes are small, usually less than 300, they can be used, under carefully controlled conditions, for determining plutonium concentrations, providing, of course, the concentration is not too low. It is worth emphasiz-

Table 2.8—ELECTRICAL MIGRATION OF Pu(III), (IV), AND (VI) IONS [39]

Oxidation state	Acid concentration	Time, hr	% plutonium migrated	
			To cathode	To anode
III	1*M* HCl	8	79	21
III	10*M* HCl	5	69.5	30.5
III	0.5*M* H_2SO_4	17.5	97	3
III	16.6*M* H_2SO_4	17	16	84
IV	2*M* HCl	17	99.95	0.05
IV	10*M* HCl	17.5	0.2	99.8
IV	0.1*M* H_2SO_4	16	25	75
IV	0.5*M* H_2SO_4	5	6	94
IV	1*M* H_2SO_4	4	1	99
IV	1*M* HNO_3	18	98.5	1.5
IV	10*M* HNO_3	17	1.2	98.8
VI	2*M* HCl	17	100	-------
VI	10*M* HCl	17	-------	100
VI	1*M* H_2SO_4	16	27	73
VI	2*M* HNO_3	17	99.1	0.9
VI	14.6*M* HNO_3	3.5	5	95
VI	9*M* $HClO_4$–0.1*M* HNO_3	16.5	99.9	0.1

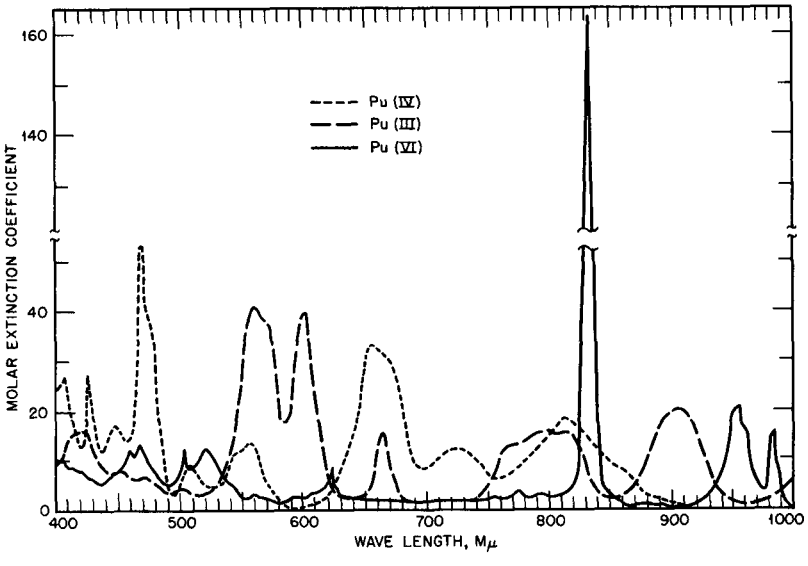


Fig. 2.6—The absorption spectrum of Pu(III), Pu(IV), and Pu(VI) in 1*M* perchloric acid.

ing, however, that the data mentioned above point very clearly to the necessity for accurate knowledge of kind and concentration of anion and oxidation state (or states) of the plutonium before quantitative use can be made of these absorption spectra for determining plutonium concentrations.

In chemical analysis considerable use is being made of coordination complexes in the separation of plutonium from other metal ions. For example, in the spectrographic determination of impurities, Pu(IV) is first quantitatively separated by anion–exchange resins either from 12*M* hydrochloric acid,[40] 7*M* to 10*M* nitric acid,[41, 42] or 12*M* hydrochloric–1*M* nitric acid mixture.[43] For the separation of plutonium from uranium, thorium, alkalies, alkaline earths, rare earths, zirconium, niobium, ruthenium, and other fission products, the plutonium is oxidized to the (VI) oxidation state and extracted from 4.8*M* hydrochloric acid with a 5 per cent solution of triisoöctylamine in xylene. The Pu(VI) is stripped from the organic phase with 0.1*M* hydrochloric acid. Over 99 per cent recovery has been reported.[44]

(2) *Chelate Complexes.* Plutonium reacts with various chelating agents to form neutral, stable complexes, many of which are soluble in nonpolar organic solvents. Of these, the complexes formed with thenoyltrifluoroacetone (TTA) are of most importance.[45] Several factors affect the extractability of metal–TTA complexes; included are acidity, TTA concentration, mixing time, and the equilibrium constant for the complex formation. The relationship between acidity, TTA concentration, and extraction coefficients for the various oxidation states of plutonium are shown later (Table 2.20).

The separation of plutonium by TTA extraction is used in determining total plutonium in uranium-product solutions and in waste streams containing high salt content, americium, neptunium, and uranium, as well as in various other solutions containing alpha emitters. In the analysis of irradiated reactor fuel, Pu(IV) is first quantitatively separated from uranium and fission products by extraction from 1*M* nitric acid into 0.05*M* TTA in xylene.[46]

Solvents other than xylene have been found useful in the TTA chelate system, and several other chelating agents have found use in plutonium analytical chemistry. For example, extraction coefficients of 3, 10^5, and approximately 10^{-1} have been reported for Pu (III), (IV), and (VI), respectively, between TTA–benzene and 0.5*M* nitric acid. In addition, the extraction of Pu(III) cupferrate into an ether-chloroform mixture is used to remove plutonium from most metallic impurities, which are then determined by a spectrochemical method.[47] Ethylenediaminetetraacetic acid (EDTA), which forms highly stable complexes with plutonium, is used as a holding agent during the

extraction of mercury diethyldithiocarbamate[48] and in other determinations. The extraction of other chelate complexes of plutonium have also been described.[49]

2–2.3 Qualitative Detection

Detection of the first minute quantity of plutonium that was produced by bombardment experiments was made possible by its radioactive nature. Since that time, other characteristic properties and behavior of the element have been investigated. Some of these may also serve for its qualitative detection as described below.

(a) *Radiochemical.* The radioactive-disintegration characteristics of the more common isotopes of plutonium are described in Table 2.6. From these data it is obvious that its radioactive properties can be used to detect an extremely small amount of the element. Usually, the half life of a radioactive isotope is considered its chief characteristic, and it is frequently used to advantage in identifying that particular isotope. A comparison of the half lives of the plutonium isotopes in Table 2.6 clearly shows that these isotopes can be identified by measuring their half lives. Details of these procedures are beyond the scope of this chapter but are adequately covered in Chap. 14. It often happens that the energies of the α particles resulting from radioactive decay are sufficiently different among individual isotopes to be used for identification. In the case of plutonium, however, the α-particle energies of the Pu^{239} and Pu^{240} isotopes are so close together that modern detection equipment is unable to resolve them. Because of this, these two isotopes will be counted together. The energies of the α particles from the Pu^{238} and the Am^{241} isotopes cannot be resolved by modern counting equipment either. Hence Am^{241}, which is always present as a daughter of Pu^{241} except in recently purified material, will, if present, interfere in the counting of the Pu^{238} isotope. The magnitude of the error introduced by the Am^{241} will, of course, be directly proportional to its concentration. Unfortunately, its concentration builds up rapidly owing to the very short half life (13 years) of the Pu^{241} isotope from which it originates.

Radiochemical techniques are usually preferred for the detection of plutonium, although the techniques outlined in the following sections can also be applied.

(b) *Emission Spectrum.* Characteristic lines in the emission spectrum of plutonium which can be used to identify the element [50] are as follows: 3989.7; 3985.5; 3907.2; 3312.6; 3000.4; 2993.9; and 2988.1 A. The sensitivity, defined as the smallest amount of the oxide of the element which will produce a line barely visible when excited by the copper-spark technique, is about 1 μg in most of these cases.

Table 2.9—PROMINENT ABSORPTION BANDS OF PLUTONIUM[52]

Solution	Wave length, Å	Molar extinction coefficients (ϵ)			
		Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
Pu(III) in 0.1*M* $HClO_4$	9000	19. 30			
	6650	14. 65	30. 9		
	6030	35. 40			
	6000	35. 30			
	5600	36. 10	11. 64		
Pu(IV) in 0.5*M* HCl	8150	14. 63	19. 61		
	7300		14. 60		
	7000		10. 88		
	6550		34. 4		
	*4700		49. 6		11. 25
Pu(V) in 0.5*M* HCl	*7750	12. 40	11. 90	17. 10	
Pu(VI) in 0.1*M* $HClO_4$	9830				8. 90
	9530				19. 90
	*8330	5. 25	15. 5		300
					†553

*Extremely sharp.

†See Ref. 52.

(c) *Absorption Spectra.* Table 2.9 shows the wave lengths and the molar extinction coefficients (ϵ) of the principal absorption bands of plutonium in its various oxidation states which can be used for qualitative identification of the element. With care, these absorption bands can also be used as the basis for rather insensitive spectrophotometric methods for the quantitative determination of various states of oxidation of plutonium [see Sec. 2.2.5(c)].

(d) *X-ray Fluorescence Spectra.* Characteristic X-ray emission (fluorescence) lines for plutonium have been reported[51] as follows: $\alpha_2=14.083$; $\alpha_1=14.278$; $\beta_2=17.252$; $\beta_4=17.551$; $\beta_5=17.946$; $\beta_1=18.290$; $\beta_3=18.535$; and $\gamma_1=21.410$. All energies are expressed as thousand electron volts (kev).

(e) *Color of Ions in Various Oxidation States.* Table 2.4 shows the color range of solutions of the various oxidation states of plutonium.

The colors of such solutions are not intense and obviously vary with the concentration of the ion. For these reasons, they are not of significant importance in the qualitative identification of the element. Of more practical importance is the change in color that always accompanies a change in the oxidation state of the element. For example, a tan-colored solution of Pu(IV) will always change to blue when hydroxylamine or some reducing agent of similar potential is added.

690-457 O—64——13

Likewise, a blue solution of Pu(III) will always change to tan when an oxidizing agent such as bromate, nitrite, concentrated nitric acid, oxygen, or ceric ion is added. Unfortunately the visual color test is insensitive. Dilute solutions of plutonium ions are always colorless.

2–2.4 Determination of Isotopic Composition

The isotopic composition of plutonium is of considerable importance, both from the standpoint of production in a reactor and use as a reactor fuel. This arises from the fact that the Pu^{239} isotope is by far the most abundant and is also the isotope whose fissionable properties are the most useful, as a reactor fuel or otherwise. The producer of plutonium is always interested in its isotopic composition primarily because the monetary value of this product is related to the Pu^{239} content, i.e., the higher the Pu^{239} content, the higher price per unit weight it can command. In addition, the behavior of plutonium as a fuel is influenced by its isotopic composition, which should be known before use.

The isotopic composition of the element, as it is normally produced, is a complex function of several conditions existing in the reactor at the time of its operation. Two of these important conditions are the neutron spectrum and the total neutron irradiation. In case of a uranium-fueled reactor operated either for the production of power or for the production of plutonium, the isotopic population of the plutonium produced therefrom is influenced by the above factors in the following manner.

One of the most common and important series of nuclear reactions in a reactor is that resulting in the formation of the Pu^{239} isotope:

$$_{92}U^{238}(n,\gamma)_{92}U^{239} \xrightarrow[23.5\ \text{min}]{\beta^-} {}_{93}Np^{239} \xrightarrow[2.3\text{d}]{\beta^-} {}_{94}Pu^{239} \tag{2.10}$$

In addition, other reactions involving neutrons occur

$$_{92}U^{238}(n,2n)_{92}U^{237} \xrightarrow[6.8\text{d}]{\beta^-} {}_{93}Np^{237}(n,\gamma)_{93}Np^{238} \xrightarrow[2.1\text{d}]{\beta^-} {}_{94}Pu^{238} \tag{2.11}$$

$$_{92}U^{238}(n,\gamma)_{92}U^{239}(n,\gamma)_{92}U^{240} \xrightarrow[14\text{h}]{\beta^-} {}_{93}Np^{240} \xrightarrow[7.3\ \text{min}]{\beta^-} {}_{94}Pu^{240} \tag{2.12}$$

$$_{94}Pu^{238}(n,\gamma)_{94}Pu^{239}(n,\gamma)_{94}Pu^{240}(n,\gamma)_{94}Pu^{241}(n,\gamma)_{94}Pu^{242}(n,\gamma)_{94}Pu^{243} \tag{2.13}$$

If enriched uranium is the fuel, the reaction

$$_{92}U^{235}(n,\gamma)_{92}U^{236}(n,\gamma)_{92}U^{237} \xrightarrow[6.8\text{d}]{\beta^-} {}_{93}Np^{237}(n,\gamma)_{93}Np^{238} \xrightarrow[2.1\text{d}]{\beta^-} {}_{94}Pu^{238} \tag{2.14}$$

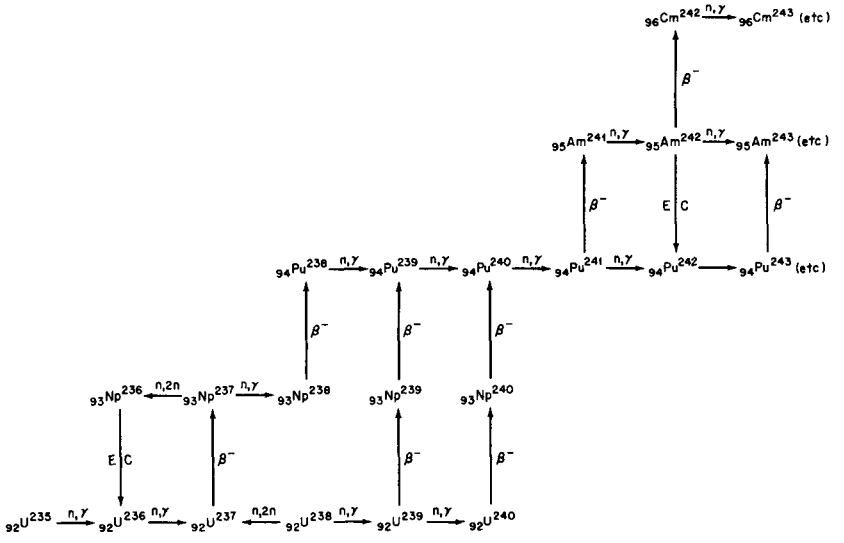


Fig. 2.7—Some nuclear species produced during neutron irradiation of uranium and plutonium.[53]

becomes more important on a relative basis as the degree of enrichment in the U^{235} isotope becomes greater.

In addition, if there is a significantly large percentage of fast neutrons produced in the reactor, Eq. 2.15 occurs to a measurable extent:

$$_{92}U^{238}(n,2n)_{92}U^{237} \xrightarrow[6.8d]{\beta^-} {}_{93}Np^{237}(n,2n)_{93}Np^{236} \xrightarrow[2.9d]{\beta^-} {}_{94}Pu^{236} \qquad (2.15)$$

Equation 2.13 is one of the more important neutron reactions and is the one largely responsible for the presence of the isotopes heavier than 239. Figure 2.7, which is taken from Seaborg and Katz,[53] is given in order to more clearly indicate the interrelationships in the reactions described by Eqs. 2.10 through 2.15.

It is beyond the scope of this chapter to discuss in detail the mathematical relationships between isotopic distribution and the parameters of the reactor, but mention is made of the above reactions to point out the complexity of the problem and to emphasize the necessity for isotopic measurements for the complete characterization of any particular quantity of plutonium.

(a) *Mass Spectrometer Techniques.* The mass spectrometer is the most satisfactory instrument available for rapid, precise, and routine measurement of isotopic abundances. Because the instrument will not distinguish between isotopes of different elements having the same ratio of charge to mass (e/m), it is advisable to have the sample of

as high purity as possible. In the case of plutonium, it is especially important to purify the sample from Am^{241} immediately before analysis, because this daughter product would obviously interfere with measurement of the Pu^{241} abundance. The plutonium is separated from uranium and fission-product mixtures by any of the methods of ion exchange, liquid-liquid extraction, coprecipitation, etc., mentioned in Sec. 2–3.2.

The details of the method of isotopic analysis are described in Chap. 13. The mass spectrometric methods in common use for plutonium isotopic analysis utilize the high-sensitivity surface ionization technique. Because of the radioactivity hazard of plutonium, the most sensitive variations of this technique are used: the "multiple filament" or the "canoe filament" technique. In these techniques, the sample, in the form of a nitrate solution, is evaporated to dryness on a tungsten or rhenium filament in air. This filament, placed in the proper position of the ion source of the mass spectrometer, will emit ionized plutonium atoms when heated to high temperatures. The mass spectrometer measures the relative intensities in the ion beam of the different isotopic species Pu^{239}, Pu^{240}, Pu^{241}, Pu^{242}, etc. Except for small corrections, the relative intensities are equal to the relative concentrations of the isotopes in the sample. These corrections are determined by analyzing known standard samples. In the absence of plutonium isotopic standards, uranium standards could probably be used with very little error.

(b) *Radiochemical Techniques.* Radioanalysis techniques are important but of limited use in the quantitative determination of isotopic abundances in plutonium. Their limited use arises from the fact that the α particles of the Pu^{239} and Pu^{240}, which normally are the most abundant, have nearly the same energies and cannot be resolved by modern α-counting equipment. Hence, the sum of the α particles from these two isotopes is always obtained in α-energy analysis. Plutonium-241 is a beta emitter, although the maximum energy of the beta particles is small (20 kev maximum), making their measurement rather difficult. However, this measurement has been successfully accomplished by dissolving the plutonium in a scintillator solution whose emission spectrum matched the peak spectral response of the photomultiplier tubes of a coincidence type liquid scintillation spectrometer.[54] The Pu^{238} isotope (α energies of 5.495, 5.452, and 5.352 Mev) can be measured in an α-energy analyzer, providing Am^{241} (α energies of 5.482 and 5.439 Mev) has been removed immediately before counting. The Pu^{242} isotope (α energies of 4.898 and 4.854 Mev) theoretically can be measured in an α-energy analyzer with little or no interference from other plutonium isotopes. However, its long half life

($3.75 \pm 0.05 \times 10^5$ years) compared to that of Pu^{239} (2.436×10^4 years) actually means that the high specific activity of the latter does cause interference.

It is obvious from what has been said that radioanalysis techniques do not give complete information regarding isotopic abundances of plutonium. They are more useful in measuring ultramicro amounts of plutonium, providing, of course, the specific activity of the material in question is known. For a more complete discussion of the radiochemistry of plutonium and applications of radiochemical techniques, it is suggested that Seaborg [53] be studied in detail.

2–2.5 Quantitative Determination

(a) *Electrometric Methods.* Because plutonium exhibits, in solution, several oxidation states, each having a well-defined redox potential, the precise measurement of plutonium by potentiometric titration techniques is possible. In most cases, the element is first quantitatively reduced to the (III) oxidation state by Ti(III), zinc amalgam, Cr(II), or in a silver reductor. Oxidation to the (IV) state is then accomplished with a standard solution of either Ce(IV), Cr(VI), or Mn(VII). The most widely used methods involve reduction of the plutonium to the (III) oxidation state with either Ti(III) or zinc amalgam followed by oxidation to the (IV) state with standard ceric solution. In these titrations, the end point is determined potentiometrically.

In one very precise method, quantitative oxidation to the (VI) oxidation state is followed by reduction to the (IV) state with excess Fe(II); the excess Fe(II) is then titrated potentiometrically with standard ceric solution.

Applications of polarographic and coulometric techniques are later developments. All these reported methods are discussed in brief detail in the following paragraphs.

Common to the potentiometric titration methods, in which Pu(III) is titrated to Pu(IV), are the interference caused by iron and the use of a standardized solution of the oxidant. Iron does not interfere in the method requiring reduction of Pu(VI) to Pu(IV) by Fe(II), but a standardized solution of Ce(IV) is employed in this determination. The most common oxidant is $0.05M$ to $0.1M$ solution of Ce(IV) bisulfate, which is prepared in $1N$ sulfuric acid and allowed to age one week, taking care that dust or other organic material does not enter the solution. This reagent, which is stored in a dark bottle, is standardized by one of the following methods or by using arsenous oxide, Mohr's salt, or iron wire as a standard.[55] This standardization is either by weight or by volume, depending upon the type of buret

used in the titration of plutonium. The following procedures describe standardization by weight, and appropriate changes should be made if volumetric burets are to be used.

Procedure for Standardization of Ce(IV) Solution With Sodium Oxalate. Primary standard sodium oxalate is dried at 120°C for 1 hr. Approximately 350 mg is weighed to the nearest 0.1 mg, transferred to a 50-ml beaker, and dissolved in distilled water. The solution is thoroughly mixed and quantitatively transferred into a tared weight buret of 60-ml capacity. Five aliquots are weighed, by difference, into 50-ml beakers and each is diluted to 25 ml with 1*M* sulfuric acid. Each is heated to 75 to 80°C and titrated with the Ce(IV) solution, determining the end point potentiometrically using a saturated calomel–bright platinum electrode system. The end point is at about −850 mv, although the potential may vary somewhat from this value. A satisfactory technique for establishing the end point is to add final increments of the titrant from a weight buret until no downward drift of the potential is observed. The plutonium titre (grams of plutonium per gram of titrant) is calculated as follows:

$$\text{Pu titre} = \frac{(\text{Grams } Na_2C_2O_4 \cdot H_2O)\,(239.06)}{(67.007)\,(\text{grams titrant})} \qquad (2.16)$$

(The atomic weight of plutonium is influenced by the isotopic composition, which must be determined by mass spectrometer measurements on the sample. The value shown above is the chemical atomic weight of the 239 isotope, but, if the plutonium is produced from a high burn-up of a relatively low enrichment fuel, the presence of several per cent of higher isotopes will significantly increase this number. For standardizations by volume, calculate either the plutonium titre by volume or the molarity of the Ce(IV) solution.)

Procedure for Standardization of Ce(IV) Solution With Pure Plutonium Metal. A better method of standardization is to use high-purity plutonium metal as a primary standard, provided metal of at least 99.98 per cent purity is available. In this case, the metal is cleaned either mechanically or by electrolysis. In the latter cleaning technique, the sample, approximately 600 mg, is placed in a wire-mesh basket (tantalum or tungsten) (see Fig. 2.8), and immersed in a 20 per cent solution of potassium carbonate. With the wire basket and sample serving as the anode and a platinum wire dipping into the carbonate solution serving as the cathode, a direct current of approximately 0.1 amp is passed for 1 or 2 min. The sample should turn bright as a result of a small amount of the metal being anodically dissolved, which mechanically removes the oxide layer. The basket and sample are removed, washed immediately in concentrated nitric acid, water, and acetone, in that order. An accurately weighed portion of about 600 mg of the cleaned metal is dissolved in a 25-ml volumetric flask by the dropwise addition of 6*M* hydrochloric acid. Dilution to volume is made with 3*M* hydrochloric acid. Weight aliquots, each containing approximately the same weight of plutonium as titrated for actual samples, are used for the standardization, which is carried out in the same manner as the analysis of a metal sample (see individual method to be used).

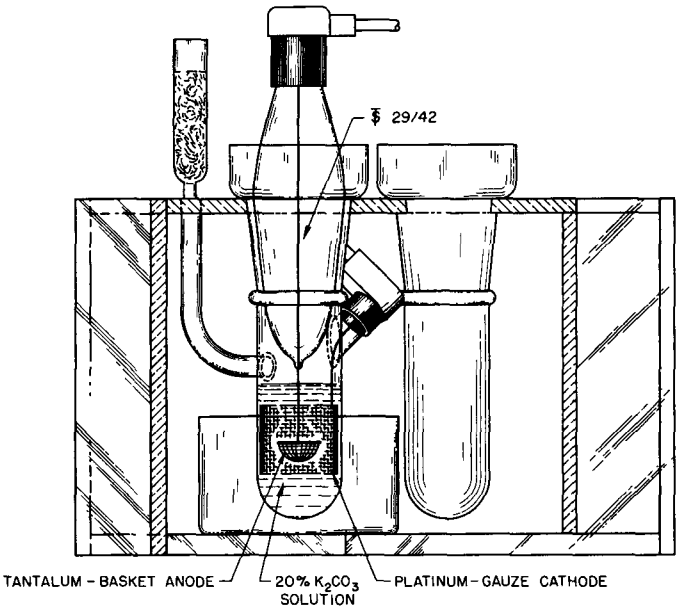


Fig. 2.8—Apparatus used in electropolishing plutonium.

Procedure for Determination and Correction for Iron. The interference caused by iron in most of these titration methods requires that iron, if present, be determined separately. Using an aliquot of the original sample solution, the acidity is adjusted to less than 0.5*M* free acid. The plutonium, in the (III) or (IV) oxidation state, is then precipitated as the oxalate, and the precipitate is removed by centrifuging. The acidity of the solution is adjusted to pH 6 with ammonium hydroxide, hydroxylamine hydrochloride is added to completely reduce the iron to the ferrous state, *o*-phenanthroline is added, and the solution is allowed to stand for 30 min. The absorbance is then read at a wave length of 515 mμ. The amount of iron is determined from a standard curve. The plutonium equivalent of the iron, or the iron correction, is calculated as follows:

$$\text{Fe correction} = \frac{(\text{Grams Fe/grams sample})\,(239.06)}{55.85} \qquad (2.17)$$

(The atomic weight of plutonium is influenced by the isotopic composition, which must be determined by mass spectrometer measurements on the sample. The value shown above is the chemical atomic weight of the 239 isotope, but, if the plutonium is produced from a high burn-up of a relatively low enrichment fuel, the presence of several per cent of higher isotopes will significantly increase this number.)

(1) *Titanous Reduction: Ceric Oxidation Method.*[56, 57] The sample may be either metal or an inorganic solution of the element. If metal, it is dissolved in 6*M* hydrochloric acid. [Please observe the

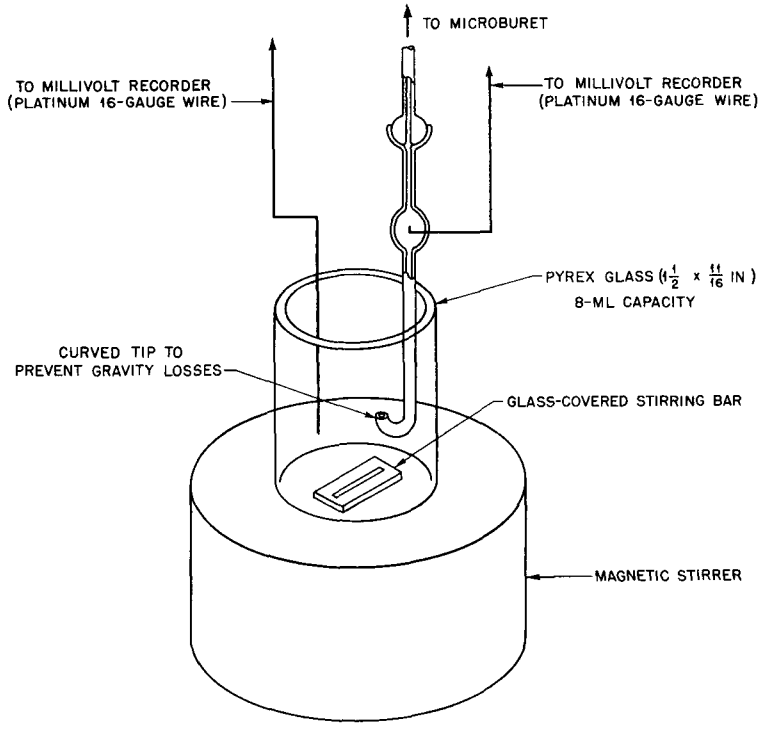


Fig. 2.9—Plutonium titration system.

precautions taken in cleaning metal samples as described under "Procedure for Standardization of Ce(IV) With Pure Plutonium Metal."]

Procedure.. To an aliquot containing 6 to 10 mg of plutonium in an 8-ml platinum crucible is added 1 ml of 1*M* sulfuric acid. Evaporation to copious fumes of sulfur trioxide is made with infrared heaters. This fuming operation is repeated twice, and before each fuming the sides of the crucible are washed down with 0.4 to 0.5 ml of distilled water. The purpose of these fumings is to remove all nitrate and fluoride ions and organic materials. The sulfuric acid solution of the sample is then quantitatively transferred to a special titration vessel (see Fig. 2.9). (This titration vessel is a simplified design of that described in the original reports[56, 57] and seems to be preferred.) The crucible is rinsed three times with 0.3 ml of 0.1*M* sulfuric acid, and the rinses are added to the titration vessel. The solution is stirred magnetically at a moderate rate. The platinum indicating electrode is positioned to within ¼ in. of the bottom of the titration vessel. A Gilmont microburet is filled with 0.1*N* Ce(IV) bisulfate solution, and the buret is lowered into the titration vessel so that upon the addition of the Ce(IV) solution it will not flow directly over the indicating electrode. A platinum wire sealed into the Gilmont buret several inches from the tip is in continuous contact with the standard Ce(IV) solution and therefore acts as a reference electrode during the titration. The electrode system is calibrated by adjusting

resistors in the potentiometer–millivolt meter circuit to give a reading of zero on the meter. A freshly prepared solution of titanous chloride, made by diluting 200 μl of the 20 per cent solution to 1 ml with 1*M* sulfuric acid, is added dropwise from a 100-μl micropipet until the meter reads approximately −1900 mv on an arbitrary scale. The sample solution is then titrated by adding the 0.1*N* Ce(IV) bisulfate solution from the Gilmont micropipet to the first end point at about −1200 mv. At this potential all the excess titanous ion has been oxidized. Additional standard solution is added until a second end point is reached at about −700 mv. In the vicinity of each end point, the standard solution is added in increments of 1 μl, and after each addition the total volume of titrant is recorded as well as the meter reading in millivolts. The end points are calculated as follows:

$$\text{End points } P_1 \text{ or } P_2 = A + \frac{(B-C)E}{2B-(C+D)} \qquad (2.18)$$

where

P_1=volume (ml) of titrant added to obtain *first* end point
P_2=volume (ml) of titrant added to obtain *second* end point
A=total volume (ml) of titrant added prior to maximum Δ EMF
B=maximum Δ EMF (mv)
C=Δ EMF immediately preceding B (mv)
D=Δ EMF immediately following B (mv)
E=increment volume (μl) of titrant added in the vicinity of the end points

The plutonium in the sample is calculated as follows:

$$\% \text{ Pu} = \frac{(\text{Pu titre, g}/\mu\text{l})\,(P_2-P_1)-(K\times L)}{\text{Grams of sample}} \qquad (2.19)$$

where

K=iron present in sample (g/g) and L=factor for converting grams iron to grams plutonium$=\frac{239.06}{55.85}=4.28$. (The chemical atomic weight of plutonium should be determined by mass spectrometer measurements.)

The iron correction (K×L) is calculated from a separate determination of the iron content on a separate portion (aliquot) of the sample as described above.

A reagent blank is determined on 1 ml of 1*M* sulfuric acid, carrying it through the identical procedure in the absence of plutonium. This value is usually zero. The method is rapid and has been reported[58] to have a coefficient of variation of 0.15 per cent using a 4- to 6-mg sample.

Iron, chromium, gold, platinum, and vanadium interfere.

(2) *Zinc-amalgam Reduction: Ceric Oxidation Method* (*Los Alamos Scientific Laboratory*).[59] The sample may be in the form of metal or a solution of inorganic salts of the element. The method also applies to binary alloys of plutonium with aluminum (90 per

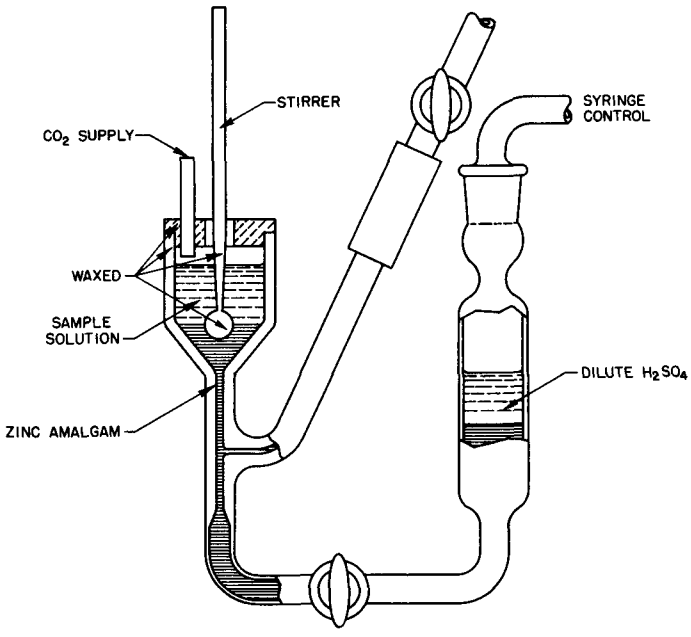


Fig. 2.10—Schematic diagram of titration cup (LASL type), plutonium reduction step.

cent), cerium (50 per cent), copper (3 per cent), magnesium (25 per cent), nickel (1 per cent), silicon (2 per cent), tin (10 per cent), thorium (15 per cent), and strontium (5 per cent). If the sample is plutonium metal or an alloy and is visibly oxidized, the oxide surface should be removed with fine abrasive cloth or a file. If the sample is plutonium metal and is not too badly oxidized, the surface layer may be removed, prior to weighing, by electrolysis, as described above.

Procedure. For the most precise results it is recommended that immediately following cleaning approximately 600 mg of the sample be weighed and transferred to a weighed 25-ml volumetric flask and that 6*M* hydrochloric acid be added dropwise until dissolution is complete. Spray and violent action should be avoided by controlling the rate of addition of hydrochloric acid. If the sample is an alloy, it may be necessary to use concentrated hydrochloric acid to start the dissolving action. When dissolution is complete, the solution should be diluted to volume with 3*M* hydrochloric acid, mixed well, and the flask and contents weighed. Then 1 ml, or perferably an aliquot weighing between 1 and 1.3 g, should be transferred to a 10-ml platinum crucible. Add 0.5 ml of 2*M* sulfuric acid, and evaporate the solution to copious fumes of sulfur trioxide, but not to dryness. This evaporation proceeds smoothly if infrared heating lamps are used. This fuming process is repeated twice, with the addition of 0.5 ml of water between fumings. Following the fuming process, a precipitate of Pu(IV) sulfate tetrahydrate will be

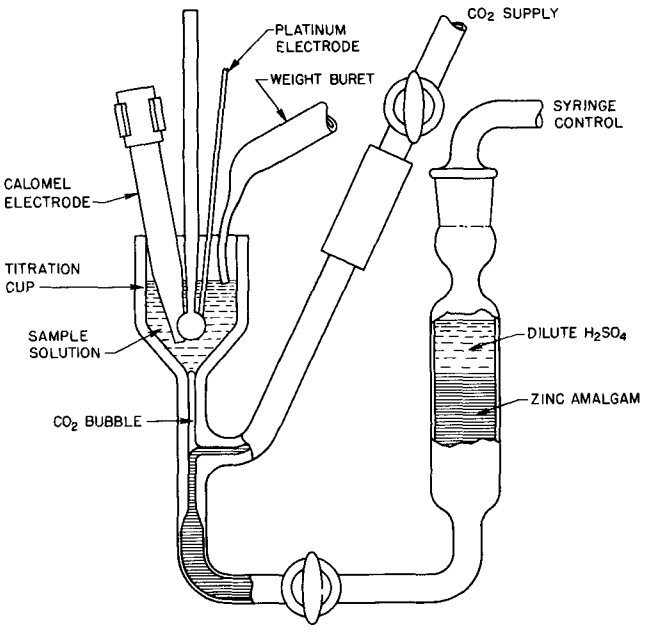


Fig. 2.11—Schematic diagram of titration cup (LASL type), plutonium titration step.

found in the crucible. Several drops of 0.5*M* sulfuric acid are added to slowly dissolve the precipitate. The sample solution is transferred to a special titration cup (Fig. 2.10), and the crucible is rinsed with 0.5*M* sulfuric acid. The solution at this point should be between 1.5*M* and 2.5*M* in sulfuric acid.

By means of a glass syringe attached to the amalgam reservoir, zinc amalgam is forced into the titration cup. The carbon dioxide gas flow (through cover as shown in Fig. 2.10) is adjusted to a rate of at least 100 cm^3/min. A wax-tipped electric-driven stirrer is inserted so that half the stirring surface dips into the zinc amalgam (Fig. 2.10). The solution and amalgam are stirred continuously while the plutonium is being reduced to the (III) oxidation state, which usually requires between 30 and 45 min. The solution will turn from tan, or rose color, to a characteristic blue color as the reduction proceeds to completion.

By means of slight suction from the syringe, the amalgam is withdrawn from the titration cup into the reservoir. The end of the thread of amalgam below the reservoir is adjusted so that its position is at the junction of the stem of the titration cup and the tube to the carbon dioxide supply (through side arm, Fig. 2.11). A bubble of carbon dioxide gas is introduced through this supply tube so that it occupies a position above the junction and between the end of the amalgam thread and the bottom of the titration cup. This separation of amalgam and sample solution must be done carefully so that no droplets of solution remain in that part of the capillary bore between the end of the amalgam thread and

the bottom of the titration cup. Also, no droplets of amalgam should remain in the titration cup. The electrode system, consisting of a saturated calomel electrode and a bright platinum wire, is lowered into the solution, the stirrer is again started, and the Pu(III) is oxidized to the (IV) oxidation state by titration with standard Ce(IV) bisulfate solution.

In this titration, the previously standardized Ce(IV) bisulfate solution is added from a weight buret (see Fig. 2.12) until the potential of the electrode system is between −600 and −650 mv, which corresponds to about 95 per cent of the plutonium being oxidized to the (IV) oxidation state. The Ce(IV) solution is added dropwise until the potential rises to −700 mv. Smaller increments are then added by touching the waxed tip of the weight buret to the surface of the solution until the end-point potential of −750 to −780 mv is reached. The plutonium content, expressed as weight per cent, is calculated as follows:

$$\%\text{Pu} = \frac{[(\text{Wt. standard solution} - \text{blank})(\text{Pu titre}) - (\text{Fe correction})](100)}{\text{Grams of sample}} \tag{2.20}$$

If a reagent blank is to be determined, the above procedure is repeated with a weighed aliquot of an accurately known solution of iron containing approximately 0.1 mg of iron per 1-g aliquot. The sample is omitted, and the standard Ce(IV) solution may be diluted 1 to 10 to obtain a more precise value for the blank. The difference in grams between the weight of the standard Ce(IV) solution actually consumed in the titration of the iron solution and the calculated weight of solution to react with the iron in the aliquot is taken as the reagent blank. Experience has shown that the reagent blank usually is insignificantly small.

(3) *Cr(II) Reduction: Ce(IV) Oxidation Method (Oak Ridge National Laboratory)*.[60] This method involves the reduction of Pu(IV) to Pu(III) with excess Cr(II). The excess Cr(II) is then oxidized with standard Ce(IV), and the oxidation of the Pu(III) to Pu(IV) oxidation state is made in the same solution by the continued addition of standard Ce(IV). The end point is determined potentiometrically. The method is quite similar to the one in which the plutonium is reduced to the (III) oxidation state with excess Ti(II) and then oxidized to the (IV) state with standard Ce(IV) solution.

An automatic titrator [61] consists of a microburet, a Brown recorder, and a drive unit that simultaneously actuates the buret plunger and the Brown chart drive. Calibration of the Brown recorder chart in terms of a known weight of high-purity iron serves as an indirect standardization of the ceric sulfate titrant. The known weight of iron used is stoichiometrically equivalent to a definite weight of plutonium.

The electrode system consists of a bright gold wire dipping into the titration vessel and the platinum buret plunger, which is in contact with the Ce(IV) titrant. The gold wire is subject to poisoning and

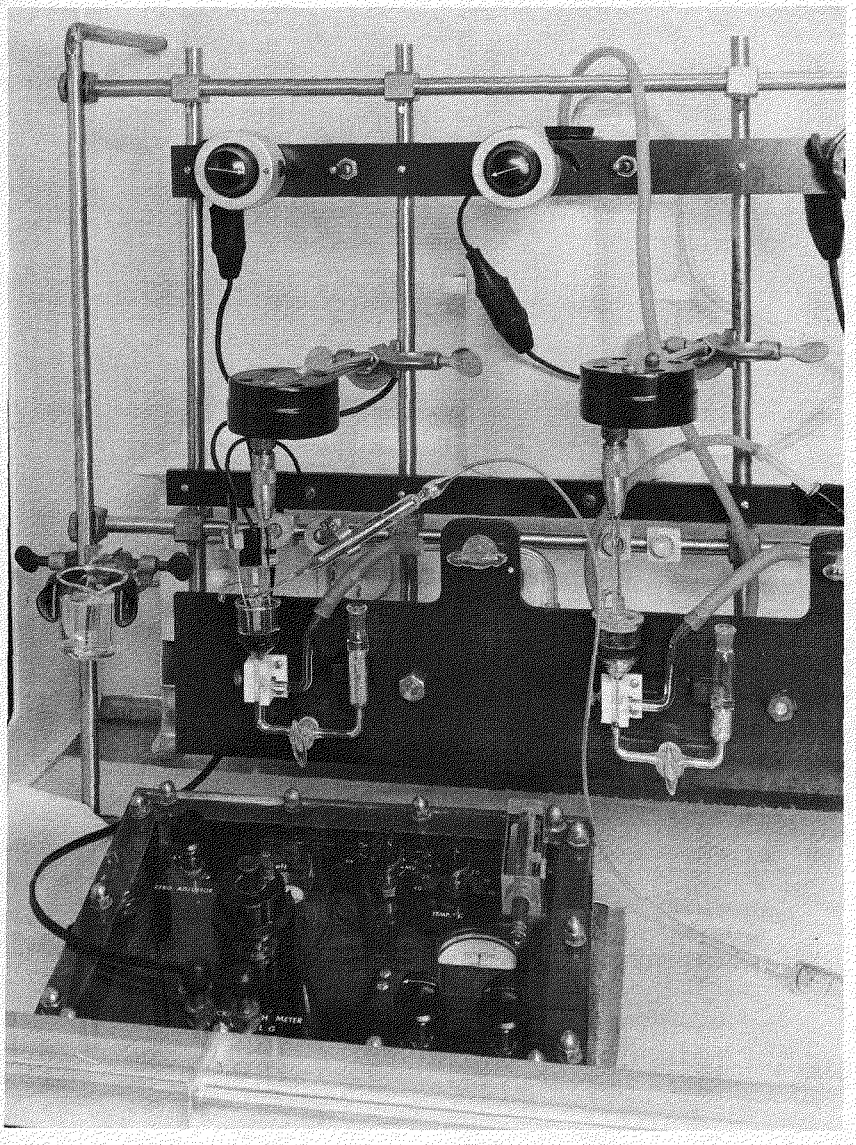


Fig. 2.12—Complete titration apparatus (LASL type).

must be cleaned frequently by immersion in a solution of potassium dichromate in sulfuric acid. It may be necessary occasionally to polish the gold wire with emery cloth.

The major interferences are nitrates, chlorides, organic material, iron, and uranium. Fuming with sulfuric acid eliminates the above non-metal interferences. Iron and uranium, if present, must be deter-

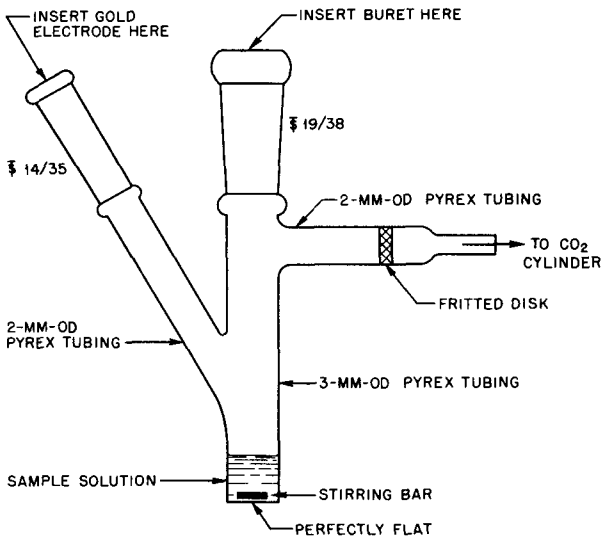


Fig. 2.13—Schematic diagram of titration vessel (ORNL type).

mined separately, and a correction must be applied to the total titre of the sample.

Procedure. The sample, containing between 8 and 12 mg of plutonium in the form of nitrate or chloride, is pipetted into a 10-ml volumetric flask. One milliliter of concentrated sulfuric acid is added, and the temperature is slowly increased to 300°C and held there until copious white fumes of sulfur trioxide emerge from the flask and reddish-brown crystals of Pu(IV) sulfate appear. The flask is cooled, and the solution is diluted to volume. An aliquot containing between 100 and 200 μg of plutonium is pipetted into the titration vessel (see Fig. 2.13). The electrode assembly is then inserted, and the microburet is placed so that the tip is just beneath the surface. A magnetic stirring bar is added to the vessel, and while the solution is being stirred, a quantity of Cr(II) sulfate solution is added sufficient to reduce the plutonium to the (III) oxidation state, which is indicated when the recorder pen reaches its maximum position at the left of the chart.

The sample solution is then titrated with standard Ce(IV) sulfate solution, which is added in an automatic manner* from the microburet. On the Brown recorder chart, the distance in inches between the Cr(II)-Cr(III) break and the Pu(III)-Pu(IV) break is taken as a measure of the amount of plutonium in the sample.

Calibration of Brown Recorder Chart. The milligrams of plutonium equivalent to 1 in. of chart travel is determined as follows:

*The automatic titrator referred to in this procedure was developed at the Oak Ridge National Laboratory and is designated as ORNL model Q-945 Automatic Recording Titrator. Anyone interested in building one of these instruments may obtain assistance from ORNL. It is beyond the scope of this chapter to include operational details of this highly specialized instrument.[61]

A standard iron solution containing 5 mg of iron per milliliter is prepared by dissolving 500 mg of pure iron in concentrated sulfuric acid and diluting to 100 ml with distilled water.

An aliquot of the standard iron solution containing 50 μg of iron is pipetted into the titrating vessel. The iron is then titrated as described for plutonium.

Calculations:

Let A=iron titrated (mg)

B=inches of chart travel on the Brown recorder between the Cr(II)-Cr(III) break and the Fe(II)-Fe(III) break

239.12=atomic weight of plutonium (the atomic weight of the plutonium should be determined by mass spectrometer measurements)

55.85=atomic weight of iron

Then, plutonium equivalent to 1 in. of recorder chart travel:

$$\text{Mg}=\frac{A}{B}\cdot\frac{239.12}{55.84}=C \tag{2.21}$$

The plutonium in the sample (mg/ml) is equal to $C\times D\times E$, where C=plutonium equivalent to 1 in. of chart travel, D=inches of chart travel between the Cr(II)-Cr(III) and Pu(III)-Pu(IV) breaks, and E=dilution factor.

Repeated titration of a known solution containing 2.292 mg of plutonium per milliliter gave an average result within 0.1 per cent of the known value and a coefficient of variation of 0.5 per cent when a total quantity of 0.229 mg of plutonium was determined.

(4) *Cr(II) Reduction: Ce(IV) Oxidation Method (British).*[62] A simplified modification of the ORNL method has been developed by British workers. In this method, the plutonium, in sulfate solution, is reduced to the (III) oxidation state by the addition of excess Cr(II) sulfate in sulfuric acid. The excess Cr(II) is air oxidized until a steady potential is observed from the bright platinum–saturated calomel electrode system. The Pu(III) is then oxidized to Pu(IV) with a standard solution of Ce(IV) sulfate delivered manually from a micrometer syringe microburet. A coefficient of variation of 0.2 per cent was attained using samples from 2 to 10 mg in weight. A schematic diagram of the apparatus is shown in Fig. 2.14.

Procedure. To an acid solution of the sample containing between 2 and 10 mg of plutonium, 5 ml of 3N sulfuric acid is added, and the solution is evaporated under an infrared lamp to fumes of sulfuric acid. The solution is allowed to cool and then is transferred to the potentiometric titration vessel and diluted to 5 ml with water. While the solution is being stirred mechanically, the plutonium is reduced

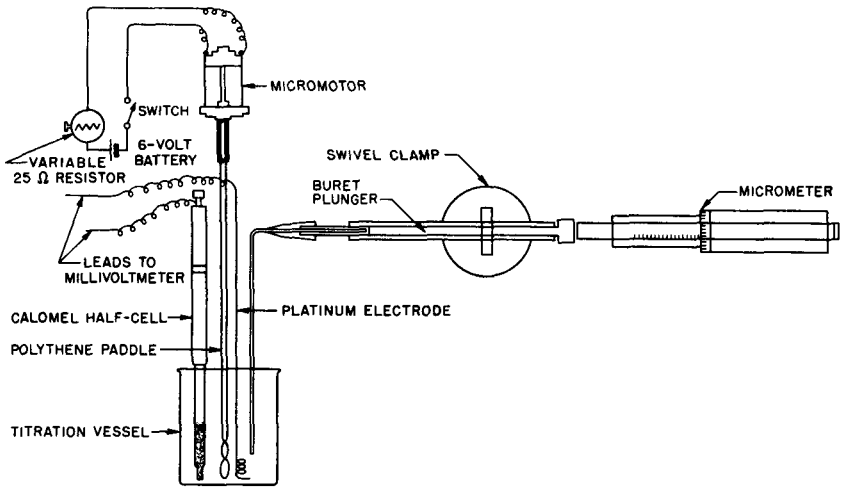


Fig. 2.14—Block diagram of titration apparatus (AERE type).

to the (III) oxidation state by the dropwise addition of Cr(II) sulfate solution (a slight excess). A slight excess of reductant is indicated by a large change in potential of the platinum–saturated calomel electrode system. The solution is allowed to stand until the excess Cr(II) is air oxidized to the (III) state. (The oxidation potential of Cr (II)/(III) is −0.4 volt, and the potential change at the end of the reduction of Pu(IV) to Pu(III) is about 1.1 volts and hence readily observed.) The Cr(II) is assumed to be completely oxidized when the potential remains at a constant value.

The Pu(III) is then oxidized to the (IV) oxidation state by the manual addition of a standard Ce(IV) sulfate solution from a microburet. The microburet recommended is one having a capacity of 0.5 ml and graduated in 0.0002 ml. The titration of 10 mg of plutonium requires 0.4184 ml of a 0.1*N* Ce(IV) sulfate solution. The potential following the addition of each increment of Ce(IV) solution is recorded, and the equivalence point is determined from the maximum value of $\Delta E/\Delta V$.

When interfering elements such as iron and uranium are present, a preliminary separation of the plutonium is recommended. A quantitative separation and recovery of the plutonium is obtained by adjusting its oxidation state to (IV), which is then adsorbed on an anion-exchange resin from 8*M* nitric acid. The column is washed successively with 8*M* nitric acid and 1*M* hydrochloric acid. The plutonium is then eluted in the (III) oxidation state by the addition of 1.5*M* hydroxylamine hydrochloride in 1*M* hydrochloric acid. Following destruction of the hydroxylamine hydrochloride by the dropwise addition of hydrogen peroxide, the solution is fumed with perchloric acid to ensure complete destruction of all organic matter. Plutonium is then determined as above.

(5) Fe(II) Reduction of Pu(VI) to Pu(IV): Potentiometric Titration of Excess Fe(II) With Ce(IV) (Waterbury–Metz

Method).[63] This method is based on the fact that Fe(II) will quantitatively reduce Pu(VI) to Pu(IV) in sulfuric acid solution according to the equation:

$$Pu(VI)+2Fe(II)\rightarrow Pu(IV)+2Fe(III) \qquad (2.22)$$

The amount of Fe(II) required to complete the reduction of the Pu(VI) is determined by initially adding a known weight (to slight excess) of Fe(II) in the form of a standard solution of Mohr's salt, then titrating the excess Fe(II) with standard Ce(IV) solution using a potentiometric end point.

Procedure. The sample, which may be a plutonium salt, a hydrochloric acid solution of the metal or of a plutonium alloy, or a nitric–hydrofluoric acid solution of an alloy, should contain more than 200 mg of plutonium in each aliquot. The aliquot, in a 250-ml tall-form beaker, is evaporated to near dryness using a combination of electric hot plate and infrared heaters. After being cooled, the walls of the beaker are washed down with 6 to 10 ml of 70 per cent perchloric acid containing 2 to 3 ml of 6*M* nitric acid. The solution is evaporated in the same manner (and without boiling) to strong fumes of perchloric acid. After it has cooled, the beaker is washed down with a few milliliters of 20 percent perchloric acid and fumed to a final volume of 2 to 3 ml. If the solution should evaporate to dryness, the residue may not redissolve in perchloric acid. In such cases, a few milliliters of 16*M* nitric acid–1*M* hydrofluoric acid mixture will usually dissolve the residue. A double fuming with perchloric acid is then again necessary. Regardless of the dissolution steps, it is essential that the fuming operation completely remove fluoride, nitrate, and phosphate because these seriously interfere in the remainder of the procedure.

To the fumed and cooled solution is added about 50 ml of water, and the following steps are carried out immediately. A glass tube connected to a supply of carbon dioxide is inserted into the beaker so that the end is less than 1 in. above the surface of the solution, and a flow of carbon dioxide is started to exclude air. Approximately 10 ml of 50 per cent sulfuric acid is added, and the electrode system of saturated calomel–bright platinum electrodes is placed in position. A sensitive vacuum-tube potentiometer is used for measuring the potential of the indicating electrode. With continuous stirring of the solution, a standard Fe(II) solution (Mohr's salt) is added from a weight buret until a sudden large change in potential indicates complete reduction of the Pu(VI) to the (IV) oxidation state. A slight excess of reducing solution is added, which is then back-titrated to a potential of —780 mv with standardized Ce(IV) solution from a weight buret. An automatic titrator may also be used for the titration.[64] The total amount of Ce(IV) solution required is usually less than 1 g (0.05 milliequivalent); whereas over 4 g (2 milliequivalents) of Fe(II) solution is required. The percentage of plutonium in the sample is calculated as follows:

$$\%\ Pu=\frac{(\text{Net grams of titrant})\ (\text{Pu titre of titrant})\ (100)}{\text{Grams of sample}} \qquad (2.23)$$

where net grams of titrant is the total grams of titrant minus the grams back-titrated.

690–457 O—64——14

Use of a large-size sample and also of weight burets are advantageous in obtaining good precision. For a 200-mg sample, the coefficient of variation is less than 0.03 per cent.

In addition to the anions listed above, chromium, gold, manganese, platinum, and vanadium interfere.

One advantage of the method is that iron, one of the common impurities in plutonium, does not interfere.

Standardization of the Ce(IV) Solution. The Ce(IV) solution, which is about 0.05*N* in Ce(IV) and 1*M* in sulfuric acid, is standardized against primary sodium oxalate as previously described. There would be no advantage, in this case, in using high-purity plutonium metal for this purpose.

Standardization of Fe(II) Solution. The Fe(II) solution is prepared by dissolving 200 g of Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, in 1 liter of 0.5*M* sulfuric acid. Nitrogen is bubbled through the solution to remove any dissolved oxygen. The solution should be standardized immediately before use. High-purity (99.98 per cent) plutonium metal is preferred in this case, and the standardization is carried out as described above for the determination of plutonium.

(6) *Zinc Reduction: Cr(VI) Oxidation Method (New Brunswick Laboratory).*[63a] Plutonium in sulfuric acid solution is reduced in a Jones reductor to Pu(III) which is oxidized to Pu(IV) with a standard solution of potassium dichromate. Standard solutions of two concentrations are used in the titration, and the end point is determined potentiometrically. The major interferences are iron, uranium, organic materials, nitrate, and platinum. A coefficient of variation of 0.04% was reported[63a] for the determination of 70 to 141 mg of plutonium in the high-purity metal.

The electrode system consists of two gold electrodes polarized by a constant current of about 2 μamp supplied by a 45-volt B battery through a 20-megohm resistor. Platinum electrodes are unreliable because they become poisoned and unresponsive. The gold electrode system is very sensitive to the acidity of the solution being titrated. In 2*N* sulfuric acid solution the change in potential is not adequate to distinguish the end point; a much sharper inflection occurs in 4*N* sulfuric acid solution.

Procedure. Approximately 100 mg of the cleaned metal is weighed to ± 0.02 mg and dissolved in 10 ml of 4*N* sulfuric acid in a covered beaker. When dissolution is complete (in usually 15 to 20 min), the solution is poured into a Jones reductor, which is then covered with a watch glass. The solution is passed through the reductor at a flow rate of about 3 ml/min and collected in a beaker. The original beaker and the watch glass on the reductor are washed with 4*N* sulfuric acid, which is added to the reductor, and the reductor is washed twice with 15-ml portions of 4*N* sulfuric acid and once with 15 ml of water. The gold

electrodes are inserted into the combined effluents from the reductor, and standard potassium dichromate solution, A, containing about 0.7 mg of the salt per gram of solution is added rapidly from a weight buret until the color of the solution turns from blue to light orange. Gentle stirring of the solution and measurements of the potential across the gold electrodes with a suitable vacuum-tube voltmeter are started at this point. The titrant is added quickly in 5-drop portions until a potential change of 10 mv is noted, then in 2-drop increments until a second 10-mv change in potential occurs, and, finally, the titrant is added dropwise until a third 10-mv increment in potential is observed. This cautious addition of the titrant from the weight buret ensures that more than 99% of the Pu(III) is titrated without danger of adding excess oxidant. The weight buret is weighed and the quantity of solution A added is determined from the weight change. The titration is continued immediately by adding from a microburet 0.05-ml increments of a standard potassium dichromate solution, B, containing about 0.25 mg of the salt per ml. The titration is continued for at least two increments beyond the end point which is taken at the point where the largest change in potential was obtained for a 0.05-ml increment.

For the determination of the reagent blank, the above procedure is repeated using 10 ml of 4*N* sulfuric acid but omitting the sample. The quantity of the dilute standard potassium dichromate solution, B, to produce the same potential as that obtained for the end point in the titration of the sample is taken as the blank. In addition, the iron correction must be determined as described above.

The plutonium equivalent of the net quantity of the two titrants added and the plutonium concentration in the sample are calculated as follows:

$$\text{Pu equivalent} = (\text{Grams of titrant A})(\text{Pu titre}) + (\text{milliliters of titrant B—blank})(\text{Pu titre}) \quad (2.23a)$$

$$\%\ \text{Pu} = \frac{(\text{Pu equivalent} - \text{Fe correction})(100)}{\text{Grams of sample}} \quad (2.23b)$$

Recently this method was modified to use a 0.3- to 1.0-g sample of plutonium which is titrated with a more concentrated titrant added entirely from a weight buret, thus eliminating the secondary microvolumetric titration. The modified method was applied to a limited extent to the determination of plutonium in plutonium oxide–uranium oxide and plutonium carbide–uranium carbide mixtures, following separation from uranium by ion exchange, and in plutonium salts such as the sulfate and dicesium plutonium hexachloride.[63b] Details of the modified method and its applications were not given.

(7) *Coulometric Methods.* Methods have been devised for the determination of plutonium either by applying the principles of constant-current or constant-potential coulometry.

Constant-current Coulometry. The plutonium is reduced to the (III) oxidation state by adding a slight excess of Cr(II) [65, 66] or Ti(III).[67] Titration is then made [65, 66] with electrolytically generated bromine or Ce(IV), and the end points are determined potentiometrically. Large reagent blanks and diffusion within the titration cell

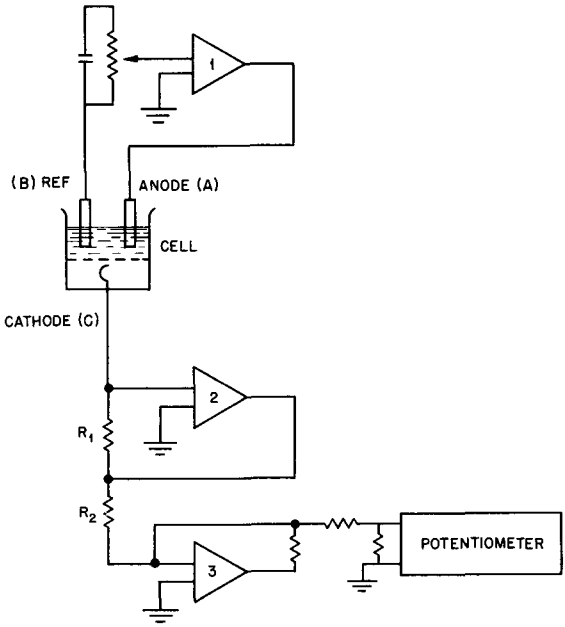


Fig. 2.15—Block diagram of controlled-potential coulometer (HAPO type). R_1 and R_2 are resistors; 1, 2, and 3 are electronic amplifiers.

combine to make the method not very satisfactory. However, better reagents and further work may overcome these difficulties.

More recently a method [67] was developed in which the plutonium is first oxidized to the (VI) oxidation state by bismuthate or permanganate. Following destruction of the manganese dioxide by the addition of sodium azide or formaldehyde, the Pu(VI) is titrated with electrolytically generated Fe(II) using a potentiometric end point. The method will measure very small amounts of plutonium. The reported coefficient of variation for a 3-μg sample is about 5 per cent, and that for a 1-mg sample is 1 per cent. Several elements cause interference, but all except cerium and oxygen can be removed by an initial lanthanum trifluoride separation of the plutonium.

Constant-potential Coulometry. The coulometric determination of plutonium at constant or controlled potential is a more recent development in coulometric techniques and seems to be preferred to the constant-current technique by many chemists. The controlled-potential technique is simpler in that pretreatments to adjust oxidation states and the need for end-point detection are both eliminated. The availability of simple and reliable controlled-potential coulometers [68, 69] has resulted in applications [69-71] of the method to the determination of plutonium in dissolver solutions of spent reactor fuels and also to its

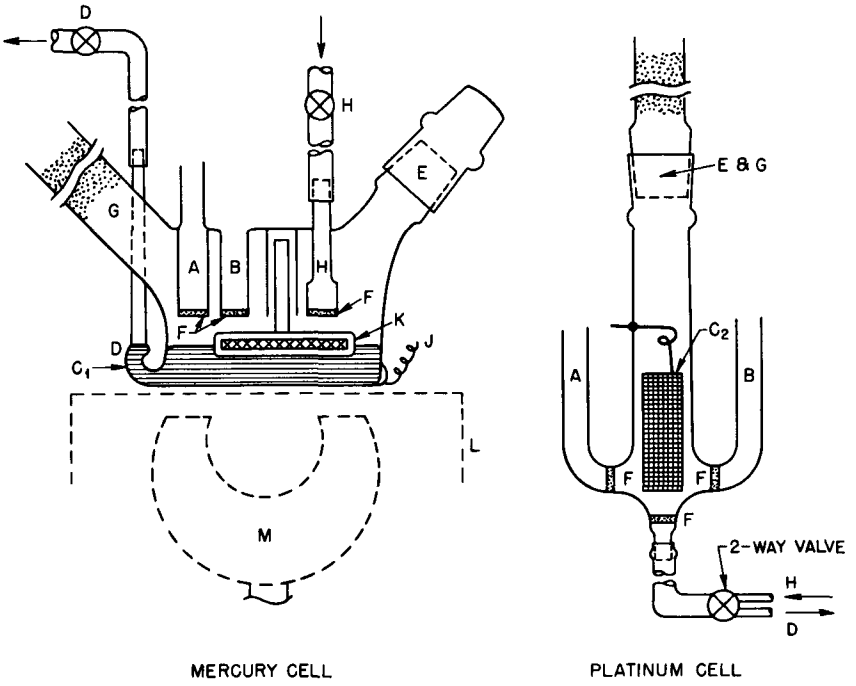


Fig. 2.16—Titration cells (HAPO type). A, anode compartment. B, reference electrode compartment. C_1, mercury-pool electrode. C_2, platinum-gauze electrode. D, connection to vacuum flask. E, entry port (ground-glass joint). F, frits (sintered glass). G, vent with glass-wool filter. H, helium gas for deaeration. J, mercury contact. K, magnetic stirring bar. L, stainless-steel support. M, rotating magnet.

determination in product solutions. The electrode reaction of interest is

$$Pu(IV) + e^- \rightleftarrows Pu(III) \qquad (2.24)$$

Either the oxidation or reduction reaction may be used for the determination of the plutonium. If oxidation from the (III) to the (IV) oxidation state is used, a mercury-pool working electrode seems to be preferable; whereas for the reduction reaction a bright platinum working electrode is satisfactory. Each of the two working electrodes has its desirable features. The most notable advantage of the mercury cell is the high degree of reproducibility of the electrode surface and the high electrode efficiency. The outstanding feature of the platinum cell is its simplicity, both in construction and operation. Figures 2.15 and 2.16 show a coulometer block diagram and schematic cross sections of the two types of cells, respectively.

Briefly, the operational procedure is as follows: If the mercury-pool electrode is to be used, a citrate buffer solution is prepared by dissolving 1 mole of citric acid and 0.1 mole of aluminum sulfate in water. The pH is adjusted to 4.5 with potassium hydroxide, and the solution is diluted to 1 liter. If the platinum cell is to be used, titrations are carried out in a supporting electrolyte of 1*N* hydrochloric acid or nitric acid. However, if the latter is used or if considerable nitrate is present in the sample, a trace of sulfamic acid is added to prevent interference from nitrite ion.

The titrating medium and the solution of plutonium sample are placed in the cell, and the solution is deaerated for 5 min. The plutonium is then reduced to the (III) oxidation state by applying a potential of about 0.12 volt below the $E^{0\prime}$ of the system, where $E^{0\prime}$ is the working standard reduction potential obtained by replacing activities by concentrations in the Nernst equation. (In the citrate buffer medium, $E^{0\prime}$ is about +0.19 volt vs. the saturated calomel electrode. In 1*M* nitric and 1*M* hydrochloric acids, $E^{0\prime}$ is about −0.67 volt and −0.71 volt, respectively, vs. the saturated calomel electrode.) The reduction requires from 5 to 30 min, depending on the

Table 2.10—TOLERABLE AMOUNTS OF INTERFERING IONS

Element	Ion-to-plutonium ratio to cause 1% bias*		
	Citrate	1*M* HNO_3†	1*M* HCl‡
Copper	0. 006	>100	
Gold	>100	0. 020	
Iron	0. 014	0. 17	1. 0
Lead	4. 6	>100	
Mercury	>1000	0. 025	
Molybdenum	(§)	>100	
Palladium	>100	0. 04	
Ruthenium	(¶)	>10	
Silver	>100	1. 7	
Tin	(§)	>100	
U(VI)	**20	>1000	>1000

*Based on a titration span of 0.120 volt on either side of $E^{0\prime}$ for plutonium.

†Containing 0.01*M* sulfamic acid.

‡Values left blank were not determined.

§Tin and molybdenum undergo irreversible reaction in the potential region of interest in the citrate medium. Samples containing these elements should be analyzed in the acid media.

¶Ruthenium interferes in the citrate medium by reducing the hydrogen overvoltage of the mercury. Therefore, the tolerable amount of ruthenium is independent of the plutonium concentration and is an absolute quantity. This amount is about 2×10^{-4} millimoles for the cell described in the original report.[67]

**Uranium(VI) reduction is not reversible.

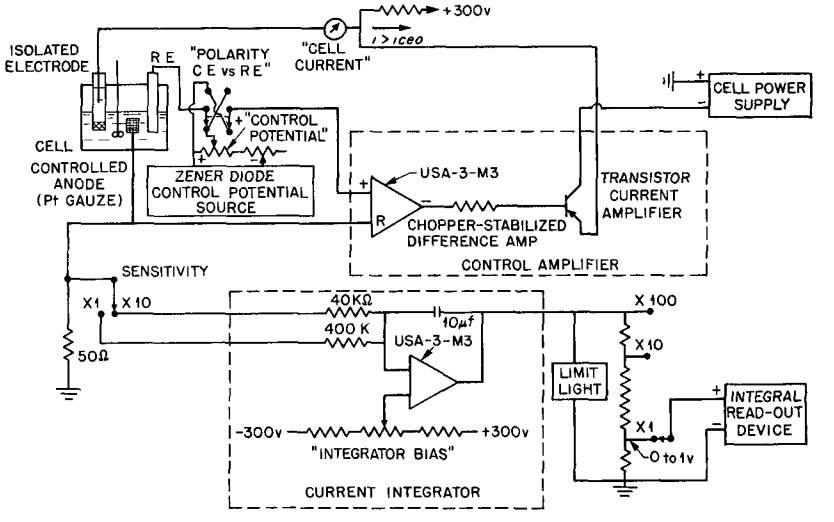


Fig. 2.17—Block diagram of modified electronic controlled-potential coulometric titrator (ORNL type).

amount of plutonium present and the initial oxidation state. The completion of the reduction step is indicated when the current falls to the residual-current level. The potential on the working electrode is then changed to a value that will cause oxidation from the (III) to the (IV) oxidation state. This oxidation voltage is normally about 0.12 volt greater than the $E^{0\prime}$ for the system. Ten minutes will usually suffice for the oxidation in cells of the type shown in Fig. 2.16. When oxidation is complete, the plutonium content is calculated from the reading of the calibrated integrator portion of the coulometer. For greatest accuracy the integrator reading should be corrected for the current that flows during a blank run in which conditions are identical except for the presence of plutonium. Interfering elements are those that can enter into redox reactions at the working electrode within the voltage range employed in the reduction and oxidation of the plutonium. Table 2.10 shows the conditions under which the interference by certain elements was not greater than 1 per cent.

The method applies to the determination of plutonium concentrations in the range of 0.05 to 50 g/liter. At concentrations of 0.05 g/liter, the coefficient of variation is about 0.3 per cent, and, at 20 g/liter, the coefficient of variation is 0.05 per cent.

The method appears to be reliable, although it was noted that the first determination made at the beginning of a day is usually low. It would seem that some inherent characteristic in cell design might be responsible for this.

In more recent work [72] a controlled-potential method very similar to the above [69] was thoroughly investigated to evaluate the precision

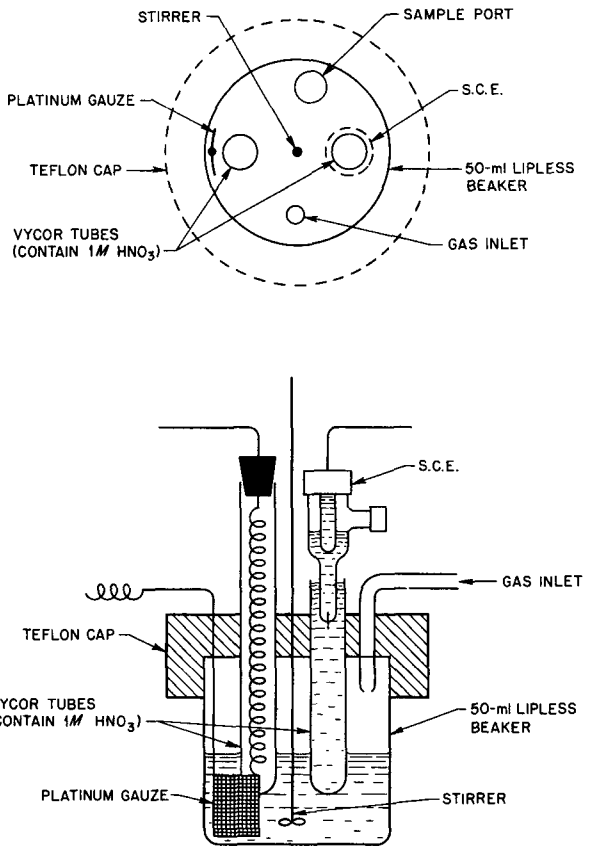


Fig. 2.18—Schematic diagram of titration vessel (ORNL type).

of the method on a routine basis when applied to the analysis of power-reactor fuel-reprocessing pilot-plant samples. With a coulometric titrator [73] similar to that used above, but with certain changes (see Fig. 2.17) making it more adaptable to the particular intended use, and with a modified titration cell (see Fig. 2.18) with a platinum working electrode, the method was applied routinely to plutonium "product" samples having approximate compositions of 4.5*M* nitric acid and 40 to 60 mg of plutonium per milliliter. It was found that iron caused very little interference and that uranium caused no interference if the reduction of the plutonium were made in a 1*M* perchloric acid solution. The potentials of the working electrode during the reduction and oxidation steps were, respectively, −0.560 and −0.880 volt vs. the saturated calomel electrode. The sample size was approximately 5 mg of plutonium. Table 2.11 shows a comparison of this method with a potentiometric method under routine operating conditions.

Table 2.11—COMPARISON OF POTENTIOMETRIC AND COULOMETRIC METHODS UNDER ROUTINE OPERATING CONDITIONS [72]

(Standard plutonium solution = 10.027 mg Pu/ml ± 0.2%)

Method	No. of determinations	Av. mg Pu/ml	Relative standard deviation, %
Potentiometric	24	10. 058	0. 68
Coulometric	37	10. 027	0. 27

As a result of this work, it was decided that the coulometric technique was adequate for the analysis of this type of sample and that a considerable saving in time could be effected by its use in place of standard potentiometric titration method.

(8) *Amperometric Titration of Pu(VI) with Fe(II) (Argonne National Laboratory).*[73a] In this method the plutonium in 0.25*M* sulfuric acid solution is oxidized to the (VI) oxidation state with argentic oxide. The excess oxidant is removed by heating, and the Pu(VI) is titrated with Fe(II) to an amperometric end point. The coefficient of variation for determining 10 mg of plutonium is 0.05 per cent. For smaller amounts of plutonium, 0.1 to 0.2 mg, the coefficient of variation of the method is 0.5 per cent. Cerium, chromium, manganese, vanadium, nitrate, and chloride are the principal interferences, and the latter two can be removed by evaporating the sample to fumes with sulfuric acid. Although the initial experimental work has shown this method to be highly promising, application to the routine determination of plutonium has not been made yet.

The equipment necessary in the amperometric titration includes a synchronous electrode rotator revolving at 600 rpm, a rotating platinum electrode, and an amperometric titration apparatus (similar to the Ampot No. S–29710, made by E. H. Sargent & Co.). The reference electrode is of the mercurous sulfate type with a potassium sulfate–salt bridge. For the standardization of the Fe(II) solutions, either potassium dichromate or high-purity plutonium metal is the primary standard. The latter is preferred, especially for standardization of the dilute (0.001*M*) Fe(II) solution.

Procedure. An aliquot containing between 10 and 20 mg of plutonium is transferred to a 50-ml beaker, 0.5 ml of 9*M* sulfuric acid is added, and the solution is evaporated to dryness. After the solution cools, the residue is dissolved in about 10 ml of 0.25*M* sulfuric acid. While the solution is swirled slowly, argentic oxide is added in small portions to oxidize the plutonium to the (VI) oxidation state. A slight excess of oxidant should be added. The presence of this excess is shown by a

characteristic blackish-brown color in the solution and the formation of a black precipitate (possibly Ag_2O_3). Fifteen minutes after addition of oxidant, the solution is diluted to about 25 ml with 0.5*M* sulfuric acid and then heated to 80°C to eliminate the excess argentic oxide and the black precipitate. The solution is cooled to 40°C, and the platinum microelectrode and the salt-bridge arm of the mercurous sulfate reference electrode are inserted into the solution. Ten milliliters of 9*M* sulfuric acid is added slowly, and the initial current is measured at an applied potential of +0.6 volt relative to the reference electrode. The current should be steady and not greater than 0.2 μa. Standardized 0.05*M* Fe(II) solution is added in small increments from a weight buret until a steady current of about 2 μa is obtained. The exact current and the weight of the buret are recorded. Then more Fe(II) solution is added until the current reaches 25 to 30 μa, and the new buret weight and the exact current are recorded. The end point of the titration is determined graphically by plotting the current as a function of the grams of titrant added, assuming the current is zero prior to the end point. The weight of plutonium in the aliquot is calculated from the weight of titrant required to reach the end point and the titre of the Fe(II) solution.

For determining between 0.1 and 0.2 mg of plutonium, less argentic oxide is required to effect the oxidation and 0.001*M* Fe(II) solution is the titrant. In addition, the residual current must be considered in determining the end point.

(b) *Volumetric Methods.* Complexiметric and redox titrations have been applied to the volumetric determination of plutonium. In the complexiметric titrations, ethylenediaminetetraacetic acid invariably is the titrant and one of several metal indicators is used in determing the end point. The methods involve either direct or indirect titration of the plutonium. The redox titration methods are, in general, similar to potentiometric methods except for the end-point detection. One of the earliest methods [74, 75] for determining plutonium involved reduction to Pu(III) in a Jones reductor and subsequent oxidation to the (IV) oxidation state with standard Ce(IV) solution using ferrous *o*-phenanthrolate as a color indicator to establish the end point. Reproducibilities were reported as being between 0.25 and 3 per cent for 2.5-mg samples. Larger samples make the color change of the indicator difficult to detect by visual means. The difficulties of visual detection of the end point are eliminated when the color change is determined spectrophotometrically.

(1) *Volumetric Titration of Plutonium With Ce(IV) With a Spectrophotometric Determination of the End Point (Rocky Flats Division, Dow Chemical Co.).*[76] In this recently developed method for the assay of plutonium metal, the sample is cleaned and dissolved in hydrochloric acid. The Pu(III), which is the only oxidation state of plutonium formed during the dissolution in hydrochloric acid, is titrated in a sulfuric acid solution with Ce(IV), using ferroin as a color indicator. The end point is deter-

mined spectrophotometrically with a special photometric end-point detector. A coefficient of variation of 0.03 per cent is reported for a single determination. Iron, vanadium, uranium, titanium, and molybdenum are among the interfering metals. A correction factor, based on a spectrophotometric determination of the iron concentration using a separate aliquot of the sample, corrects for the interference caused by iron.

The photometric end-point detector consists of a light source, a 510-mμ interference filter with a half-band width of 10 mμ, a cadmium sulfide detector cell, a sample cell compartment for a 250-ml electrolytic beaker, and a 200-μa meter driven by the output from the detector cell.

Procedure. The metal sample is cleaned by filing away the oxidized surface. Two 0.5-g pieces are cut from the polished sample and weighed. Each piece is dissolved and analyzed separately to eliminate any waiting periods during which some of the Pu(III) may be oxidized by air. The weighed sample is placed in a 250-ml electrolytic beaker with a polyethylene cover and dissolved in 5 ml of 6*M* hydrochloric acid. The beaker cover and walls are washed down with 0.5*M* sulfuric acid, and the solution is diluted to about 100 ml with this acid. Five drops of ferroin indicator (1,10-o-phenanthroline ferrous sulfate, 0.025*M*) are added, the beaker is placed in the cell compartment, and the Pu(III) is titrated immediately with 0.05*M* Ce(IV) standard solution from a 50-ml buret. [This titration must be completed within 5 min following the dissolution of the sample to prevent air oxidation of the Pu(III).] Near the end point the meter pointer begins to move slowly. From this point increments of about 0.02 ml of the titrant are added until no significant deflection of the meter pointer occurs upon further additions. Volume readings are recorded after each increment has been added. The second piece of the sample is then assayed in the same manner, and a blank is determined using the same quantities of reagents as in the analysis of the sample. The titration of the blank should require no more than 0.1 ml of titrant. The plutonium concentration is calculated for each determination using the following equation:

$$\% \text{ Pu} = \frac{(\text{Ml of titrant} - \text{ml of blank})(\text{Titre of titrant}) - \text{Fe correction}}{(\text{Grams of sample})(0.01)} \qquad (2.25)$$

For the determination of the iron correction and standardization of the Ce(IV) solution, refer to Sec. 2–2.5(a).

This method of end-point detection may also be applied to the titration methods in which the plutonium is first reduced with a reductant such as titanous or zinc amalgam before the titration. Therefore the method is applicable to samples other than plutonium metal. However, in analyzing plutonium solutions, most of the methods, including the potentiometric titration methods, require removal of nitrate ion by fuming with sulfuric acid. One exception is the method recently published[76a] in which the plutonium in a 1*N* nitric acid–1*N* sulfuric

acid solution is reduced to Pu(III) by adding Ti(III) and sulfamic acid. The nitric acid concentration should not exceed $1N$; higher concentrations of this acid rapidly oxidize Ti(III) and incomplete reduction of the plutonium might result. The excess Ti(III) is oxidized by nitrate ion and air, and the nitrite ion so formed is removed by the sulfamic acid. Ferroin indicator is added, and the Pu(III) is titrated with Ce(IV) standard solution without interference from the nitric acid.

(2) *Indirect Titration of Plutonium With Ethylenediaminetetraacetic Acid (Great Britain Atomic Energy Research Establishment)*:[77] The ability of ethylenediaminetetraacetic acid (EDTA) to form a stable 1 : 1 complex with Pu(IV) is the basis for this indirect titration method. The method applies best to milligram amounts of plutonium. An "error of less than 1 per cent" was reported [77] for the determination of 10 mg of the element. If the amount of plutonium is greater than 15 mg, the sharpness of the color change of the indicator is reduced. Interference is caused by metals such as gallium, iron, titanium, thorium, and vanadium, which form strong complexes with EDTA.

Procedure. To an aliquot containing about 10 mg of plutonium in hydrochloric acid solution is added an excess of 0.01M standard EDTA solution. Following adjustment of the pH to 2.5 with aqueous ammonia, the excess EDTA is back-titrated with 0.01M standard thorium nitrate solution. Alizarin S indicator containing a small amount of methylene blue is the color indicator normally used, although a 2 per cent solution of salicylic acid in methanol is considered a second choice. The color change of the Alizarin S indicator at the end point is green to purple. Because a 1 : 1 complex is formed between the EDTA and plutonium, its atomic weight is used as the equivalent weight in calculating the amount of plutonium in the sample.

For avoiding interference by various ions found in nitric acid dissolver solutions of irradiated uranium, the indirect titration method was modified to include an extraction separation.[77a] The plutonium is quantitatively converted to Pu(IV) using Fe(II) in the presence of nitrite ion. The Pu(IV) is then selectively extracted into 1 per cent Hyamine (long-chain quaternary ammonium base) in benzene. A two-stage extraction cycle separates 99.8 per cent of the plutonium with decontamination factors of 10^5 from mixed fission products and 10^2 from uranium. The extract is converted to a nitric acid-acetone medium, and an excess of EDTA is added. A back-titration with standard zinc solution to the color change of dithizone indicator completes the determination. Neptunium is the only likely interference. A coefficient of variation of 0.3 per cent in determining between 0.1 and 0.5 mg of plutonium is obtained under ideal conditions.

Procedure. To an aliquot containing between 0.1 and 0.5 mg of plutonium are added 2 ml of 1.3*M* nitric acid, 3 drops of 20 per cent ferrous ammonium sulfate solution, and 3 drops of 1*M* sodium nitrite in that order. Additional 1.3*M* nitric acid is added to reduce the final acidity to less than 2*M*. Then the plutonium is extracted into 2 ml of benzene containing 1 per cent Hyamine 1622, and the aqueous phase is washed with an additional 2 ml of this extractant. The combined organic phases are washed with 2 ml of 4*M* nitric acid and evaporated in small increments without charring in the titration vessel. To the cooled residue are added, with mixing, 1 drop of 4*M* nitric acid, 0 120 ml of 0.025 *M* EDTA solution (a slight excess), 1 ml of acetone, 1 ml of pH 4.75 buffer, and additional acetone to give a clear solution. Three drops of 0.04 per cent dithizone solution are added, and the excess EDTA is titrated with 0.004*M* zinc solution using a photometer to determine the end point. A 1-ml aliquot of 1.3*M* nitric acid, but omitting the sample aliquot, is analyzed in the above manner to determine the reagent blank. The plutonium content is calculated from the net quantity of EDTA used, assuming a 1:1 complex for plutonium-EDTA.

(3) *Direct Titration of Plutonium with Ethylenediaminetetraacetic Acid (Mound Laboratory, Monsanto Research Corp.)*[77b] In this recent method between 8 and 40 mg of plutonium in sulfate solution at a pH between 2.5 and 3.0 and at boiling temperature are titrated directly with EDTA standard solution. Copper-1-(2-pyridylazo)-2-naphthol (Cu-PAN) or Xylenol orange metal indicator is added to permit visual determination of the end point. Following the direct titration, the method is continued by adding ammonium fluoride solution at pH 3 to destroy the plutonium chelate, and the uncomplexed EDTA is titrated with standard copper solution to the color change of PAN metal indicator. The coefficient of variation in the determination of 14 mg of plutonium was 0.6 per cent by the direct titration and by the indirect method. Cations that are partially or completely complexed by EDTA at pH 2.5 to 3.0 interfere in the direct titration. These cations include Ni(II), Fe(III), Al(III), Cu(II), Bi(III), Ce(III) and (IV), Cr(III), Cd(II), Mn(II), Zn(II), and Th(IV). Ce(III) and (IV), Zn(II), Th(IV), and Al(III) also interfere in the indirect titration. Phosphate is the only anion listed as an interference.

Procedure. To the sample aliquot containing between 8 and 40 mg of plutonium are added 2 ml of 36*N* sulfuric acid, the solution is heated to fumes, and nitric acid is added dropwise to destroy organic material. Then the sample is evaporated to incipient dryness, the residue is dissolved in 10 ml of 0.25*N* sulfuric acid, and 3 to 5 ml of glacial acetic acid are added. A 10 per cent sodium acetate solution is then added dropwise until the pH is between 2.5 and 3.0. The solution is heated to boiling, 3 drops of 0.1 per cent solution of PAN are added, and the plutonium is titrated with standard EDTA. About 1 min is allowed between additions of titrant as the end point is approached. A change

in the color of the indicator from pink to lemon-yellow shows complete complexing of the plutonium.

To continue the method with the indirect titration, 1 to 2 ml of 4 per cent ammonium fluoride solution, containing sufficient hydrofluoric acid to adjust the pH to 3, are added, and the released EDTA is titrated with standard copper solution. As the end point is approached, 1 to 2 drops each of the buffered fluoride solution and of PAN indicator solution are added. The color change at the end point is yellow to faint pink.

In another direct complexiметric titration method,[77c] Pu(IV) in 0.1 to 0.2*N* hydrochloric or nitric acid is titrated with 0.005 to 0.01*M* EDTA solution using Arsenazo I, 3-(2-arsonophenylazo)-4,5-dihydoxy-2,7-naphthalenedisulfonic acid, as the color indicator. The color change at the end point is from blue violet to rose and is most clearly defined at plutonium concentrations of 0.1 to 0.2 mg/ml. Zirconium, thorium, and iron interfere in this titration, but lanthanum, uranium, chromium, lead, and nickel do not. A coefficient of variation of about 1 per cent apparently was obtained.[77c]

(c) *Spectrophotometric Methods.* The rare-earth type absorption spectra exhibited by each of the oxidation states of plutonium make it almost a foregone conclusion that spectrophotometric methods are applicable to the determination of plutonium. Unfortunately, the molar extinction coefficients of the various oxidation states in any of the inorganic acids are small, usually less than 40, except for Pu(VI) in perchloric acid, where the value is over 300 (see Table 2.8). For this reason the concentration of the plutonium must be relatively high, greated than 0.5 mg/ml, before these absorption bands are usable. For example, the 6030-A absorption band of Pu(III) in 0.1*M* perchloric acid is usable at concentrations in the range of 2 to 4 mg/ml with absorption cells of 1-cm light paths. Measurements of Pu(IV) at 4760 A and of Pu(VI) at 8330 A require concentrations of 1 mg/ml and 0.5 mg/ml, respectively.

The value of ϵ (molar extinction coefficient) is sensitive to acid type, acid concentration, and temperature, making it necessary that these be carefully controlled. In addition, all four oxidation states may be present simultaneously in one solution, making it necessary to measure absorbances at selected wave lengths. Advantageous wave lengths for these measurements are 4760, 5960, 6030, and 8330 A. If these measured absorbances with the corresponding molar extinction coefficients are used and if the absorbances are assumed to be additive, a set of four equations can be set up and solved for the concentration of each oxidation state. This technique has been used for determining the concentration of each oxidation state in various aqueous media, such as sulfuric acid [52, 78-81] and nitric acid.[52, 82, 83] It must always be remembered that the wave length of maximum absorption varies somewhat with the acid media.

If the solution is pretreated to ensure the presence of a single oxidation state and if a standard is used (differential spectrophotometry), wider application can be made of the above technique, and better precision results. For example, in a 1*M* hydrochloric acid solution containing 8 to 13 mg of plutonium reduced to the (III) oxidation state per milliliter, measurement of the absorbance of the plutonium at 5650 A relative to an accurately known standard containing 8 mg of plutonium per milliliter is reported [84] to have a coefficient of variation of 0.05 per cent, or a precision of 0.1 per cent at the 95 per cent confidence level.[85] Calcium, Ce(III), thorium, and uranium in molar ratios of 4 to 1 and Fe(II) in equimolar ratios do not interfere, but Fe(III), molybdenum, aluminum, and zirconium do interfere.

In a method [74] in which the absorption of Pu(IV) is measured, hydroxylamine is added to reduce the element to the (III) state, which is then precipitated as the hydroxide. The precipitate is dissolved in 16*M* nitric acid, and the solution is warmed to quantitatively oxidize the plutonium to the (IV) oxidation state. The resulting solution is diluted to a nitric acid concentration of 3.1*M*, and the absorbance is read at 4760 A and compared with standards in the concentration range of 0.00224*M* to 0.00896*M* in Pu(IV). Neither iron nor uranium interfere, and the method is reported to be "precise to within 1 per cent." [74]

In the determination of milligram quantities of plutonium in solutions containing significant concentrations of fission products and uranium, the plutonium is oxidized with Ag(II) to Pu(VI), which is extracted as the tetrapropylammonium trinitrate complex from an acid-deficient aluminum nitrate salting solution into methyl isobutyl ketone. A direct measurement of the absorbance at 502 mμ of the plutonium complex in the separated organic phase completes the determination. The molar absorptivity of the complex is small, 65.3, and between 2 and 15 mg of plutonium are required for this determination. In the determination of 12.3 mg of plutonium, the coefficient of variation is 0.3 per cent. The method is virtually free of diverse ion interference. Uranium and neptunium are coextracted, but their spectra are sufficiently discrete that no interference is caused in the plutonium determination.[74a]

Spectrophotometric methods have been made far more sensitive by the use of specific color-forming reagents. For example, sodium alizarin sulfonate forms a highly colored complex [86] with Pu(IV) in solutions buffered to pH 3. The molar extinction coefficient was determined to be 9870 when measured at 530 mμ. The reagent is not highly selective, requiring removal of some interfering metal ions by electrolysis into a mercury cathode. Citrate, fluoride, oxalate, and

tartrate cause low results. Over the concentration range from 2.5 to 15 μg of plutonium per milliliter, the coefficient of variation was reported to be 1.84 and 0.46 per cent, respectively.

Thoron (Thorin, Thoronol) also forms a complex [87, 88] with Pu(IV) which is somewhat more intensely colored, having a molar extinction coefficient of 11,000 when measured at 540 mμ. Two methods for determining plutonium are based on this fact. The plutonium, in hydrochloric acid, is reduced to the (III) oxidation state with hydroxylamine and then oxidized to the (IV) oxidation state with sodium nitrite. A solution of the color-forming reagent is then added, and the absorbance is measured at 540 mμ. Thorium, U(IV), zirconium, fluoride, oxalate, phosphate, and large concentrations of sulphate interfere. A coefficient of variation of 1 per cent for a plutonium concentration level of 4μg/ml was reported.[87] Plutonium (III) and (VI) form less intensely colored complexes with the reagent, thereby making it possible to determine the concentrations of the (III), (IV), and (VI) oxidation states in the same solution, providing the sample is in dilute hydrochloric acid. In this case, following adjustment of the acidity to about 0.1*M* in hydrochloric acid, Thorin reagent is added, and the absorbance is measured at 540 mμ. Neglecting the small absorbance of the (III) and (VI) oxidation states at this wave length, this measurement determines the Pu(IV) present in the original sample. The concentration of the (III) oxidation state is determined by treating an aliquot with sodium nitrite, which oxidizes all the (III) to (IV). Following addition of the Thoron reagent, the (IV) state of oxidation is again determined by measuring the absorbance at 540 mμ. The increase shown, if any, must be due to the (III) oxidation state initially present in the sample. The concentration of the (VI) oxidation state is then obtained by determining the total plutonium as described above and subtracting the combined (III) and (IV) concentrations.

A second method [89] employing Thoron as the color reagent is used primarily for determining plutonium in solutions containing interfering ions. The plutonium, in the (IV) oxidation state, is extracted into a solution of a quaternary ammonium base in benzene. The Thoron reagent is added to the organic phase, a dilution is made with alcohol, and the absorbance is measured. In the plutonium concentration range from 4 to 100 μg/ml, no bias was reported, and the coefficient of variation at the 80 μg/ml level was 8 per cent.

The most sensitive reagent discovered [90] so far for the spectrophotometric determination of plutonium is Arsenazo,3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid. The (IV) oxidation state forms a 1:1 complex with the reagent in the pH range 0.95 to 1.35 and has a molar extinction coefficient of 21,000 at a wave length

of 580 mμ, the wave length of maximum absorbance. The molar extinction coefficient is acid dependent at these low pH values but has been found [91] to be essentially independent of acidities in the range from 0.1*M* to 0.4*M* nitric acid. The advantage of using the higher acidity is that interference from U(VI) is virtually eliminated. As in the case of Thoron, the (III) and (VI) oxidation states also form colored complexes with Arsenazo, although with this reagent the molar extinction coefficients are about the same for the colored complexes of all the oxidation states. Optimum conditions for their formation are pH 5.5 to 6.5 for Pu(III) and pH 8.5 to 9.5 for Pu(VI). The wave length of maximum absorption seems to be 590 to 600 mμ. Interferences include chromium, iron, zirconium, uranium, and rare earths.

(d) *Radiochemical Methods.* As has been indicated in Sec. 2–2.3(a), the radioactive property of plutonium affords the most sensitive technique for its qualitative detection and also for its quantitative determination. Remembering that the half life of the 239 isotope is 2.436×10^4 years, it can be calculated that the specific activity is 1.372×10^5 disintegrations/μg/min. If it is assumed, for purposes of calculation, that an acceptable precision for the determination of a small amount of plutonium is 2 per cent at the 95 per cent confidence limit, it would be necessary to register 10,000 counts with an alpha counter. Assuming this is done over a period of 100 min and that the counter has a geometry of exactly 50 per cent, it would be possible to measure 1.46×10^{-9} g of plutonium with the above certainty. In making this calculation, however, it should be clearly indicated that the uncertainty in the measurement is that arising solely from the counting procedure and is inherent in all counting procedures owing to the random nature of radioactive decay.

In actual practice the uncertainties in other parts of the method would be added (statistically) to the above inherent counting uncertainty to arrive at the over-all precision of the method for determining plutonium in a particular sample. This means, of course, that if the over-all uncertainty is to remain at 2 per cent for the 95 per cent confidence limit, the total number of counts to be registered on the counter would need to be in excess of 10,000. Significant steps that contribute to the uncertainty are the efficiency of the chemical separation step, if required, and also that of preparing the plate for counting. In the above calculation, the specific activity of the 239 isotope has been used for simplification. However, in the case of production plutonium, the specific activity is always larger and may be larger by several per cent than that of the 239 isotope, owing to the presence of significant concentrations of isotopes of shorter half lives, particularly Pu^{238} and Pu^{240}.

690–457 O—64——15

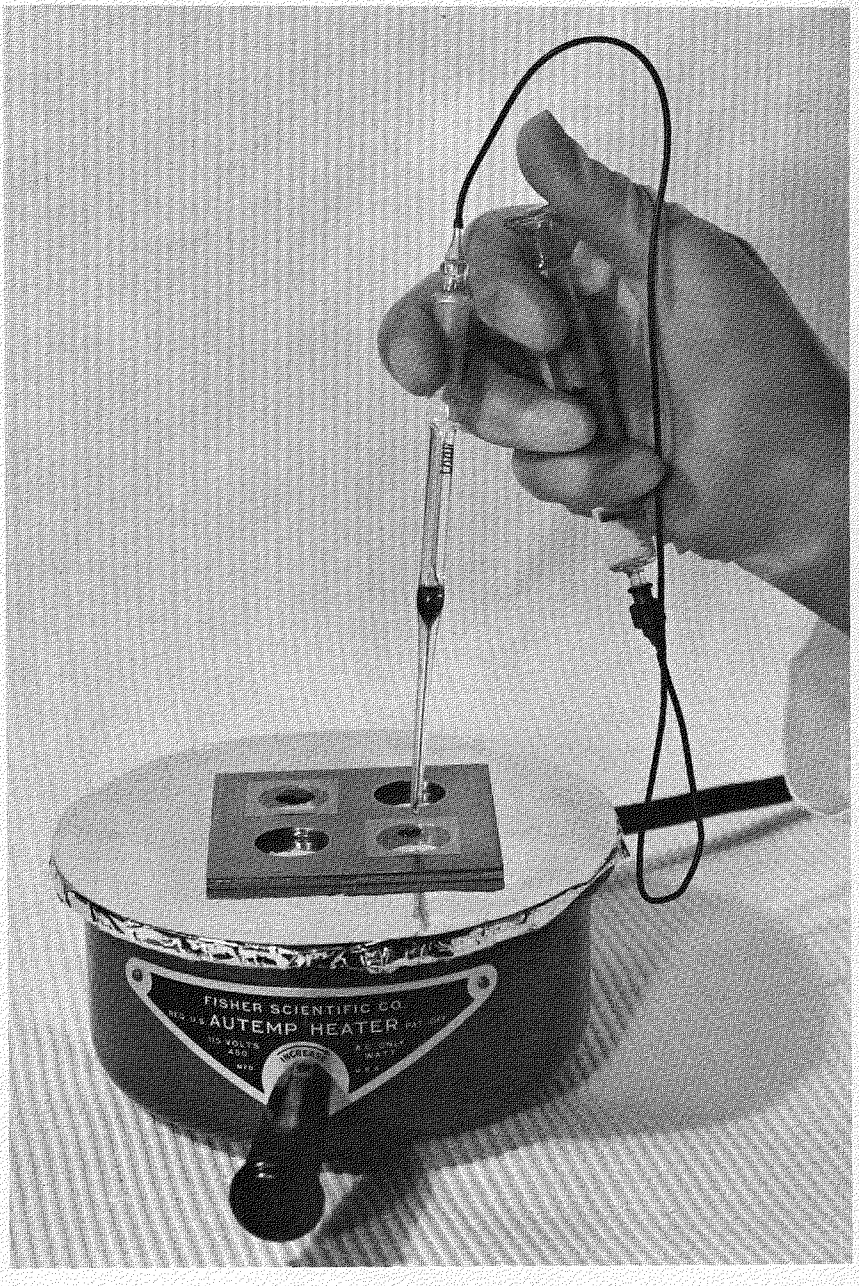


Fig. 2.19—Preparation of samples for radiometric analysis.

Details of counting instruments and equipment are covered in Chap. 14, as are the details of counting techniques and various radiochemical methods of analysis. The remainder of this section will discuss, in a general way, certain radiochemical methods and their important applications.

(1) *Direct Evaporation.* Direct evaporation is a simple procedure designed for the determination of plutonium in "clean" solutions. By clean is meant the absence of other radionuclides and dissolved salts that would interfere in the determination. The size of the aliquot to be used will depend on the concentration of the plutonium present and on the required precision of analysis. Following selection of an aliquot of suitable size, dilution is made, if necessary, to an appropriate volume with $2M$ nitric acid. A selected volume is carefully added to the counting plate with a waxed-tip syringe-controlled calibrated pipet (Fig. 2.19). The counting plate is carefully heated around the edges to prevent the solution from spreading. The pipet is rinsed once with 2 to 3 drops of $2M$ nitric acid, the washing being added to the counting plate. The aliquot on the counting plate is carefully evaporated to dryness without spattering. The plate is held with tweezers and is flamed momentarily over a burner to remove volatile and combustible materials. The plate is then placed in the counting chamber and counted in a suitable manner.

The precision of the direct-evaporation procedure is a function of several parameters, and, in general, it is rather inconclusive to state the precision obtainable over a wide range of conditions. However, the best coefficient of variation from a practical or operating standpoint is probably around 0.5 per cent.

(2) *Coprecipitation.* Coprecipitation applies to a general method of separating the radionuclide of interest from other constituents in the sample, which, if present on the counting plate, will interfere with the accurate measurement of the disintegration rate of the radionuclide. This interference may result from the presence of other radioactive elements or from the presence of dissolved salts in such concentrations as to absorb a significant percentage of alpha particles, thereby causing a negative bias of an unknown and indeterminable amount. The precision obtainable in coprecipitation methods varies greatly with the nature and composition of the sample. Where possible, radioactive tracers are added prior to the separation to establish the percentage of recovery in a particular case. It is never advisable to assume 100 per cent recovery is actually obtained in any separation by a coprecipitation method.

The most widely used coprecipitation, or "carrying," agents for the separation of plutonium from diverse impurities are bismuth phos-

phate, cerium tri- and tetrafluorides, lanthanum hydroxide, and lanthanum trifluoride. Others include zirconium phosphate; thorium pyrophosphate; the oxalates of thorium, U(IV), bismuth, and lanthanum; and the iodates of cerium, thorium, and zirconium.

The choice of coprecipitating agent is usually dependent on the composition of the sample. For example, lanthanum trifluoride is used for removing neptunium, plutonium, or americium in the (III) or (IV) oxidation states from solutions containing fluoride-soluble elements or the noncarrying higher oxidation states of the actinides. Bismuth phosphate is used as a coprecipitating agent for Pu(III) and Pu(IV) from solutions containing high concentrations of aluminum, calcium, and magnesium. However, Am(III) follows along with the plutonium and is not separated. An additional step is required to oxidize the plutonium first to the (VI) oxidation state in which it is not carried (see Chap. 14). Cerium trifluoride (or tetrafluoride) is an excellent coprecipitating agent for the separation of americium and plutonium from solutions containing uranium and lanthanide fission-product elements. Plutonium(III) is carried most efficiently. Lanthanum hydroxide is an efficient coprecipitating agent for removing plutonium in the (III) or (IV) oxidation state from solutions containing elements whose hydroxides are soluble.

Lanthanum Trifluoride. A suitable aliquot of the sample is made 2*M* in nitric acid, and the oxidation state (III or IV) of the plutonium is made certain by the addition of hydroxylamine. A small amount of lanthanum, 0.25 mg, is added in the form of nitrate, and lanthanum trifluoride is precipitated by the addition of hydrofluoric acid. The precipitate, which contains the plutonium, is centrifuged, washed, slurried onto a counting plate as a uniform deposit, flamed, and alpha counted in an approved manner. If necessary, the separation procedure should be repeated to obtain better separation. A correction is always necessary owing to absorption of a fraction of the alpha particles by the lanthanum trifluoride on the counting plate.

Cerium Trifluoride or Tetrafluoride. Cerium trifluoride (or tetrafluoride) is used much like lanthanum trifluoride. It is particularly convenient in separating americium from plutonium in a preliminary step. This is accomplished by adding a small amount of Ce(IV) solution to the hot nitric acid solution of the sample. The Ce(IV) quantitatively oxidizes the plutonium to the (VI) oxidation state. Hydrofluoric acid is then added to precipitate cerium trifluoride. The Am(III) is coprecipitated, and the Pu(VI) remains in solution. The Pu(VI) is then reduced to the (III) oxidation state with hydroxylamine hydrochloride, which also reduces the remaining

Ce(IV) to the very fluoride-insoluble (III) oxidation state. Any Pu(III), and also Np(IV), present are coprecipitated by the cerium trifluoride. The precipitate is transferred to a suitable counting plate and counted in an approved manner. It is necessary to employ a multichannel alpha-energy analyzer to count separately the neptunium and plutonium.

Bismuth Phosphate. Bismuth phosphate is precipitated from a suitable aliquot of the sample by the addition of bismuth nitrate followed by phosphoric acid. The pH of the solution is about 6. The fine, white, heavy precipitate carries Pu(III) and Pu(IV) but not Pu(VI). The plutonium-carrying bismuth phosphate precipitate is centrifuged and dissolved in concentrated hydrochloric acid. The plutonium is then again coprecipitated with lanthanum trifluoride, which is quantitatively transferred to a suitable counting plate, prepared for counting, and counted in an approved manner. Chloride and oxalate interfere and must be removed by preliminary treatment of the sample. Iron and chromium also interfere if present in concentrations greater than 0.3*N*.

If significant amounts of americium are present, it is necessary to make a separation of the two elements. This is accomplished by first dissolving the bismuth phosphate precipitate, which contains Am(III), Pu(III), and Pu(IV), in concentrated hydrochloric acid. Sodium dichromate is added, and the solution is heated to 80 to 90°C for 30 min to oxidize the plutonium to the (VI) oxidation state. The solution is cooled, and lanthanum trifluoride is precipitated as described above. The Pu(VI) is not carried, but the Am(III) is quantitatively removed. If americium is to be determined, the above precipitate is separated, washed, and mounted for alpha counting. Plutonium is determined in the filtrate.

Lanthanum Hydroxide. Lanthanum hydroxide is particularly useful in separating plutonium from solutions containing high concentrations of elements whose hydroxides are soluble. The lanthanum hydroxide is precipitated in the usual manner, following addition of hydroxylamine hydrochloride to ensure that the plutonium is present in the (III) and (IV) oxidation states. However, the hydroxide is not a satisfactory form for counting, primarily because of the difficulties in obtaining suitable reproducibility of the counting plate. For this reason it is always necessary to redissolve the hydroxide and carry the plutonium from solution on lanthanum trifluoride.

(e) *Gravimetric Methods.* The development of gravimetric methods for the determination of plutonium has lagged behind the development of other methods that have been mentioned earlier in this section. This is primarily due to the health hazard involved in the

handling of dry, powdery plutonium oxide or compounds. The danger from dry, powdery solids is greater than from solutions because ingestion into the human system is much easier via the respiratory tract. Although solutions containing plutonium can be safely handled in open front dry boxes, dry, powdery materials must always be handled in glove boxes.

Some of the early work [27, 92, 93] on the stoichiometry of plutonium compounds indicated that anhydrous Pu(IV) sulfate was stable in air and could be weighed as such. Later work involving thermogravimetric studies [94] showed that it was not a suitable weighing form. More recent work [95] of a preliminary nature indicates that Pu(IV) sulfate tetrahydrate is stable over a range of temperatures and humidities and is therefore suitable as a weighing form. This work is being continued.

Plutonium trifluoride has been reported [96] to be a satisfactory weighing form and also suitable as a chemical standard. A limited investigation indicated a plutonium content of 78.5 ± 0.2 per cent, as compared to a stoichiometric percentage of 80.7 for the compound. However, the compound was found to contain 2.3 per cent water when dried at room temperature. Although plutonium trifluoride is a fairly insoluble compound, its actual use as a precipitating form in a gravimetric procedure has not been reported.

Considerable attention has been given to the stoichiometry of plutonium dioxide, primarily for two reasons: (1) If the conditions of its stoichiometry could be established, it might be useful as a primary plutonium standard, and (2) the ignition of most plutonium compounds results in the formation of the dioxide. If stoichiometric and stable, it could be useful as the weighable form for a gravimetric procedure involving a primary precipitation of plutonium as an insoluble compound and subsequent ignition to the dioxide.

It has been reported [93, 97] that the only oxide stable to ignition in air is the dioxide. Other work [27] involving the complete hydrolysis of the tetrafluoride verified the formula PuO_2. Quantitative use of the dioxide ignited to 700 to 900°C has been reported [92, 98-101] for the determination of specific activity of the element. A constant-weight dioxide has been reported [102] from ignition of the nitrate at 1100°C. Assuming the dioxide obtained was stoichiometric, the amount of plutonium found was within 0.2 per cent of the amount taken (in the form of pure metal).

Oxides have been prepared [103] by the individual ignition in air at 870°C of metal, hydride, nitride, carbide, plutonium (III) and (IV) chloride, fluoride, hydroxide, nitrate, oxalate, iodate, and sulfate. The physical and chemical properties of these oxides were found to

depend upon the starting material and temperature of ignition. Oxide produced by the ignition of sulfate at 700 to 1000°C appeared to be nonstoichiometric, and the calculated formula was $PuO_{2.10}$ as compared to the "standard" that was prepared from specially purified plutonium metal. Direct ignition of the metal to oxide at 870°C yielded a product having a composition $PuO_{2.010}$ (σ=0.05 per cent). At any particular temperature between 870 and 1180°C, the weight of the oxide was constant, but, as the temperature was increased in this range, the product lost weight. The weight was reported to be reproducible within ±0.02 per cent after ignition at 1200°C. Hence it was concluded that ignition at 1200°C was necessary to obtain a stoichiometric oxide.

Unpublished and incomplete work [104] using a thermogravimetric balance and large samples (10 g) has indicated that the dioxide slowly loses weight at 1250°C and has an excess of oxygen after 4 hr at this temperature. It would appear from this work that a higher temperature is necessary to obtain a stoichiometric oxide. In support of this statement, brief mention is made by Ferguson et al.[105] of a "crystalline stoichiometric oxide," $PuO_{2.000}$, being prepared at 1600°C upon heating "plutonia" for several days in an argon atmosphere. Details were not given.

At the present time there is no known gravimetric method that is being routinely used for the determination of plutonium. Furthermore, in view of the several excellent methods discussed in earlier paragraphs of this section, there seems to be little need for such a method.

However, the need for a primary chemical standard does exist, and more information is needed concerning the stoichiometry of plutonium compounds before the chemical-standard problem can be solved.

(f) *Polarographic Methods.* Use has been made of square-wave polarography [106] in determining plutonium in the concentration range from 2×10^{-6} to 7.5×10^{-6} moles/liter. The Pu (IV)/(III) couple in nitric or hydrochloric acid is utilized. Nitrite and Fe(III) are known to interfere. This method has not been widely used. Preliminary work [107] has been reported on the determination of plutonium and uranium in the same solution, using a cell with two platinum electrodes. No data are available.

(g) *X-ray Methods.* (1) *Absorption.*[108] In a manner similar to the absorption of visible and ultraviolet light by ionic and molecular species in solution, X rays are also absorbed, although certain basic differences exist. Also, the absorption of X rays as they pass through matter may be used as a basis for measuring the concentration of an element in solution. The absorptive effect on X rays is dependent

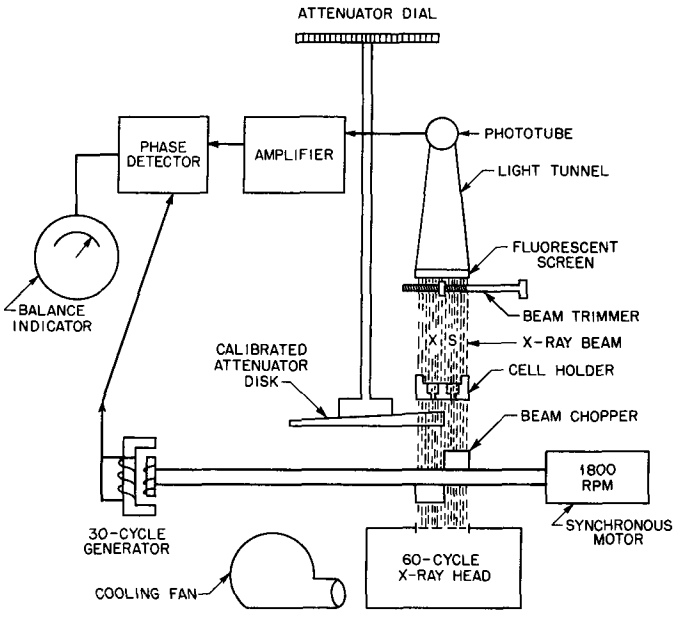


Fig. 2.20—Block diagram of X-ray absorption apparatus (HAPO type).

on the atomic numbers of the elements in the solution traversed and is also proportional to their concentrations. Total X-ray absorption by any particular element is independent of isotopic composition and oxidation state. Because the absorptive effect of any particular element is proportional to the atomic number, a method based on this effect will be the most sensitive for elements of high atomic numbers. Also, because the total absorption is the sum of the absorptions of all ionic species, both anions and cations, certain restrictions are thereby imposed on the nature of the solutions. The major absorbing constituent of the solution being analyzed must be the element in question, or the amounts of the other absorbing constituents must be accurately known so that a correction can be applied.

The instrument that has been developed [108] to the highest state of performance consists essentially of an X-ray incident beam split by a synchronous motor-driven chopper so that its two halves alternately pass through a standard cell (X) and a sample cell (S). The emergent X-ray beams impinge alternately on the left half and right half of a fluorescent screen, as shown in Fig. 2.20. Light from this screen is reflected by the mirror walls of the light tunnel to the phototube. The electrical output of the phototube, the result of alternate signals of emergent X-ray beams from the two cells, X and S, is amplified and fed to the phase detector. A calibrated aluminum wedge attenu-

ator disk may be rotated about its axis in beam X so as to insert a known thickness of aluminum metal in the beam. Relative absorption of the two beams is measured by rotating the disk until the balance meter reads zero, indicating that the beams after passing through X and S are of equal intensity. The absorption of the unknown, then, is equal to that of a certain thickness of aluminum. In addition to the attenuator disk, standard solutions or aluminum blocks of known thickness may be placed in either beam to balance their intensities. This is sometimes referred to as the "aluminum reference method." [108] The "direct comparison method" [108] is another technique in which the total absorptions of the sample solution and of a standard solution of nearly identical concentrations are measured at the same time against the same reference solution. This technique seems to be the most accurate and precise. A third method is referred to as the "crisscross method." In this method an instrument reading is obtained with the sample in one beam and the reference solution in the other; then a second reading is obtained with the sample and reference solutions in switched positions. In more general cases, the crisscross method has been found to give the best precision in routine work.

It perhaps should be repeated that the method measures total absorption of all solutes, solvents, and cell and therefore applies best to routine analysis of samples having fairly constant compositions of impurity ions. Optimum conditions of a 12-cm cell path and a plutonium concentration of 36 g/liter in a solution of known acidity have been established.[108] Under these established conditions, an instrument precision of 0.3 per cent at the 95 per cent confidence limit has been achieved. The method is less time consuming than potentiometric titration techniques. It is obvious, however, that it could not be applied to dissolver solutions of irradiated fuel elements unless a preliminary separation of the plutonium was made.

(2) *X-ray Fluorescence.* A method has been reported [109] for the determination of plutonium in either 1*M* hydrochloric or 1*M* nitric acid solutions. The total sample required is 0.5 ml, containing less than 1 mg of plutonium. The plutonium concentration should be between 2 and $8 \times 10^{-3} M$, and the counting time is that required for 128,000 counts to be registered. Obviously, clean solutions are highly desirable, if not actually necessary, which may require prior separation of the plutonium by any suitable method such as ion exchange, carrier precipitation, or solvent extraction. At the limits of the concentration range stated above, the coefficients of variation of a single measurement are 1.5 and 0.6 per cent, respectively. This, of course, refers to instrument precision. Although apparently not as precise as the X-ray absorption method, it requires a much more dilute solution

of the sample (1 to 2 g/liter), hence making it applicable to concentrations of plutonium found in dissolver solutions of spent uranium fuel elements. Prior separation of the plutonium would, of course, be necessary. Unless the efficiency of the separation of the plutonium from the remaining elements is 100 per cent, the over-all precision of the method would, of course, not be as good as that indicated above. In addition, a bias would be introduced. This method has not been used routinely. It does not appear to have any outstanding advantages.

An X-ray fluorescence method for determining plutonium in solids, liquids, and sludges reportedly applies to plutonium concentrations between 10 ppm and 100 per cent. It is rapid, independent of isotopic concentrations of the plutonium, free from interference by other radioactive materials, and reasonably accurate.[109a] Samples that are difficult to analyze by other methods can be analyzed readily by this method. For determining plutonium at the 88 per cent concentration level, the coefficient of variation is 0.6 per cent; at the 10 to 1820 ppm level, it is about 10 per cent.

Procedure. Solid samples of high plutonium content are dried, ground to a fine powder, and mixed with yttrium, which serves as an internal standard, and an aluminum hydroxide–magnesia matrix mixture. This matrix was chosen for ease of handling and its slow drying property. Sludges having a low plutonium concentration are mixed with only the yttrium internal standard; the sludge serves as the matrix material. Liquid samples are analyzed by adding yttrium in solution form and diluting to appropriate concentration. The samples are placed in plastic holders and analyzed in an X-ray spectrograph equipped with a scintillation counter, a lithium fluoride analyzing crystal, a single-channel pulse-height analyzer, and a molybdenum-target X-ray tube. The tube is operated at 50 kv and 40 ma. The pulse-height analyzer is operated at a base-line voltage of 25 volts and a channel width of 12 volts. The intensities of the fluorescence X-rays from plutonium and yttrium at 2θ angles of 24.90° and 23.75°, respectively, are measured for the samples and corrected for background intensities. The ratio of the corrected intensities is compared to ratios obtained in a similar manner for known samples prepared from plutonium dioxide for high plutonium concentrations, aluminum hydroxide–magnesia matrix with added plutonium for sludges, and plutonium solutions with added yttria.

In another X-ray emission method,[109b] thorium is used as an internal standard in determining plutonium and uranium in refractory oxide mixtures and fused alloys. The refractory materials are fused in a potassium pyrosulfate flux, cooled slowly to form pellets, and the $L\alpha$ X-rays of uranium, plutonium, and thorium are measured. For pure preparations of oxide mixtures, the thorium internal standard is omitted and the plutonium to uranium intensity ratio is measured. The coefficient of variation in determining each element is 3.2 per cent,

but this can be reduced to 0.9 per cent by polishing the pellets prior to analysis.

The X-ray spectrograph used in these determinations consists of a lithium fluoride analyzing crystal, a tungsten-target X-ray tube operated at 50 kv and 35 ma, a scintillation counter, a pulse-height analyzer, and a scaler. The sample-holder compartment is enclosed in a glove box to contain the radioactive material in the event a sample is spilled.

Procedure. A sample containing between 20 and 30 mg of uranium and 1 to 10 mg of plutonium is mixed with 40 mg of thorium and 10.0 g of potassium pyrosulfate and fused at 450°C for 2 hr, or until the melt becomes clear. The melt is allowed to cool to room temperature very slowly, usually overnight, and the pellet formed is polished with fine sandpaper. The polished pellet is placed in a sample holder having a Mylar window and then into the X-ray spectrograph. The intensities of the $L\alpha_1$ X rays are measured at 24.90° for plutonium, 26.15° for uranium, and 27.46° for thorium, and an appropriate background intensity is subtracted from each. The background correction is calculated from measured intensities at 29.18° and 24.18°, assuming that the background variation is linear in this range. The fixed-count technique and a minimum of 128,000 counts for measurement of each element in the sample is recommended. Ratios of the intensities of the X rays from plutonium and uranium relative to the thorium X ray and of the plutonium X ray relative to the uranium X ray are calculated and compared to similar ratios obtained for known samples. Generally, the intensity ratios for the known samples are plotted as functions of the weight ratios for each two metals to prepare calibration curves. From these curves the weight ratios, corresponding to the intensity ratios calculated for each sample, are obtained. The quantity of uranium and plutonium is calculated from the respective weight ratio and the known quantity of thorium added. For mixtures of pure uranium oxide and plutonium oxide, the sample is heated to 850°C in air to ensure that all the uranium is oxidized to U_3O_8. The oxides are cooled, weighed, and fused with potassium pyrosulfate, but no thorium is added. The pellet is polished, and the ratio of the intensities of the $L\alpha_1$ X ray of plutonium to the $L\alpha_1$ X ray of uranium, each corrected for background intensity, is obtained as described above. The weight ratio of plutonium to uranium is obtained from a calibration curve prepared from data for known samples. The plutonium and uranium concentrations are calculated from the weight ratio, the known formulas for the respective oxides, and the sample weight.

(3) *Electron-microprobe X-Ray Fluorescence Methods.* The electron-microprobe X-ray analyzer recently has been applied to the chemical analysis of plutonium-containing materials.[109c-109f] Semiquantitative determination of most elements of atomic number greater than about 12 is possible. The surface area of the sample examined is of the order of 1 to 3 μ in diameter. A metallographically polished specimen is required. The specimen is coated with a thin film of

Formvar plastic or ultrasonically cleaned in methyl chloroform until no loose radioactive particles are removed when the sample is wiped lightly with a tissue. This instrument has been applied to the examination of several reactor fuel materials including various plutonium–iron alloys and uranium–plutonium dioxides.

(h) *Emission Spectrographic Methods.* Emission spectrographic methods have found very limited application in the determination of plutonium in any kind of material. This is probably a result of the relatively poor precision of such methods and also of the simplicity, rapidity, and general applicability of radiochemical methods.

However, in solids containing plutonium dioxide in the concentration range of 0.5 to 100 per cent, it has been reported [110] that plutonium can be determined by an iron-flux technique in which the sample is diluted with at least a 10-fold excess of a flux consisting of equal amounts of anhydrous ferric sulfate and ammonium sulfate. The prepared sample is excited on a copper electrode in a d-c arc. The iron is used as an internal standard. At 50 per cent concentration of plutonium dioxide in the sample, the coefficient of variation was reported to be 6.6 per cent. The method has no inherent advantage at such high concentration levels of plutonium. In fact, the only value of emission spectrographic methods now in existence lies in the identification of the element and the determination of trace impurities therein.

2–2.6 Determination of Impurities in Plutonium

Because traces of some impurities cause significant changes in the physical and nuclear properties of plutonium or have a deleterious effect on container materials for plutonium reactor fuels, determination of trace concentrations of several elements in plutonium is required. Of course, existing methods for the determination of each foreign element are used wherever possible. In other cases, modifications of existing methods or new methods are developed for specific analyses. At the present time methods are available for determining most of the known elements in plutonium. Of these methods the determinations of only the impurity elements that affect the use of plutonium as a nuclear fuel are included here.

(a) *Spectrochemical Methods.* Many of the impurity elements may be determined spectrographically, but the line-rich spectrum of plutonium makes it necessary that the plutonium spectrum be suppressed, either by use of a carrier-distillation technique or by removal of most of the plutonium by chemical means. A much less sensitive technique does not require separation but depends for its success upon limiting the quantity of plutonium on an electrode to 50 μg. This technique,

identified as the direct copper-spark technique, is not recommended for high-purity plutonium. More-detailed descriptions of these various spectrochemical techniques are given in Chap. 12. In the direct copper-spark technique,[37, 111] the sample is dissolved and converted to the sulfate by evaporation to fumes with sulfuric acid. Following proper dilution a known volume is evaporated on a copper electrode and excited using an a-c spark discharge. Plutonium serves as an internal standard. The line-rich plutonium spectrum limits the amount of plutonium on the electrode to 50 μg and thus limits the sensitivity of the direct copper-spark method, as shown in Table 2.12.

Carrier-distillation methods, in which the added carrier suppresses the plutonium spectrum and carries the impurities into the excitation zone, are quite sensitive for most impurity elements. (See Table 2.12). Either gallium sesquioxide at a concentration of 4 percent relative to the plutonium oxide [37] or sodium fluoride [112] are effective carriers. In the method using gallium oxide as a carrier, the plutonium sample is ignited in air, and a weighed portion of the oxide is mixed intimately by grinding with 4 wt. % gallium sesquioxide. One hundred milligrams of the mixture is weighed into a cratered graphite electrode and excited in a d-c arc. Standards prepared with a plutonium dioxide matrix and containing impurity elements in the appropriate concentration ranges are excited similarly to the samples, and their spectra are photographed on the same plate for comparison with the spectra from the samples. Limits of detection of some elements are given in Table 2.12.

The method in which sodium fluoride is used as the carrier is similar to the procedure described above. This method has been combined with the direct-spark technique [112] to lower the limits of detection of some elements without sacrificing the speed of the direct-spark method. In this combined procedure, 0.5 mg of plutonium in nitrate solution is added to 0.8 mg of sodium fluoride in a cratered graphite electrode and evaporated to dryness. During excitation with an a-c arc, the sodium fluoride quenches the plutonium spectrum and thus increases the sensitivity as compared to the direct-spark method (see Table 2.12). However, the small sample size limits the sensitivity of this method for most elements as compared to the gallium sesquioxide carrier-distillation method or to methods involving separation of the plutonium from the impurities.

Methods of greatest importance in separating impurities from plutonium are given in Table 2.13. After separation, the impurity elements are determined using d-c arc excitation or the copper-spark technique.[114, 115] Limits of detection for a few elements are given in Table 2.12.

In addition to the spectrochemical determinations of several impurity elements simultaneously, methods have been developed for the determination of specific elements or groups of elements. Included

Table 2.12—DETECTION LIMITS OF IMPURITIES IN PLUTONIUM [43, 111, 113]

Element	Detection limit by various methods, ppm				
	Direct copper spark (50-μg sample)*	Direct spark–NaF (0.5-mg sample)*	Ga_2O_3 carrier distillation (100-mg sample)*	Cupferron extraction (300-mg sample)	Ion exchange–copper spark (200-mg sample)
Ag	300	10	1	----	----
Al	----	25	20	5	----
As	----	2000	10	----	----
Au	----	200	----	----	----
B	300	25	0.1	----	5
Ba	200	25	5	20	----
Be	200	4	0.1	0.1	0.02
Bi	----	----	0.5	----	----
Ca	200	25	----	3	5
Cd	----	----	10	20	----
Co	----	1000	5	10	----
Cr	300	25	5	2	----
Cu	300	25	5	----	----
Fe	300	50	5	----	----
Hg	----	----	5	----	----
K	----	----	----	50	1
La	----	2000	----	10	----
Li	----	----	0.1	0.1	0.01
Mg	300	25	2	3	----
Mn	----	25	----	0.5	----
Mo	----	25	20	----	----
Na	----	----	1	5	10
Ni	100	25	2	2	----
Pb	300	50	1	2	----
Sb	----	1000	10	----	----
Si	300	----	5	----	----
Sn	----	25	1	----	----
Sr	200	----	10	10	----
Ti	200	200	50	----	----
V	----	50	20	----	----
Zn	200	----	50	50	----
Zr	100	2000	----	----	----

*Sample weight actually placed on the electrode.

Table 2.13—SEPARATION METHODS USED IN SPECTROCHEMICAL DETERMINATIONS OF IMPURITIES IN PLUTONIUM

Type of separation	Plutonium species involved	Medium	Reference
Extraction	Pu cupferrate	Ether-chloroform or trichloroethylene.	47
	Pu(IV)-TTA	Benzene or xylene	116
	Pu(VI) nitrate	Hexone	116
Ion exchange	$Pu(NO_3)_6^{-2}$ in 7 to 10*M* HNO_3.	Dowex-1 anion-exchange resin.	41, 42
	$PuCl_6^{-2}$ in 12*M* HCl.	Dowex-1 anion-exchange resin.	40
	$PuCl_6^{-2}$ in 12*M* HCl-1*M* HNO_3.	Dowex-1 anion-exchange resin.	43

are special procedures for determining boron, phosphorous, cerium, lanthanum, and zirconium. In the method for determining boron and phosphorous in plutonium,[117] the plutonium sample, uranium, and gallium are mixed as their nitrate solutions to provide final weight ratios of 5 : 14 : 1 (25, 70, and 5 per cent), respectively, for the three metals. An aliquot containing a total of 10 mg of the metals is dried, and the residue is converted to the oxides, which are excited in a cratered electrode. In a comparison of gallium sesquioxide, ammonium and sodium fluorides, and silver chloride as carriers, gallium sesquioxide was the most effective in reducing the uranium background spectra, and the fluorides were the least effective. The method is sensitive to 1 ppm of boron and 200 ppm of phosphorous, and the coefficient of variation is 9 per cent for a single determination.

For determining cerium and lanthanum in plutonium,[118] europium carrier is added, the plutonium is oxidized in fuming perchloric acid, and the rare earths are precipitated as the fluorides leaving Pu(VI) in solution. The fluoride precipitate is fumed with perchloric acid and dissolved in hydrochloric acid, and an aliquot of the solution is evaporated on a copper electrode and excited in an a-c spark discharge. The coefficient of variation of the method is 10 per cent for a single determination.

In the spectrochemical determination of zirconium in plutonium, the anion nitrate complex of plutonium is absorbed on Dowex-1, and the zirconium in the effluent is determined by graphite spark excitation using cobalt as an internal standard. The coefficient of variation of a single determination is 8.5 per cent, and concentrations greater than 20 ppm can be determined.[119]

(b) *Spectrophotometric Methods.* An impressive number of spectrophotometric methods have been developed for the determination of trace concentrations of a significant number of impurity elements in plutonium. The broad applicability of spectrophotometry lies in the ease with which plutonium can be tightly complexed into a noninterfering state and also in the ease with which it can be separated from a large number of impurity elements. From the many spectrophotometric methods in existence, several have been selected for discussion here.

(1) *Boron.* Boron in plutonium is determined using the curcumin color reaction in a modification of Naftel's spectrophotometric method.[120] Isolation of the boron is accomplished by distillation as methyl borate from a hydrochloric, nitric, or sulfuric acid solution of the plutonium containing less than 2 millimoles of free nitric or hydrochloric acid.[121] In another modification, plutonium is first removed by precipitation as the oxalate.[122, 123] The boron-curcumin color is developed at 55°C in the presence of accurately measured quantities of calcium hydroxide, oxalic acid, hydrochloric acid, and 0.1 per cent curcumin in alcohol. The color is extracted into ethanol, and the absorbance is measured at a wave length of 540 mμ. The coefficient of variation of these methods is about 5 per cent for 0.1 to 0.5 μg of boron.

(2) *Cerium.* Cerium is separated by oxidizing the plutonium to the (VI) oxidation state with argentic ion and precipitating the Ce(IV) along with lanthanum carrier as the fluorides. After centrifuging, the precipitate is dissolved by heating with sulfuric acid, the cerium is reoxidized by argentic ion, and the absorbance of the Ce(IV) is measured at a wave length of 320 mμ. To obtain a reliable blank the Ce(IV) is reduced with hydrogen peroxide, and the absorbance is remeasured. For 0.01 and 0.3 wt. % cerium in plutonium, the coefficients of variation are 5 and 1 per cent, respectively.[124] Large concentrations of chloride and ruthenium interfere with the determination and are removed by evaporation to fumes with perchloric acid.

Following a preliminary separation by precipitation as the fluorides, as described above, cerium and other rare-earth elements, collectively, are precipitated as the oxinates, which are dissolved in hydrochloric acid and measured spectrophotometrically.[125] More details of this procedure are given in the section on *Lanthanum.*

(3) *Chromium.* Chromium is conveniently separated from 10 mg of plutonium by precipitating the latter as the hydroxide from 10 ml of weakly basic solution containing hydrogen peroxide to oxidize the chromium to the hydroxide-soluble (VI) oxidation state.[126] After

warming and centrifuging, the chromium in the supernatant solution is determined either by measuring the absorbance of the chromate ion at a wave length of 370 mμ or by using diphenylcarbazide as a colorimetric reagent. The first spectrophotometric method is applicable for determining 0.01 to 0.10 mg of chromium per 10 mg of plutonium (0.1 to 1 per cent chromium). In the diphenylcarbazide spectrophotometric method, which is used for chromium concentrations between 10 and 1000 ppm, an aliquot of the supernatant solution, following precipitation of the plutonium, is brought to 0.2*M* acidity by adding sulfuric acid, and the diphenylcarbazide color is developed. Measurement of the absorbance at 540 mμ permits estimation of 0.1 μg (10 ppm of chromium) with a coefficient of variation of about 29 per cent. Over the range of chromium concentrations between 40 ppm to 1 per cent, the coefficients of variation range from 7 to 1 per cent when the appropriate spectrophotometric method is used. Of twenty-six foreign ions tested, only uranium causes interference if the absorbance of the chromate ion is measured, and phosphate interferes in the diphenylcarbazide method.

In an alternate method for determining chromium as the diphenylcarbazide,[127] the plutonium sample in hydrochloric acid solution is oxidized with bromine, and the Pu(IV) is complexed with cupferron, using an ethereal solution of the reagent, and extracted as the cupferrate into chloroform. The organic phase is evaporated, and the residual organic material and the chromium are oxidized with ammonium peroxy disulfate. An acid solution of diphenylcarbazide is added to develop the color. Ions interfering in this determination were not listed.

(4) *Fluoride.* Low concentrations of fluoride in plutonium are determined either by microtitration with a standard thorium solution [128, 129] or by a spectrophotometric procedure.[129a] For the spectrophotometric determination, a sample containing 0.25 to 2.5 μg of fluoride is dissolved in perchloric acid, and the fluoride is distilled as fluosilicic acid. Reaction of the fluoride with the zirconium salt of *p*-dimethylaminoazophenylarsonic acid liberates the free acid, which is dissolved in a mixture of acetone and hydrochloric acid and measured spectrophotometrically at a wave length of 500 mμ. For the determination of 0.5, 1.5, and 2.0 μg of fluoride in 50 mg of plutonium, the coefficients of variation of this method are about 8, 6, and 12 per cent, respectively.

In addition to the spectrophotometric method, several microtitration methods for fluoride are used. In one method a plutonium sample containing less than 10 μg of fluoride is dissolved in dilute sulfuric acid, and about 90 per cent of the plutonium is precipitated by increasing

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the sulfuric acid concentration to between 5*M* and 5.5*M*. The fluoride in the supernatant solution is separated by distillation at 135°C in an all-glass still and titrated at pH 3.4 with 0.001*M* thorium nitrate solution, using Chrome Azurol S indicator. For fluoride concentrations of 5 to 30 ppm, the coefficient of variation of the method is about 10 per cent.[128] Fluoride in plutonium fluorides has also been determined by a similar procedure in which the fluoride is distilled from 12*M* sulfuric acid and titrated at pH 3.05 with standard thorium solution to an Alizarin Red S end point. In determining 1 to 4 mg of fluoride, the coefficient of variation is 2.0 per cent.[130]

Separation of microconcentrations of fluoride can also be accomplished by pyrolysis of the sample at 1000°C in moist air or steam. The fluoride is then determined by titration with standard alkali solution.[131]

(5) *Iron.* The usual color reagents, *o*-phenanthroline or α,α′-dipyridyl, are employed in the spectrophotometric determination of iron. For low concentrations of iron, separation from plutonium is necessary for good accuracy. If the iron concentration is high enough to permit the use of samples containing less than 1 mg of plutonium, no separation is required. In the latter case, the iron and plutonium in hydrochloric acid solution are reduced with hydroxylamine, the pH is adjusted to 3 to 9 with a sodium acetate buffer, and the Fe(II)-*o*-phenanthrolate color is developed during a 30-min period. The absorbance is measured [132] at a wave length of 515 mμ.

For the separation from plutonium, either extraction of Fe(III) into a carbon tetrachloride-dichloroethylether mixture from 7*M* hydrochloric acid [133] or precipitation of plutonium as the oxalate is satisfactory.[134] Extraction of Fe(II)-dipyridyl into chloroform from an acetate-buffered aqueous phase containing sodium alkyl sulfonate, and measurement of the absorbance of the extract has also been reported for the determination of iron.[135] Of these separation methods, extraction of Fe(III) into the mixed solvent has the advantage of not requiring reduction of the iron. Following extraction of the Fe(III), it is reduced and back-extracted by contacting the organic phase with an aqueous solution containing reductant, buffer, and *o*-phenanthroline. The absorbance of the aqueous phase is measured at a wave length of 515 mμ. For the determination of 5 to 50 μg of iron in 50 mg of plutonium, the coefficient of variation of the method is 2.4 per cent.

(6) *Lanthanum.* No specific spectrophotometric method for determining lanthanum exists, and this element is normally determined in mixtures of other rare earths by the spectrochemical method described in Sec. 2–2.6(a). A method for determining combined rare earths has been applied to samples of plutonium containing only lanthanum.[125]

In this method the plutonium is oxidized by fuming perchloric acid or by argentic ion, and the lanthanum is precipitated as the fluoride. Following dissolution of the precipitate in hot perchloric acid, the lanthanum is precipitated as the oxinate, which is then dissolved in 0.1*M* hydrochloric acid. The absorbance of the resulting solution is measured at 365 mμ. Other rare-earth elements, the higher actinides, and thorium are among the interfering ions. This method is applicable for determining 25 to 1000 μg (0.05 to 2.0 per cent) of lanthanum with coefficients of variation of 8 to 1.5 per cent, respectively.

(7) *Molybdenum.* Several spectrophotometric methods for the determination of molybdenum in plutonium have been developed. In one of these methods, 10 to 100 μg of molybdenum is separated by extraction into 4-methyl-2-pentanone from a 6*M* hydrochloric–0.4*M* hydrofluoric acid solution of the plutonium. Back-extraction of the molybdenum into water and precipitation of any iron as the hydroxide completes the separation from most foreign metals. The filtrate is evaporated to dryness, and the molybdenum is dissolved in 1.4*M* hydrochloric acid and reacted with chloranilic acid. The absorbance of the chloranilate is measured at a wave length of 350 mμ. The coefficient of variation of the method is less than 2 per cent, and tin, tungsten, and bismuth are the only foreign metals that cause serious interference.[136]

Molybdenum can be determined also by the usual thiocyanate spectrophotometric method in which 5 to 50 μg of molybdenum is extracted as the thiocyanate into *n*-butylacetate from approximately 2*M* sulfuric acid solution containing Sn(II) chloride. Following centrifuging of the extract, its absorbance is measured at a wave length of 470 mμ. The coefficient of variation of the method is about 3 per cent.[137] At least one other modification of the thiocyanate method for determining molybdenum has been reported.[138]

A modification of a method proposed first by Miller [139] and later by Greenberg,[140] in which Mo(VI) is extracted as the dithiol complex into *n*-amyl acetate from 5*M* hydrochloric acid, is a very rapid procedure for determining molybdenum. The absorbance of the extract is measured at a wave length of 685 mμ. For the determination 5 to 50 μg of molybdenum in 1 g of plutonium, the coefficients of variation are 3.5 and 1.5 per cent, respectively.[141] Following extraction of the molybdenum, tungsten in the aqueous phase can also be determined by extracting as the W(V) dithiol complex into *n*-amyl acetate at 80 to 90°C and measuring the absorbance of the extract at 640 mμ. For satisfactory extractions, the aqueous phase is 10*M* to 11*M* in hydrochloric acid and contains Ti(III) chloride to reduce the tungsten to the (V) oxidation state. Coefficients of variation of 3.0 and 1.4 per

cent for determining 10 and 120 μg of tungsten in 1 g of plutonium were reported.[141]

(8) *Nickel.* The spectrophotometric methods for determining this element are based upon the color formed with dimethylglyoxime or with α-furildioxime. The nickel must be separated from plutonium, and in one method [142] this is accomplished by precipitating plutonium iodate from 1.5*M* hydrochloric–0.1*M* potassium iodate solution. The nickel in the supernatant solution is oxidized with bromine and then reacted with dimethylglyoxime in a weakly basic ammoniacal solution. The absorbance of the solution at a wave length of 534 mμ is measured immediately. Using a 40-mg sample, coefficients of variation of a single determination of 0.010 and 0.160 per cent nickel are 10 and 1 per cent, respectively. Twenty parts per million of nickel can be detected by this method. Copper, cobalt, and manganese are among the interfering metals.

A cation-exchange method is also used in separating microgram quantities of nickel from milligram quantities of plutonium.[143] The sample, in hydrochloric acid, is loaded onto Amberlite–IR–120 30- to 60-mesh cation-exchange resin in the hydrogen form. The nickel is eluted with potassium cyanide or 1.0*M* hydrochloric acid, the latter eluant being preferred. The normal dimethylglyoxime method for the spectrophotometric determination of nickel is then applied. The precision of the method and the effects of other ions on the determination were not stated in the original report.

In the determination of nickel using α-furildioxime [144, 145] as the color reagent, the sample is dissolved in hydrochloric or sulfuric acid, and an aliquot containing between 1 and 20 μg of nickel is taken for analysis. One drop of 1*N* potassium dichromate solution is added to oxidize any Fe(II) present, and sodium citrate is added to complex plutonium, Fe(III), and uranium. Nickel is then extracted as the α-furildioxime complex from ammoniacal solution into chloroform, and the absorbance of the extract is measured immediately at a wave length of 435 mμ. Alkali-metal salt concentrations above 0.1*M* interfere in this determination.

(9) *Phosphorous.* In addition to the spectrochemical method discussed in Sec. 2–2.6(a), a modification of the molybdophosphate spectrophotometric procedure is used for determining phosphorous.[146] Following dissolution of the sample in nitric and hydrochloric acids and fuming with hydrofluoric and sulfuric acids to volatilize any silicon present, an aliquot containing between 0.5 and 5.0 μg of phosphorous is treated with ammonium molybdate, and the molybdophosphate is extracted into *n*-butanol. Tin(II) chloride is added, and the absorbance of the reduced complex is measured at a wave length of 730

mμ. The coefficient of variation is 2.5 per cent for determining less than 4 μg of phosphorous in 50 mg of plutonium. Arsenic interferes with this determination. Other modifications of this method have been used for determining phosphorous in plutonium.[147]

(10) *Rhodium and Platinum.* Rhodium and platinum are determined simultaneously without separation from plutonium by a modification of the spectrophotometric method reported by Ayres, Tuffly, and Forrester.[148] In the modified method [149] an aliquot of the sample containing not more than a total of 200 μg of both noble metals in hydrochloric acid is reduced with Sn(II) at 95°C. After the solution has been cooled, the absorbances of the reduced platinum and rhodium-chloro complexes are measured at wave lengths of 399 and 470 mμ, respectively. The contributions of Pu(III) to the absorbances at these wave lengths are corrected for by measuring its absorbance at 665 mμ, which is directly related to its absorbances at 399 and 470 mμ; correction factors are then calculated using empirically determined equations. Ruthenium, palladium, osmium, gold, and chromium interfere with these determinations. For concentrations of rhodium and platinum from 5 to 14 ppm, the coefficient of variation of the method is 2 per cent. In applying the method for determining the concentrations of rhodium and platinum in plutonium ternary alloys, the sealed-tube method is required for dissolving the samples (see Sec. 2–3.1), and the coefficient of variation is reduced to about 1 per cent.

(11) *Silicon.* For the determination of microgram quantities of silicon in plutonium and its alloys, separation of the silicon is usually required. One of the cleanest separations for quantities not greater than 50 μg of silicon is effected by distillation as silicon tetrafluoride from perchloric-nitric-hydrofluoric acid solution in an all-platinum still.[150] The silicon tetrafluoride is trapped in a solution of boric and molybdic acids, and the molybdenum blue color is developed and measured at a wave length of 815 mμ. For the determination of 5 and 32 μg of silicon in 0.3 g of plutonium, the reported coefficients of variation are 16 and 2.5 per cent, respectively.

Silicon can be determined by a molybdenum blue method similar to the procedure described in (9) for determining phosphorous. Ammonium molybdate and sodium sulfite are added to a 2*M* hydrochloric acid solution of the sample, and the silicomolybdate complex is reduced by ascorbic acid and extracted into *n*-butanol.[151] The extract is washed with 0.5*M* hydrochloric acid, and the absorbance is measured at 815 to 825 mμ (using 608 Ilford filters). Another application of the molybdenum blue method includes separation of the plutonium as the insoluble fluoride.[152] The sample is dissolved in hydrochloric acid, and hydrofluoric acid is added to activate the silicon and to pre-

cipitate the plutonium. Aluminum chloride is added to the supernatant solution to complex excess fluoride, the pH is adjusted to 0.6 using ammonium hydroxide, and ammonium molybdate is added. The silicomolybdate complex is reduced by 1-amino-2-naphthol-4-sulfonic acid in the presence of tartaric acid and sulfite ion, and the absorbance is measured at a wave length of 825 mμ. Phosphorous, germanium, arsenic, chromium, iron, and nickel interfere. The reported coefficients of variation for determining 22 and 110 ppm of silicon in plutonium were 9.1 to 4.4 per cent, respectively.

(12) *Sulfur.* In the most frequently used method for the determination of sulfur,[134] the plutonium sample, containing 5 to 25 μg of sulfur, is dissolved in hydrochloric acid, and the sulfur is distilled as hydrogen sulfide and absorbed in zinc acetate solution. Addition of Fe(III) chloride and *p*-amino dimethylaniline and digestion at 25°C develops the methylene blue color, which is measured spectrophotometrically. In a recent revision of this method,[153] the sample in the distilling flask is treated with hydriodic and hypophosphorous acids to ensure reduction of sulfur compounds. After distillation as hydrogen sulfide into a zinc acetate trap, *p*-phenylenediamine, Fe(III) chloride, and hydrochloric acid are added to form Lauth violet by reacting with the sulfide. After 1 hr, the absorbance is measured at a wave length of 595 mμ. For the determination of 20 to 50 μg of sulfur in a maximum of 500 mg of plutonium, the coefficient of variation of the method is 2 per cent. For determining 5 μg of sulfur in 500 mg of plutonium, the coefficient of variation is 4 per cent. Separation of the plutonium by absorption on cation-exchange resin and formation of a barium sulfate suspension, which is measured with a spectrophotometer, has also been reported recently as a method for determining sulfur.[154]

(13) *Zirconium.* For the determination of trace concentrations of zirconium, a spectrophotometric method is generally used. A plutonium sample size is selected to contain between 15 and 100 μg of zirconium. The zirconium precipitates as the *p*-bromomandelate from dilute hydrochloric acid containing hydroxylamine as a holding reductant for Pu(III). The precipitate, which is too small to be weighed conveniently, is heated with nitric and perchloric acids to destroy the organic material, and the zirconium is reacted with chloranilic acid in 1.4*M* perchloric acid. The absorbance of the zirconium chloranilate is measured [155] at a wave length of 350 mμ. A recovery of 98.4 per cent of between 25 and 100 μg of zirconium and a coefficient of variation of 3.4 per cent were reported for this determination. Of 23 foreign ions tested, only hafnium and fluoride interfere. Larger quantities of zirconium in plutonium can be determined gravimetrically as the *p*-bromomandelate.[156]

Absorption of Pu(IV) onto Dowex-1 anion-exchange resin from 10*M* nitric acid also serves to separate plutonium from zirconium, which is not absorbed. The acidity of the effluent solution is adjusted to 0.1*M*, and the zirconium is reacted with Alizarin Red S and determined [157] spectrophotometrically at a wave length of 520 mμ. Hydrofluoric and sulfuric acids interfere in this determination. The method is recommended for quantities of zirconium between 40 and 100 μg. Coefficients of variation in this concentration range were reported to vary between 5 and 3 per cent.

(c) *Radiochemical Methods.* Methods for the radiochemical determination of radioactive isotopes of many elements in plutonium have been developed. Procedures for determining over forty of these isotopes, individually or in combinations, have been compiled in a recent report,[158] and other reviews or manuals of this type are available.[159–161] In addition, methods for determining major long-lived fission-product elements in irradiated plutonium-rich reactor fuels have been described.[113] Many of these methods are also applicable to the analysis of expended uranium-rich reactor fuel and are discussed in Chap. 6, entitled "Expended Reactor Fuels." They are also generally applicable to the radiochemical determination of the isotopes in various materials and therefore are discussed in Chap. 14, entitled "Radiochemical Methods." To prevent duplication, the radiochemical methods for determining only the radioactive isotopes that are commonly found in "product" plutonium and affect the radioactive properties of plutonium-rich fuels prior to their irradiation are within the scope of this chapter. Americium and neptunium fall in this category.

(1) *Americium.* Because of its relatively short half life of 470 years, Am^{241}, the most abundant isotope of americium, interferes with the direct radiochemical estimation of plutonium by alpha counting and must be determined if the plutonium results are to be corrected. This determination is accomplished by gamma counting without separation from the plutonium or by alpha pulse analysis.[162] When gamma counting is used as a means for determining americium with only those gamma rays with energies about 30 kv counted in a well scintillation detector, Am^{241} has a specific activity of 2.2×10^6 counts/min/μg as compared to 75 counts/min/μg for Pu^{239}. Therefore, concentrations as low as 5 ppm of americium in plutonium may be determined. The coefficient of variation is 2 per cent for determining 50 ppm of americium in a 10-μg sample.

If alpha-energy analysis is to be used in determining the americium, the americium must be separated from Pu^{238}. This is accomplished by oxidizing the latter to the (VI) oxidation state with Ce(IV) and then precipitating Am(III) fluoride using Ce(III) as the carrier.

The precipitate is washed repeatedly with nitric and hydrofluoric acids and dissolved by adding zirconyl ion, and the americium is reprecipitated as the fluoride. The final precipitate is transferred as a slurry to a counting plate and dried, and the alpha energy is analyzed.[163, 164] When this method is used for determining trace concentrations of americium in plutonium, the precision is reported to be 2.2 per cent at the 99 per cent confidence limits.

Americium can also be separated by ion-exchange techniques,[165, 166] by solvent-extraction methods,[163, 167] or by precipitation of only Pu(IV) on zirconium phenylarsonate.[168] Various chemical methods also exist for determining americium, but the radiochemical methods are generally preferred.

(2) *Neptunium.* Because of the low specific activity of 1.40×10^3 disintegrations/μg/min for Np^{237}, it is usually separated from plutonium before it is counted. Oxidation of the neptunium with potassium bromate in 0.5*M* to 3*M* sulfuric acid and coprecipitation of the unoxidized plutonium with lanthanum fluoride has been used for this separation, but yields are low. Separation by anion-exchange methods are more favorable. By absorbing Np(IV) on Dowex-1x4 (100- to 200-mesh) anion-exchange resin from 8*M* nitric acid containing Fe(II) sulfamate and semicarbazide and eluting the neptunium with 0.005*M* Ce(IV) sulfate in 0.25*M* nitric acid, recoveries of 95 per cent are obtained. An aliquot of the eluate is evaporated on a counting plate for total alpha counting, alpha-energy analysis, and gamma-energy analysis.[169]

Liquid-liquid extraction methods appear to be the most rapid and reliable. In one excellent procedure,[49] Np(IV) is extracted into thenoyltrifluoroacetone from 1*M* hydrochloric acid solution containing hydroxylamine and potassium iodide or Fe(II) to keep plutonium in the nonextractable (III) oxidation state. The neptunium is back extracted into 10*M* nitric acid, and an aliquot is taken for alpha counting of Np^{237} or gamma counting of Np^{239}. Greater than 99 per cent of the neptunium is recovered.

In an alternate method,[170] Np(IV) is extracted from 12*M* hydrochloric acid containing 0.1*M* hydroquinone and 0.1*M* potassium iodide into 0.48*F* mono(2-ethylhexyl)orthophosphoric acid in toluene. Plutonium(III) and americium(III) remain in the aqueous phase. The extract is washed repeatedly with 12*M* hydrochloric acid–0.1*M* hydroquinone, and then an aliquot of the organic phase is prepared for counting. The reported over-all precision is 10 per cent. Concentrations at least as low as 1 ppm of neptunium in plutonium can be measured.

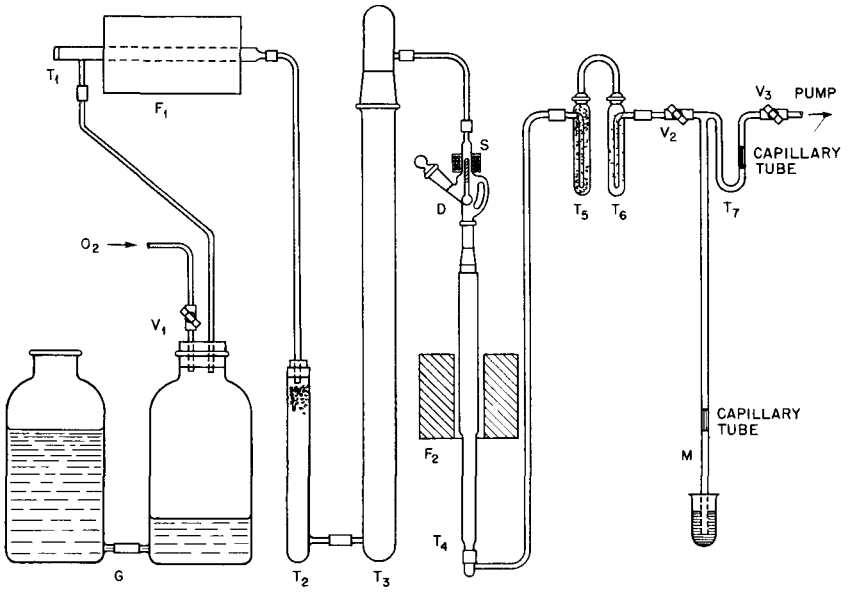


Fig. 2.21—Schematic diagram of the apparatus for the determination of carbon by the capillary-trap method. G, gasometer. T_1, preheater tube. T_2 and T_3, purifying tubes. T_4, combustion tube. T_5 and T_6, purifying tubes. T_7, capillary trap. D, dumper. V_1, V_2, and V_3, brass bellows type valves. F_1 and F_2, furnaces. S, solenoid. M, manometer.

(d) *Physicochemical Methods.* (1) *Carbon.* Conventional combustion methods can be applied to the determination of carbon in plutonium. Sample sizes from 3 to 5 g enable a carbon content of 10 ppm to be determined by absorbing the carbon dioxide on Ascarite and weighing. It is necessary, however, to burn the sample in an argon-oxygen mixture to reduce the rate of burning. The use of such large samples is not normally recommended, and the procedure should always be carried out in gloved boxes.

A micromethod [171] that has been used with considerable success requires a sample size of 80 to 150 mg and enables the carbon to be determined in concentrations of 20 ppm. With this method the sample is burned in a stream of oxygen at atmospheric pressure, and the carbon dioxide is condensed in a capillary trap and measured with a capillary manometer.

Figure 2.21 is a schematic diagram of the apparatus. Oxygen flows through the system from the gasometer (G), passing successively through the preheater tube (T_1), purifying tubes (T_2 and T_3), the sample dumper (D), the combustion tube (T_4), purifying tubes (T_5 and T_6), and through the capillary trap (T_7) to the pump. V_1, V_2,

and V_3 are ¼-in. brass bellows type valves. V_1 is opened only to refill the gasometer with oxygen, V_2 controls the flow rate, and V_3 is always open except when carbon dioxide is being measured.

The gasometer, made from two 4-liter aspirator bottles, serves to measure the oxygen and also to maintain a pressure slightly above atmospheric in all the apparatus up to valve V_2. Its operation is semiautomatic; in filling operations any excess oxygen bubbles out through the open bottle, and, when 1 liter has been delivered, an electrical contact rings a buzzer. The gasometer fluid is a potassium sulfate solution, which provides the necessary conductivity for buzzer operation. The preheater tube, heated to 900°C by furnace F_1, is made of quartz and contains a roll of platinum gauze as a catalyst. The bulk of the moisture from the gasometer is removed by silica gel in tube T_2; Ascarite and silica gel in tube T_3 complete the purification of the oxygen. T_5 contains amalgamated copper turnings to remove traces of sulfur. Magnesium perchlorate in T_6 removes the last traces of moisture; silica gel was less satisfactory in this position.

The combustion tube, T_4, is made from a McDanel 1¼-in. clay tube cut to a length of 45 cm; a standard taper is ground into the large end. It is mounted vertically, about 10 cm of its length being heated by furnace F_2. This furnace is platinum-wound and is operated continuously at 1000°C. No crucible is used, the samples being burned on a packing of loose solid material which fills the lower part of the tube. This bed consists of quartz chips, covered by a layer, 2 to 3 cm deep, of copper oxide (wire form), the latter thus being confined to the hot zone. The lower end of the tube is plugged with glass wool to retain any contaminated dust.

The glass sample dumper (D) is connected to the combustion tube through a standard-taper adapter, which is cemented with sodium silicate into the ground end of the tube. Samples are introduced into a side arm closed by a plain ground stopper, without grease or mercury seal. This is made possible by a slightly greater than atmospheric pressure inside the combustion tube. The solenoid (S), the coil of an H-B mercury relay, lifts the plunger to drop the sample into the combustion tube. A rheostat control is used to pick up and set down the plunger as gently as possible.

The manometer (M) and trap (T_7) are made of glass capillary tubing, the manometer of 1.5-mm bore, and the trap of 1-mm bore. The trap is designed to fit into a 250-ml Dewar flask. Its ends are sealed with Apiezon W into the two valves, which are oriented so that the side with the small volume is included in the trap-manometer system. The manometer is read by a millimeter scale extending downward from a zero mark etched on the tube 5 cm below the T-joint (to

allow room for overshooting). The mercury well at the base of the manometer has a screw adjustment to correct the zero for changes in atmospheric pressure. A closed manometer would avoid this adjustment, but the open construction is preferred because it permits the manometer to be cleaned. Placement of the manometer before the capillary trap allows it also to serve as a flowmeter.

The various parts of the apparatus are connected by ¼-in. copper tubing; glass-to-metal connections are made with neoprene tubing or stoppers. The combustion tube, furnace, and sample dumper are mounted in a dry box, thus confining all sources of possible contamination.

Procedure. With the gasometer filled with oxygen, the stopper of the sample dumper is removed, the sample (80 to 150 mg) is dropped in, and the stopper is replaced with a slight twist to seat it firmly. During the loading, oxygen flows out through the side arm of the dumper, excluding all air. The gasometer is then refilled, and, with valve V_3 open to the pump, V_2 is adjusted to give a manometer reading of about 50 mm, which corresponds to a flow rate of 1 liter in 10 min. The trap is immediately chilled with liquid nitrogen; the Dewar flask is kept full during analysis of the sample. As soon as violent boiling of the liquid nitrogen ceases, the sample is dumped. When the buzzer sounds, indicating that 1 liter of oxygen has passed, V_2 is closed; the gasometer is refilled; and V_3 is closed. The Dewar is removed, and the trap is warmed with warm water and wiped dry. The manometer is read to the nearest 0.5 mm; it is tapped with a rubber tube to free the meniscus. V_3 is then opened, and the next sample is loaded.

A blank is determined in the same way, omitting the loading and dumping of the sample. Blanks must be determined if the apparatus is left unused for more than a few minutes. Passing oxygen through the system at the usual rate for 30 min in the morning will reduce the blank to its operating level (0.5 μg or less).

Calibration of the Manometer. Because the volume of the capillary system (trap plus manometer) increases as the mercury level falls in the manometer, the calibration is nonlinear.

If we let x=manometer reading=pressure (mmHg), v=volume of capillary trap, including manometer (mm^3), and W=weight of carbon (μg), then by the ideal gas law

$$xv=\frac{W}{12}RT \tag{2.26}$$

The proper value of R is 62.37 liter mm $mole^{-1}$ deg^{-1} (since micrograms/mm^3=grams/liter). The temperature is taken as 24°C, or 297°K (a three-degree change in temperature produces a 1 per cent error). Substituting and solving for W,

$$W=\frac{12xv}{(62.37)(297)}=0.641(10^{-3})xv \tag{2.27}$$

If V_0 is the volume of the trap above the zero mark (mm^3) and a is the cross-sectional area of the capillary bore (mm^2),

$$v = V_0 + ax \tag{2.28}$$

Substituting in Eq. 2.27

$$W = 0.641(10^{-3})(V_0 x + a x^2) \tag{2.29}$$

Now, let us define two calibration constants:

$$A = 0.641(10^{-3})V_0 \tag{2.30}$$

$$B = 0.641(10^{-3})a \tag{2.31}$$

Then the calibration equation becomes,

$$W = Ax + Bx^2 \tag{2.32}$$

B is determined as follows: Sufficient mercury is drawn into the manometer to extend a desired length x. By careful manipulation of the valves, the upper meniscus is adjusted to the zero mark. The position of the lower meniscus (x) is read to the nearest 0.5 mm. The mercury is expelled and weighed. If the weight of the mercury is M in milligrams, the average cross section (a) is given by

$$a = 0.07388\frac{M}{x} \tag{2.33}$$

where 0.07388 is the specific volume (mm^3) of 1 mg of mercury at 24°C. Combining Eqs. (2.31) and (2.33)

$$B = 0.641\ (10^{-3})\left(0.07388\frac{M}{x}\right) = 0.4738\ (10^{-4})\frac{M}{x} \tag{2.34}$$

In practice, the capillary is usually somewhat tapered so that B is not quite constant. The above measurement is therefore repeated for various values of x, following which B is plotted as a function of x. The correct value of B in Eq. 2.32 is then read from this curve.

The volume V_0, and therefore the constant A, cannot easily be measured directly because of the brass valves. The constant A is therefore determined from B by the following procedure. A leveling bulb is attached to the bottom of the manometer tube, and the bulb is filled with mercury. A connection is opened so that valve V_3 can be opened directly to the atmosphere. With this valve open, the mercury is raised to the zero mark; the valve is closed; and the barometric

pressure h is noted. The leveling bulb is lowered to a point near the bottom of the manometer scale, and the mercury level x is noted. Valve V_3 is opened to the atmosphere, and the new mercury level $\underline{x}$ is noted. This process is repeated several times.

The pressure at the upper position of the leveling bulb was h, and the volume was proportional to A. On expanding to a volume proportional to $A+Bx$, the pressure was reduced by an amount $x-\underline{x}$. Therefore, the final pressure was $h-x+\underline{x}$.

Then by Boyle's law,

$$Ah=(A+Bx)(h-x+\underline{x}) \tag{2.35}$$

Solving for A,

$$A=\frac{Bx(h-x+\underline{x})}{x-\underline{x}} \tag{2.36}$$

Values of W can now be calculated from Eq. 2.32 and the curve of its value.

Values of W can now be calculated from Eq. 2.32 and the curve of B vs. x. For routine analysis, it is convenient to calculate a table giving W as a function of x. For values of x below 100, in which the great majority of high purity samples fall, values should be calculated for every half millimeter. It is necessary to use Eq. 2.32 only at 10-mm intervals, other values being obtained by interpolation. Values of W are usually rounded to 0.1 μg.

The actual value of A is about 0.64 μg/mm, and, of B is about 0.0014 μg/mm^2. The useful length of the scale will depend, of course, on the mean barometric pressure. Readings should be made to the nearest 0.5 mm. The capacity of the apparatus is about 700 μg, and the precision of reading the scale varies from 0.32 μg near the top to about twice this value at full capacity. The calibration is probably accurate to about 1 per cent. Certain corrections (e.g., correcting the mercury column to 0°C), which amount to a fraction of 1 per cent, have been neglected.

(2) *Hydrogen.* Hydrogen is also determined by conventional combustion methods in which a 5-g sample of plutonium is burned in an argon-oxygen mixture at 550°C, or at 900°C in the simultaneous determination of hydrogen and carbon. The combustion products are oxidized over hot cupric oxide, and the water formed is absorbed and weighed. The weighing error of about 0.1 mg causes a possible error of 2 ppm of hydrogen. However, 5 ppm of hydrogen is detected by this method, and the coefficient of variation in determining 100 ppm is less than 5 per cent.

(3) *Nitrogen.* Either the Dumas method or the Winkler method is used for determining nitrogen, but the latter is preferred because of its relative speed. Results for nitrogen obtained by each method are equal, showing that the concentration of absorbed nitrogen in plutonium is insignificant as compared to the combined nitrogen. In the Winkler method, the hydrochloric acid solution of the sample is digested with boiling perchloric acid, and, after the solution has cooled, sodium hydroxide is added until the solution is strongly basic. Nitrogen is steam distilled as ammonia, which is trapped in boric acid solution. The ammonia can be titrated with standard acid solution. However, the determination is usually completed by the addition of a modified Nessler's reagent, which permits spectrophotometric measurement at a wave length of 410 mμ. For a concentration range of 20 to 100 ppm of nitrogen, the coefficients of variation are between 10 and 3 per cent. Five parts per million can be detected reliably.

(4) *Oxygen.* Vacuum fusion methods for determining oxygen in plutonium have been largely replaced by the platinum-bath capillary-trap method.[172, 173] In this method the sample is dropped into molten platinum at 1800°C which is contained in a graphite crucible. The oxide reacts with the carbon dissolved in the bath to form carbon monoxide, which is swept by argon at atmospheric pressure. Oxidation of the carbon monoxide is accomplished using Schutzes reagent, and the carbon dioxide is condensed in a capillary **U**-tube trap at liquid-nitrogen temperature and measured at room temperature with a capillary manometer. The method reliably detects 0.3 μg of oxygen, and concentrations between 50 to 500 ppm in 50 mg of plutonium are determined with coefficients of variation of 14 to 1.4 per cent, respectively.

Figure 2.22 is a schematic diagram of the capillary-trap apparatus originally developed by Smiley.[173] The sample dumper (D) and furnace (F) are enclosed in a dry box; the remainder of the apparatus is mounted on a rack adjacent to the dry box. The parts are connected by ¼-in. copper tubing. The glass-to-metal parts are connected by brass spherical joints. Brass bellows type valves are used instead of stopcocks. They permit better flow control and on the whole are more reliable, but they do occasionally develop leaks and therefore are mounted so as to be easily replaced. Several parts are interchangeable with the carbon apparatus (see Fig. 2.21).

The entire apparatus up to valve V_5 is filled with argon at slightly more than atmospheric pressure. The manostat (M), made from two 4-liter aspirator bottles and filled with silicone oil, serves to maintain this pressure when the apparatus is not in use; its large volume compensates for barometric changes or slow leaks. When the ap-

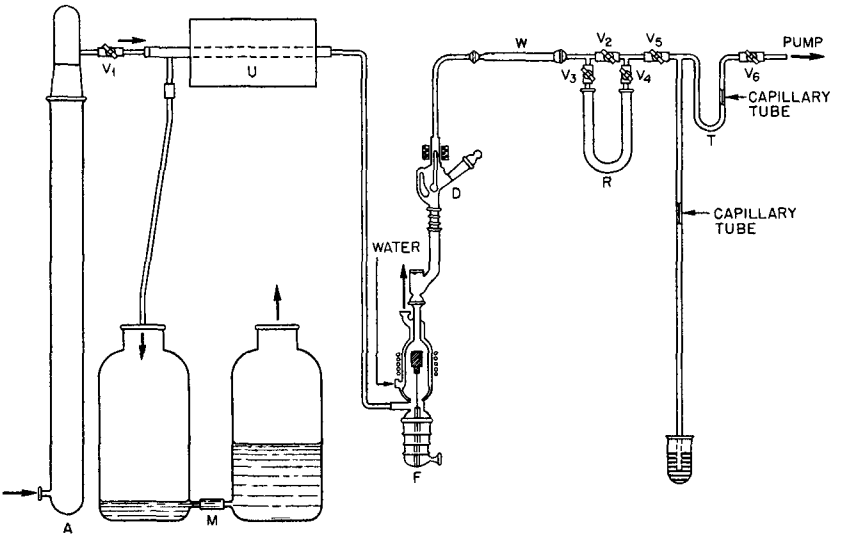


Fig. 2.22—Schematic diagram of the apparatus for the determination of oxygen by the platinum-bath carrier-gas method. A, tube containing Ascarite and magnesium perchlorate. M, manostat. U, F, furnaces. V_1 through V_6, brass bellows valves. D, sample holder. W, tube containing magnesium perchlorate and glass wool. R, U-tube containing oxidizing reagent. T, trap.

paratus is in use, valve V_1 is adjusted so that argon bubbles out slowly through M. After reduction to less than 1 psi, it passes through tube A, containing Ascarite and magnesium perchlorate, which remove most of the moisture (if any) from the argon. The argon then passes through furnace U, which consists of a 1-in. nickel tube, packed with uranium turnings, and heated over 12 in. of its length by a Nichrome winding. The temperature at the center is about 625°C, which is adequate to remove traces of water and oxygen.

From the uranium furnace, the argon passes upward through the induction furnace (F), and sample holder (D). This direction of flow is opposite to that used in the carbon apparatus and is important because it prevents any oxygen that enters the sample holder from reaching the crucible.

The induction furnace is made of vitreous silica and is water jacketed including the constricted part, which guides samples into the crucible. The graphite crucible is mounted on a 0.040-in. tungsten rod, which is supported vertically by a capillary sealed into a standard-taper joint at the base of the furnace, large enough to pass the crucible. The crucible can thus be replaced without dismounting the furnace.

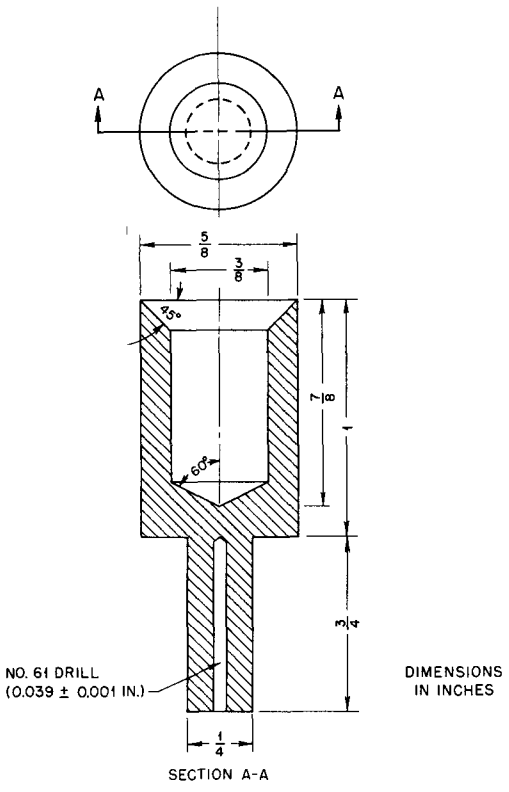


Fig. 2.23—Detail drawing of graphite crucible used in the platinum-bath carrier-gas method for determining oxygen.

Figure 2.23 shows the dimensions of the graphite crucible, which seem to be somewhat critical. If the crucible is larger than shown, frequent cracking is encountered. The crucible contains 5 to 6 g of platinum as a flux. A new crucible is heated for about a half hour at a temperature close to, but below, the melting point of platinum to remove all oxygen without evaporation of the platinum. When in use, the crucible is operated just above the melting point of platinum, or at about 1800°C. The usual practice is to observe the setting of the induction heater controls at which the platinum melts and to operate at a slightly higher setting.

The heating coil consists of 10 turns of flattened ¼-in. copper tubing and is about 2 in. high and 2 in. in inside diameter.

The sample holder is connected to the furnace through an adaptor consisting of a 19/38 standard-taper joint at the top and a spherical 18/9 at the bottom. It also contains a window to permit viewing the inside of the crucible. Samples are introduced into the holder through

the side arm; the ground joint is not greased. Both joints of the adaptor are greased with Apiezon N. Samples are dropped into the crucible by applying 110 d-c volts to a solenoid (from an H-B mercury relay) which lifts the iron-cored glass plunger. A 250-ohm rheostat is used in the coil circuit to permit lifting and lowering the plunger gently.

From the sample dumper, the argon stream passes through a tube (W) containing magnesium perchlorate and glass wool. This tube removes a small amount of moisture, which probably diffuses in through the sample dumper. It also filters out plutonium contamination and soot from the crucible.

Next, the argon flows through the oxidizing reagent (R). Valves V_2, V_3, and V_4 permit the reagent to be bypassed while the system is being flushed and while a new crucible is being degassed. The oxidizing reagent is prepared as follows: Five grams of iodine pentoxide (or the equivalent amount of iodic acid) is dissolved in 25 ml of water. The solution is allowed to saturate 50 g of coarse (6 to 16 mesh) silica gel. The silica gel is dried at 150°C for 1 to 2 hr. Ten milliliters of concentrated sulfuric acid is mixed with the dried silica gel–iodine pentoxide mixture, and the mixture is allowed to stand overnight in a closed container. The mixture is then packed into the middle section of a glass combustion tube, with glass wool pads at each end, and the ends are filled with silica gel. The tube is then evacuated, and a slow stream of air is drawn through it. Finally, the reaction mixture is heated to 220°C for about 4 hr, or until it is a uniform golden yellow color. The tube must now be kept hermetically sealed because the contents are very sensitive to moisture. The iodine pentoxide oxidizes carbon monoxide instantly to carbon dioxide, with the formation of free iodine, which appears as a brown stain. The exhaustion of the reagent can be followed by the growth of the dark zone. A single batch of reagent should last several months.

Valve V_5 is adjusted to control the flow rate; V_6 is open to the vacuum pump except during measurement. The trap and manometer are of pyrex capillary, the trap having a 1-mm bore and the manometer having a 1.5-mm bore. The U-shaped trap fits into a 250-ml Dewar flask. The dimensions of the trap and manometer are shown in Fig. 2.24. The lower end of the manometer is immersed in a beaker of mercury, and the level is adjusted by adding or removing mercury to bring the column in the manometer to the zero mark when the system is evacuated. A millimeter scale is mounted by the manometer, reading downward from the zero mark. The trap is so arranged that the manometer is at the end at which the argon enters; so the trap and manometer also serve as a flowmeter. The ends of the trap are sealed into the valves with Apiezon W. It is important to orient the valves

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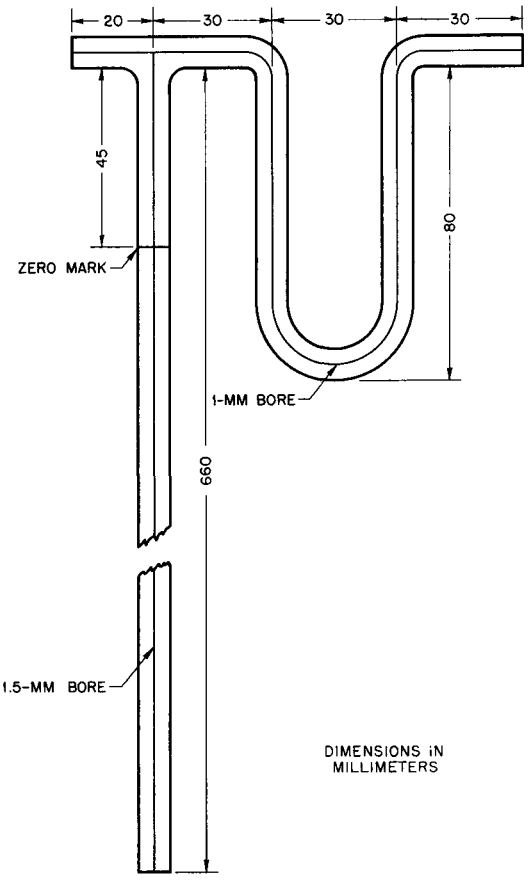


Fig. 2.24—Detail drawing of capillary trap and manometer used in the apparatuses for determining carbon and oxygen.

so that the side with the small volume (away from the bellows) is next to the trap.

Calibration of Apparatus. The calibration is carried out identically to that described under the procedure for carbon in plutonium. However, the following change is necessary because of the difference in atomic weights between carbon and oxygen. Equation 2.26 states that,

$$xv=\frac{W}{12}RT \tag{2.26}$$

where 12 is the atomic weight of carbon; for oxygen, Eq. 2.26 becomes

$$xv=\frac{W}{16}RT \tag{2.37}$$

because 16 is the combining weight of oxygen in the carbon monoxide formed in the reaction between the oxygen in the sample and the carbon of the crucible. Solving for W,

$$W=\frac{16xv}{(62.37)(297)}=0.853(10^{-3})xv \tag{2.38}$$

In the same manner Eqs. 2.30 and 2.31 now become

$$A=0.853(10^{-3})V_0 \tag{2.39}$$

and

$$B=0.853(10^{-3})a \tag{2.40}$$

Also, Eq. 2.34 now becomes

$$B=0.853(10^{-3})\left(0.07388\,\frac{M}{x}\right)=0.6302(10^{-4})\,\frac{M}{x} \tag{2.41}$$

Equation 2.36 remains the same except the value for B is calculated from Eq. 2.41 instead of from Eq. 2.34.

Sample Preparation. The metal sample should be as compact as possible. The greater the volume-to-surface ratio, the less the chance of significant oxygen contamination on the surface. In any case, it is recommended that surface oxide be removed by electrolysis immediately prior to analysis. This procedure is described in Sec. 2–2.5(a) under the heading "Standardization of the Cerium(IV) Solution." For many analyses samples weighing approximately 50 mg can be used.

Determination of the Blank. Whenever the apparatus has been idle for more than a few hours, it must be flushed to reduce the blank. This is done as follows: The argon is turned on, and valve V_1 is adjusted so that argon bubbles out through the manostat M. The vacuum pump is started, valve V_6 is opened, and the mercury column is adjusted to the zero mark by adding or removing mercury to the beaker. The manometer is tapped with a rubber tube to free the meniscus. Valve V_2 is opened (V_3 and V_4 remain closed), and V_5 is adjusted to give a manometer reading of 50 mm. This corresponds to a flow rate of about 100 ml/min. The furnace cooling water is turned on, and the crucible is heated to about 1800°C. After 30 min, V_3 and V_4 are opened and V_2 is closed, thus passing the gas stream through reagent R. Flushing is continued for 10 min; then a blank run is made.

To determine the blank, valve V_5 is closed and the zero adjustment is checked. Valve V_5 is then adjusted to give a manometer reading of 50 mm. The Dewar flask containing liquid nitrogen is placed

around the U part of the trap. The argon flow is continued for 10 min. Then V_5 is closed, and, after allowing an interval of a few seconds, V_6 is closed. The liquid nitrogen is removed, and the trap is warmed to room temperature. The manometer is then read to the nearest 0.5 mm. V_6 is opened and the zero is checked if it seems necessary. Blank determinations should be repeated until two successive values agree within 0.5 mm or less. Additional blank determinations should be made after every six samples.

Procedure. Following the determination of a satisfactory blank, with valve V_5 closed and V_6 open, the induction heater is turned off. The prepared sample is dropped into the sample holder via the side arm, and the stopper is replaced with a slight twist. The induction heater is turned on, valve V_5 is adjusted to give a manometer reading of 50 mm, the trap is chilled with liquid nitrogen, and the timer is set for 10 min. The sample-dumper rheostat is operated to drop the sample into the crucible. After 10 min, valves V_5 and then V_6 are closed. The trap is warmed to room temperature, and the manometer is read as described above.

Calculations. Convert the x values for blanks and samples into W by Eq. 2.32, or by use of a calibration table (see under "Calibration"). The W value for each sample is then corrected by subtracting the W value corresponding to the blank. If the blank shows a uniform trend, the correction for each sample is obtained by interpolation between two successive blanks. If there is no trend, the average value is used. The oxygen content is then calculated by

$$\text{Ppm oxygen} = \frac{(W, \text{sample} - W, \text{blank})(1000)}{\text{Mg of sample}} \tag{2.42}$$

2–3 ANALYSIS OF PLUTONIUM-CONTAINING MATERIALS

2–3.1 Methods of Dissolution

The plutonium-containing materials of interest in reactor technology originate from a variety of sources and differ significantly in chemical and physical properties. Consequently, several methods of dissolution are required to prepare these materials for subsequent determinations of the plutonium content. Because plutonium is formed in significant quantities in all reactors fueled with uranium of low enrichment, the dissolution of these spent fuel elements is of real interest. Methods for dissolving and analyzing expended reactor fuels are discussed in Chap. 6, and no detailed description will be given here. However, typical examples of solvents for various fuels and claddings, and in some cases the approximate compositions of the dissolver solutions, are given in Table 2.14. The mechanical and chemical dejacketing and the dissolution of specific expended fuel elements have been described in several publications.[174–176]

Table 2.14—TYPICAL SOLVENTS FOR FUEL-ELEMENT MATERIALS[174, 176-178]

Solvent	Process	Fuel-element material	Approximate concentrations of solution components
HF	Zirflex (cladding).	Zr or Zircaloy	ZrF_6^{-2}, 0.6*M*; F^-, 0.6*M*; NH_4^+, 1.92*M*; UF_4, 0.001*M*; Sn, <0.01*M*; Pu <1x10^8 counts/min/gal; Sp. Gr., 1.07.
0.5*M* HF–2.5*M* HNO_3	Zirflex (core).	UO_2-Zircaloy or U-Zr alloy.	U, 2.5*M*; HNO_3, 0.4*M*; $Al(NO_3)_3$, <0.4*M*; F^-, <0.2*M*; NH_4^+, <0.05*M*; ZrF_6^{-2}, 0.02*M*; Pu, 0.01*M*; Sp. Gr., 1.8.
6*M* H_2SO_4	Sulfex (cladding).	Stainless steel	Stainless-Steel sulfate, 0.5*M*; H_2SO_4, 3.45*M*; Fe, 0.004*M*; $U(SO_4)_2$, <0.0004*M*; Sp. Gr., 1.27; Pu<1x10^8 counts/min/gal.
2.5*M* HNO_3	Sulfex (core).	U or UO_2	U, 2.5*M*; HNO_3, 0.4*M*; $Al(NO_3)_3$, 0.4*M*; Sp. Gr., 1.8; Pu, 0.01*M*.
Aqua regia	Darex (cladding and core; 1 step).	Stainless-steel cladding and UO_2 or UO_2-stainless steel fuel.	U, 0.6*M*; stainless steel, 0.8*M*; HNO_3, 3.2*M*; Pu, 0.005*M*; Cl^-, removed by chloride stripping.
1*M* $Fe(NO_3)_3$ +5*M* HNO_3.		U-Mo alloy	U, 0.75*M*; Mo, 0.08*M*; $Fe(NO_3)_3$, 0.75*M*; HNO_3, 1*M*; Sp. Gr., 1.4.
$NaNO_3$–caustic solution.	Purex (cladding).	Al	
HNO_3	Purex (core).	UO_2 or U-Al alloy	U, 1*M* to 2*M*; Al, 0.03*M* to 0.9*M*; HNO_3, 0.2*M* to 1*M*.
Hg-catalyzed HNO_3.		Pu-Al, Pu-Al-Si, U-Al fuels or Al cladding.	
13*M* HNO_3–0.04*M* NaF–0.04*M* $Al(NO_3)_3$.		96% ThO_2–4% UO_2 fuel, U–3% Mo fuel.	
HCl gas	Zircex	Zr, Zircaloy	(Volatilizes Zr as chloride.)
2*M* HNO_3, NH_4HF_2.	Niflex	Stainless steel	
6.5*M* HF and 0.3*M* H_2O_2.	Perflex	Zr, Zircaloy	
$PbCl_2$ fused salt and Cl_2.	ARCO	Zr, Zircaloy	

Other plutonium-containing materials to be considered include the metal; various alloys, oxides, and mixed oxides: and "plutonium fissium," which is the name given to plutonium-containing material resulting from alloying with plutonium the calculated quantities of the nonradioactive species of the major fission-product elements. A typical fissium material representing 10 per cent burn-up after 130 days of fast fission contains 0.7 per cent cerium, 1.3 per cent lanthanum, 0.7 per cent molybdenum, 0.03 per cent niobium, 1.3 per cent ruthenium, and 0.8 per cent zirconium in addition to any elements added as diluents and the plutonium. As stated in Sec. 2–2.2 plutonium metal readily dissolves in the halogen binary acids, of which hydrochloric acid is the most widely used. Oxidizing acids cause an oxide film to form on the metal, reducing the rate of dissolving, or they dissolve only part of the sample, leaving an oxide residue that is difficult to dissolve. Heating with a mixture of hydrofluoric, nitric, and sulfuric acids is usually effective in dissolving these small amounts of plutonium oxide. Freshly precipitated plutonium oxide is soluble in hot concentrated sulfuric or nitric acid, but, after being heated to a temperature above 700 or 800°C, it becomes highly refractory. Refluxing with hydrobromic acid [179] or with concentrated nitric and hydrofluoric acids or fusion with potassium pyrosulfate will slowly dissolve the refractory oxide. Heating at 325°C with concentrated hydrochloric and perchloric acids in a sealed silica tube [180, 181] will effect solution in 36 to 48 hr of plutonium oxide that has been sintered at temperatures above 2000°C. In a more recent method, the oxide is fused with ammonium bifluoride, the excess fluoride flux is volatilized by heating, and the plutonium fluoride formed in the fusion is dissolved by heating with concentrated nitric acid.[182] This method has proved successful in dissolving plutonium oxide that has been heated to at least 1250°C. One of the few plutonium-containing materials that has been considered for use in a power reactor is a mixture of uranium and plutonium oxides. For the analysis of the nonirradiated material, heating with concentrated nitric acid containing a low concentration of hydrofluoric acid dissolves most of it, depending upon the temperature at which the oxides were formed. Any insoluble residue is then dissolved by the sealed-tube method or the ammonium bifluoride fusion method described above. If the sealed-tube method is used for dissolving all of a small oxide sample, the loss of volatile impurities or reaction products is eliminated.

Among the metals that have been used as alloying constituents in making plutonium-rich materials for testing purposes are aluminum, cerium, cobalt, and iron. These alloys dissolve readily in $3M$ to $12M$ hydrochloric acid. Any plutonium oxide present remains as an in-

Table 2.15—SOLVENTS FOR PLUTONIUM-RICH MATERIALS

Type sample	Element to be determined	Solvents used
Alloy	Al, Ce, Co, Fe, La, Pu, Th, U.	3*M* to 12*M* HCl.
Alloy	Al, Th, Si, Ti, Pu	$HClO_4$.
Alloy	Al, Pu	Hg-catalyzed HNO_3.
Alloy	Cu, Rh, Pu	HCl-HNO_3*.
Alloy	Pu, Ru, Mo, Zr, Ce, La, Nd, Fe, Ce, Co.	HCl-$HClO_4$ (boiling† or in sealed tube).
Oxide	Pu	HCl-$HClO_4$ (sealed tube) or NH_4HF_2 fusion-HNO_3 or HNO_3-HF-H_2SO_4.

*Rhodium requires the sealed-tube method.
†RuO_4 distilled.

soluble residue and requires one of the treatments described above. The mercury-catalyzed dissolution of plutonium-aluminum alloy in nitric acid is also used. The fissium alloys employed in the development of purification procedures are more difficult to dissolve. Treatment with hydrochloric acid and perchloric acid, followed by evaporation to fumes of perchloric acid, dissolves the alloy and simultaneously separates the ruthenium as the tetroxide by distillation. The sealed-tube method with a heating period of about 2 hr is also effective. A summary of the solvents used in dissolving the various plutonium-rich materials is given in Table 2.15.

Materials, such as reactor fuel containers, which contain small amounts of plutonium are best dissolved in solvents for the major constituent. If the plutonium is not dissolved simultaneously, the residue is dissolved by heating with nitric, hydrofluoric, and sulfuric acids, or it is fused in ammonium bifluoride.

2–3.2 Methods of Separation of Plutonium

The large ratio of uranium to plutonium and the high levels of beta and gamma radioactivities of the fission-product elements greatly increase the difficulty of separating plutonium from expended uranium reactor fuels. The methods used must provide quantitative separation from a wide variety of elements, some of which are chemically very similar to a particular oxidation state of plutonium. Therefore, these separations are long and complicated, involving several steps and many operations. Generally speaking the most widely used separation methods include coprecipitation of Pu(III) or Pu(IV) fluorides with lanthanum fluoride [4, 183] or bismuth phosphate,[183a] ex-

traction of Pu(VI) nitrate into 2-methyl-4-pentanone (Redox process),[184] extraction of Pu(IV) into tributyl phosphate (Purex process) [185] or thenoyltrifluoroacetone-benzene,[186] and ion-exchange separations using cation [187] or, of more importance, anion-exchange resins.[40, 80] The various plant processes presently used in separating plutonium from the expended reactor fuels are discussed in detail in Chap. 6 and in various publications [9, 82, 188] and will not be described here. The separation of plutonium from materials other than dissolver solutions utilizes the same general techniques, namely, precipitations, solvent extraction, and ion exchange, which are described. Other methods, such as selective volatilization of plutonium halides, electrodeposition of the oxide or metal, and extractions in molten-metal systems have not been applied in the analysis of reactor materials or are still in the developmental stages.

Separations of either micro- or macroquantities of plutonium are necessary depending upon the analytical method used. For radiochemical analyses, the quantities of plutonium required are exceedingly small, 0.01 to 1.0 μg being adequate. For spectrophotometric determinations of plutonium with a color reagent such as Arsenazo [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid], plutonium concentrations of 0.5 to 12.0 μg/ml are used. The titration methods usually require milligram quantities of plutonium. In general, the same separation techniques are employed for micro- and macroquantities except that carriers are used to increase yields and improve separation factors in precipitation separations of microquantities. These carriers precipitate when the anion or other agent forming an insoluble compound with the plutonium is added, and the plutonium is carried with the precipitate. This method is especially applicable to plutonium solutions too dilute to form a precipitate without the carrier. For example, lanthanum is frequently added to coprecipitate with and carry Pu(III) or Pu(IV) when fluoride ion is the precipitant, and strontium and zirconium holdback carriers may be added to prevent the carrying or occlusion of soluble fluorides by the precipitate. Usually, 10 to 20 mg of each carrier is used, although the amounts will vary with the method. For some separations in radiochemical analyses, a radiochemically pure product is sought in preference to a quantitative yield, but in these cases the yield must be determined. Generally, yields are estimated by adding a known concentration of an isotope of plutonium not common to the sample and determining its recovery, or by determining the recovery of a known quantity of plutonium under conditions closely approximating those for the unknown sample.

The multiplicity of oxidation states of plutonium has been widely exploited in devising methods of separation. This arises from the different chemical behavior of each oxidation state. An element that accompanies plutonium in one of its oxidation states will be separated from the plutonium if the oxidation state of the latter is changed. The use of oxidation-reduction cycles is well illustrated in the separation methods described below.

(a) *Precipitations.* As shown in Table 2.7, plutonium forms insoluble compounds with several anions under the stated conditions; the reported behavior of plutonium with several carriers is given in Table 2.16. Of the anions listed, fluoride and phosphate have been used most widely for the separation of plutonium prior to its determination. The precipitation of Pu(III) or Pu(IV) iodate from a minimum volume of solution was also shown to yield quantitative results in the determination of the element.[189] Various solubilities reported for Pu(III) and Pu(IV) oxalates have prompted a recent investigation of the solubilities of these compounds.[190] It was found that the solubility of plutonium oxalate varies markedly under different experimental conditions because of the formation of several cationic and anionic plutonium oxalate complexes. Hydroxide is not widely used for precipitating plutonium because of the noncrystalline nature of the precipitate. In addition, a recent investigation [190] showed that

Table 2.16—COPRECIPITATION BEHAVIOR OF PLUTONIUM WITH VARIOUS CARRIERS*

Carrier	Pu(III)	Pu(IV)	Pu(VI)
$Th(C_2O_4)_2$	C	C	NC
$U(C_2O_4)_2$	C	C	NC
$La_2(C_2O_4)_3$	C	C	NC
$Bi\ PO_4$	C	C	NC
$Zr_3(PO_4)_4$	NC	C	NC
$Th\ P_2O_7$	NC	C	NC
$Zr(IO_3)_4$	----------	C	NC
$Th(IO_3)_4$	----------	C	NC
$Ce(IO_3)_4$	----------	C	NC
$Na(UO_2)(C_2H_3O_2)_3$	NC	NC	C
$K_3La(SO_4)_3$	C	C	NC
LaF_3	C	C	NC
Zirconium phenylarsonate	NC	C	NC
Zirconium benzene sulfinate	NC	C	NC
Hydroxides	C	C	C
ThO_4	----------	C	

*C, carried; NC, not carried.

the solubility of the hydroxide precipitate is increased by carbonate, which causes erratic results. Wider use is made of oxalate and hydroxide, and also of peroxide, iodate, and carbonate, in the removal of plutonium from solution prior to the determination of other elements.[37, 191-193] Highly specific carriers for the Pu(IV) oxidation state are zirconium phosphate, zirconium benzene sulfinate, and zirconium phenylarsonate,[168, 194] which are used in determining the concentration of this oxidation state in solutions also containing other oxidation states of plutonium.

The use of oxidation-reduction cycles is well illustrated in the lanthanum fluoride separation cycle. The plutonium is first reduced to the (III) or (IV) oxidation state with a reductant such as sulfurous acid and then is coprecipitated as the fluoride from 1*M* to 3*M* hydrofluoric acid solution with lanthanum as a carrier. The precipitate is dissolved by heating with sulfuric or nitric acids or by adding aluminum or zirconium to complex the fluoride, and the plutonium and lanthanum are then reprecipitated as the fluorides. Metathesis with concentrated potassium hydroxide forms lanthanum and plutonium hydroxides, which are washed and then dissolved in nitric acid. The plutonium is oxidized to the fluoride-soluble (VI) oxidation state by heating with 0.15*M* bromate or argentic ion, and the fluoride-insoluble ions, such as the rare earths, are precipitated as the fluorides. The plutonium in the supernatant solution is again reduced, and the cycle is repeated to effect more complete separations. If different oxidizing and reducing agents are used, or if specific complexing agents are added, selective separations from particular elements can be accomplished. For example, in separating plutonium and uranium, sulfate ion is added to complex the uranyl ion and prevent formation of the fluoride-insoluble lower oxidation states of uranium. Plutonium is precipitated as the fluoride and separated from neptunium following oxidation of only the latter to a fluoride-soluble state with cold bromate solution catalyzed with fluoride ion.

The coprecipitation cycles using bismuth phosphate, zirconium phosphate, potassium lanthanum sulfate, zirconium benzene sulfinate, and other carriers of the same type are similar to the lanthanum fluoride cycle. In each case the lower oxidation states of plutonium are precipitated in the first separation, and the plutonium is oxidized before the second precipitation, which carries impurity elements and leaves Pu(VI) in solution. For the carriers that do not coprecipitate Pu(III), nitrite or some other oxidant is used to oxidize the plutonium to the (IV) oxidation state prior to the first precipitation in the cycle.

The sodium uranyl acetate coprecipitation cycle, which has not been used extensively with plutonium, consists of a precipitation of any

uranium present as sodium uranyl acetate while Pu(III) and Pu(IV) remain in solution. Following oxidation of the plutonium to the (VI) oxidation state, it is coprecipitated with the carrier. Few other elements, other than the lower actinide elements, follow plutonium in this separation. The uranium in the carrier is removed by precipitation from dilute acetic acid solution as the 8-hydroxyquinolate.

(b) *Solvent Extraction.* Because of their speed and efficiency, solvent-extraction methods are gaining favor for the separation of plutonium from most elements. Several procedures using a variety of extraction systems have been developed for this separation. Among the chelating agents widely used with various organic solvents in extraction systems are 2-thenoyltrifluoroacetone (TTA), cupferron, and acetylacetone. Tributyl phosphate(TBP)-nitrate, 4-methyl-2-pentanone(hexone)-nitrate, diethylether-nitrate, and, more recently, various organo-nitrogen and organo-phosphorus compounds[195–197] have been employed as extractants in ion association systems. For systems in which coordination or chelate complexes are formed, the stable oxidation state of plutonium which forms the strongest complex with the extractant is usually the most efficiently extracted. As stated in Sec. 2–2.2(e), the (IV) oxidation state has the strongest complexing tendencies. In general, the (IV) oxidation state is extracted most efficiently; the (VI) oxidation state, to a lesser extent; and the (V) and (III) states are considered not extractable. Exceptions to this rule are few but do exist. For example, Pu(III) is extracted[198] into undiluted TBP from 15.6*M* nitric acid with an extraction coefficient of 1.5. For solvents that do not form coordination complexes with plutonium nitrate, the order of extractability of the various oxidation states is (VI) > (IV) ≫ (III) and (V). Solvents of this type are hexone and diethylether. Actually, little is known about the extractability of Pu(V) because of its instability, but limited investigations have shown that the extraction coefficients are low. The differences between the extractabilities of the various oxidation states of plutonium, as shown in Table 2.17, form the basis for several separation methods. Good separations are possible by adjusting the oxidation states between the extractable (IV) and (VI) oxidation states and the poorly extracted (III) or (V) oxidation states.

Fluoride, sulfate, citrate, tartrate, and other substances that form water-soluble complexes with plutonium are avoided because they inhibit the extraction of plutonium into organic solvents. Generally, extractions are made from nitrate systems that are free of these complexing anions. Chloride systems are infrequently employed, and in those cases in which they are used, the extraction efficiencies are generally lower.

Table 2.17—VARIATION OF EXTRACTION EFFICIENCY WITH OXIDATION STATE[161,199]

Extraction system	Extraction coefficients		
	Pu(III)	Pu(IV)	Pu(VI)
19% TBP-kerosene: $4M$ HNO_3	0. 014	11. 5	2. 5
$0.5M$ TTA-xylene: $1M$ HNO_3	10^{-6}	10^4	0. 004
Diethylether: $6M$ HNO_3			2. 3
Hexone: $0.5M$ HNO_3–$11.1M$ NH_4NO_3	0. 14	1. 7	9. 8

(1) *Hexone–Nitrate and Diethyl Ether–Nitrate Systems.* Hexone, which extracts the covalent nitrate of Pu(VI), is important analytically [199] for the separation of plutonium from common salts, fission-product elements, and uranium. Because plutonium is extracted in the molecular state as the nitrate, the efficiency of the extraction is directly related to the nitrate concentration, which should be several molar. Nitric acid, ammonium nitrate, and aluminum nitrate have been used as salting agents to increase the nitrate concentration. Of these, aluminum nitrate is the most efficient because of its highly charged and readily solvated cation. Nitric acid has limited use as a salting agent because concentrations greater than $1.0M$ cause oxidation of hexone and extraction of the acid and other metals. Reductants for Pu(VI) must also be avoided, and the temperature should be kept low (10 to 25°C) to obtain best results. Vigorous mixing for 3 to 5 min usually is sufficient. Extraction coefficients for plutonium and several other metal ions, given in Table 2.18, are useful in estimating separation factors. It is evident that more than one extraction is necessary to obtain quantitative recovery of plutonium and efficient separations. For example, 99.7±0.2 per cent of Pu(VI) reportedly is extracted into hexone in four passes from $1.6M$ aluminum nitrate–$0.5M$ nitric acid.[189] Recoveries are usually slightly lower for extractions from aqueous phases containing large concentrations of several other metals. The plutonium is back extracted from the hexone phase by contacting it with an aqueous solution of a reducing agent. Plutonium(VI) in the organic phase is reduced to Pu(III) and transfers to the aqueous phase.

The Redox process [184] is widely used for reprocessing spent reactor fuels. This process utilizes hexone extraction to separate plutonium from uranium and fission-product elements. As described in detail in Chap. 6, changing the oxidation state of the plutonium in the various extraction steps effects its clean separation.

Diethyl ether is similar to hexone in its ability to extract Pu(VI), but because of the hazards in using the highly flammable ether, hexone is usually preferred. From aqueous solution containing nitric acid or ammonium nitrate as salting agents, diethyl ether quantitatively

Table 2.18—EXTRACTION COEFFICIENTS OF VARIOUS METAL IONS INTO HEXONE[199] AT 25°C

Metal ion*	Concentration, moles/liter			Extraction coefficient†
	Salting agent	NO_3	HNO_3	
Pu(III)	NH_4NO_3, 11.1	11. 6	0. 5	0. 14
Pu(IV)	11. 1	11. 6	0. 5	1. 7
Pu(VI)	11. 1	11. 6	0. 5	9. 8
Fe(II)	8	8. 2	0. 2	0. 004
Fe(III)	NH_4NO_3, 8	8. 2	0. 2	0. 0005
U(VI)	4. 3	4. 6	0. 3	0. 18
U(VI)	8. 7	9. 0	0. 3	2. 0
U(VI)	11. 0	11. 3	0. 3	14. 0
U(VI)	$Al(NO_3)_3$, 0.5	1. 8	0. 3	0. 1
U(VI)	1. 0	3. 3	0. 3	2. 0
U(VI)	2. 0	6. 3	0. 3	30. 0
U(IV)	1. 3	4. 4	0. 5	2. 1
Pu(VI)	$Al(NO_3)_3$, 2. 0	6. 3	0. 3	50. 0
F.P.‡	1. 4	4. 6	0. 4	0. 10
Ce	1. 3	4. 1	0. 2	0. 12
Ru	1. 0	3. 1	0. 1	0. 10
Np(VI)	$Al(NO_3)_3$, 0. 7	2. 6	0. 5	1. 7
Np(V)	1. 5	5. 0	0. 5	$<$0. 001
Np(IV)	1. 3	4. 4	0. 5	1. 5
Am(III)	1. 95	6. 35	0. 5	0. 002
Cs(I)	$Al(NO_3)_3$, 1. 0	3. 5	0. 5	0. 009
Na(I)	1. 3	4. 0	0. 1	0. 02
Al(III)	1. 3	3. 9	0. 0	$<$0. 0001
Cr(VI)	2. 0	6. 1	1. 7 pH	0. 011
Cr(III)	$Al(NO_3)_3$, 2. 0	6. 1	0. 1	0. 0003
Zr-Nb	1. 0	3. 25	0. 25	0. 01

*Concentration of each metal ion is 2g/liter.

†Extraction coefficient is the ratio of the concentrations of the solute in the organic and aqueous phases and is equal to the distribution ratio, D, when the volumes of both phases are equal. Percentage extraction is related to D by the following equation:

$$\% E = 100 D/(D + V_w/V_o)$$

where V_o and V_w are the volumes of the organic and aqueous phases, respectively.

‡Gamma-emitting fission-product elements after 144-day cooling period.

extracts plutonium(VI), cerium(IV), gold(III), and scandium (III), and partially extracts phosphorus, chromium(VI), arsenic(V), mercury(II), thallium(III), thorium(IV), and bismuth(III).

(2) *Tributyl Phosphate.* Tributyl phosphate (TBP) forms with Pu(IV) nitrate an organic-soluble coordination complex of the type $Pu(NO_3)_4 \cdot 2TBP$. As used in the Purex process [185] (see Chap. 6), extraction of Pu(IV) into TBP provides an efficient separation from other elements in dissolver solutions of spent reactor fuels. McKay [200] has described the role of TBP as an extraction agent and has shown its usefulness in analytical chemistry applications.

The undiluted reagent has limited application as an extractant because of its high density and viscosity, and dilution with inert solvents such as kerosene or carbon tetrachloride is advantageous. As for extractions into hexone, a high nitrate concentration enhances the extraction. Because nitric acid also forms a complex with TBP and is extracted, nitrate salts, such as ammonium, calcium, or aluminum nitrate, are preferred as salting agents. Of these, aluminum nitrate is the most efficient. Extraction efficiency is also highly dependent on the concentration of free TBP. For example, the extraction coefficient for $0.001M$ Pu(IV) in $1M$ nitric acid increases [199] about 40-fold as the concentration of free TBP is changed from $0.19M$ to $1.5M$. Plutonium(IV) is more efficiently extracted as the temperature is increased; changing the temperature from 25 to 75°C causes a 30 per cent increase in the amount extracted. Solutions of reducing agents, or even water, are efficient in stripping plutonium from the organic phase.

Extractability data for several metal ions are given in Table 2.19.

(3) *Chelating Agents.* Although many plutonium chelate complexes are extractable into nonpolar solvents,[201-204] only a few of these chelate extraction systems have found applications in analytical chemistry separations. Most widely used of these is the extraction of Pu(IV)-TTA into benzene, xylene, or similar solvent. With this method, plutonium is separated from uranium and fission-product elements,[186] uranium-product solutions, and uranium-waste solutions. Plutonium(IV) is separated from Pu(III) and Pu(VI), which are not extractable into TTA benzene.[199] Some radiochemical methods for determining total plutonium and the relative concentrations of each oxidation state of plutonium are based upon this extraction separation.[46]

The extraction coefficients of metal ions are directly dependent upon the amount of the TTA chelate formed, which, in turn, is dependent upon acidity, TTA concentration, stability of the complex, and concentrations of other complexing ions in the solution. In these chelate extraction systems, the quantitative formation of the complex between

Table 2 19—EXTRACTION COEFFICIENTS FOR VARIOUS METAL IONS INTO TBP[199]

Ion	Aqueous phase	TBP concentration, %	Extraction coefficient at 25°C
Fe (III)	2.0*M* HNO_3	12. 5	0. 003
Na (I)	2.0*M* HNO_3		0. 003
Zr (II)	2.0*M* $Zn(NO_3)_2$		0. 0001
Al (III)	4.7*M* HNO_3	15	0. 0003
Ca (II)	4.7*M* HNO_3		0. 0003
Fe (II)	4.7*M* HNO_3		0. 005
Mg (II)	4.7*M* HNO_3		0. 0003
Pu (III)	5.0*M* HNO_3	20	0. 012
Pu (IV)	5.0*M* HNO_3		16. 6
Pu (VI)	5.0*M* HNO_3		2. 7
U (IV)	4.0*M* HNO_3	25	10
U (VI)	4.0*M* HNO_3		23
Am (III)	4.0*M* HNO_3	30	0. 013
Np (IV)	4.0*M* HNO_3		3. 0
Np (VI)	4.0*M* HNO_3		12. 0
Th (IV)	4.0*M* HNO_3		2. 8
Ru (IV)	2.0*M* HNO_3		0. 15
Zr (IV)	2.0*M* HNO_3		0. 09
Nb (V)	2.0*M* HNO_3		0. 03
Rare earths (III)	2.0*M* HNO_3		0. 02

the metal ion in the aqueous phase and the chelating agent in the organic phase is not instantaneous. Therefore, extraction times of 15 to 30 min are generally employed, as compared to times of 3 to 5 min for ion association systems. The effects of some of these variables are illustrated in Table 2.20. The extractabilities of some other metal ions are given in Table 2.21. Because the extent of the reaction of TTA with an M(IV) ion is inversely proportional to the fourth power of the hydrogen-ion concentration, only the metals forming highly stable TTA complexes are extracted from strongly acid solutions. By careful control of pH, highly selective separations can be achieved, as in the extraction from solutions more acid than pH 2.5 of Np(IV) and Pu(IV), but not Am(III). The latter is then extracted[205] at a pH greater than 3.4. For metals that have similar extractabilities in a particular oxidation state, good separations result following the selective adjustment of oxidation state of one of the metals. For example, separation of Pu(IV) from Zr(IV), which coextracts into the organic phase, is effected by stripping the plutonium with a reducing agent.[186] Separation of neptunium and plutonium is achieved

Table 2.20—EFFECTS OF ACIDITY, TTA CONCENTRATIONS, COMPLEXING IONS, AND PLUTONIUM OXIDATION STATES ON EXTRACTION COEFFICIENTS FOR PLUTONIUM [199]

Organic phase	Aqueous phase	Complexing agent, moles/liter	Extraction Coefficients		
			Pu(III)	Pu(IV)	Pu(VI)
0.5*M* TTA, xylene.	0.1*M* $HClO_4$	----------	----------	----------	0.35
	1.0*M* $HClO_4$	----------	----------	4.4×10^{5}	3.5×10^{-3}
	5.0*M* $HClO_4$	----------	----------	3.5×10^{3}	----------
	10.0*M* $HClO_4$.	----------	----------	4.0×10^{2}	----------
0.5*M* TTA, xylene.	1.0*M* HCl	----------	----------	5×10^{5}	----------
0.1*M* TTA, xylene.	----------	----------	----------	800	----------
0.05*M* TTA, xylene.	----------	----------	----------	50	----------
0.005*M* TTA, xylene.	----------	----------	----------	0.005	----------
0.5*M* TTA, xylene.	0.5*M* HNO_3	0.002*M* $C_2O_4^{-2}$.	----------	448	----------
		0.2*M* $C_2O_4^{-2}$.	----------	0.003	----------
		0.024*M* F^-.	----------	11.4	----------
		0.12*M* F^-.	----------	0.07	----------
0.5*M* TTA, xylene.	0.5*M* HNO_3	0.2*M* PO_4^{-3}.	----------	62.6	----------
		1.9*M* PO_4^{-3}.	----------	0.012	----------
		0.2*M* SO_4^{-2}.	----------	1.4×10^{2}	----------
		1.7*M* SO_4^{-2}.	----------	146	----------
0.5*M* TTA, xylene.	0.5*M* HNO_3	----------	2×10^{-5}	1×10^{6}	1.6×10^{-2}

following their reduction with Fe(II) and hydroxylamine to the extractable Np(IV) and the nonextractable Pu(III).

In a typical separation procedure, plutonium is reduced with Fe(II) and hydroxylamine and then oxidized with nitrite to obtain the (IV) oxidation state exclusively. The Pu(IV) is extracted from 0.75*M* nitric acid into 0.5*M* TTA-xylene, the extract is washed with 0.5*M* nitric acid containing 1.5*M* sodium nitrite to remove uranium, and the plutonium is back extracted into 8*M* nitric acid, leaving zirconium and iron in the organic phase.

Table 2.21—EXTRACTION COEFFICIENTS [199] FOR VARIOUS METAL–TTA COMPLEXES AT 25°C

(Organic phase, 0.5*M* TTA-xylene; aqueous phase, nitric acid)

Ion	Nitric acid, moles/liter	Extraction coefficient
Am(III)	1.0	10^{-9}
Al(III)	1.0	10^{-20}
Fe(II)	1.0	<0.001
Fe(III)	1.0	375
Ce(III)	1.0	10^{-5}
Ce(IV)	1.0	10^{3}
Zr(V)	1.0	10^{7}
	8.0	250
Na(I)	1.0	10^{-20}
Nb(V)	1.0	0.4
U(VI)	1.0	3×10^{-5}
Pu(III)	1.0	3×10^{-6}
Pu(IV)	1.0	10^{4}
	8.0	<0.01
Pu(V)	1.0	$<1\times10^{-4}$
Pu(VI)	1.0	0.004

Although not as widely used as TTA, the chelating agent cupferron has found applications in the separation of plutonium from other elements. The extraction of plutonium cupferrate into an ether-chloroform mixture separates plutonium from most metallic impurities [47] and also from Am(III).[167] This separation is used to concentrate minute traces of plutonium in its radiochemical determination in waters.[206]

(4) *Organo–Nitrogen and Organo–Phosphorus Compounds.* An increasing number of applications of the extraction of plutonium into organo–nitrogen and organo–phosphorus compounds have been reported (Refs. 44, 195–197, 207, and 208). Of these, the extractions into triisooctyl amine or tri-*n*-octyl amine are probably the most useful in analytical chemistry methods.

For extractions into tri-*n*-octyl amine and trilauryl amine from nitric acid solutions, Pu(IV) is the oxidation state most completely extracted.[207, 208] Generally, nitrite ion is the holding oxidant for the (IV) oxidation state. By proper choice of oxidants and reductants, separation from most ions is effected. Extraction coefficients for plutonium between 10 per cent tri-*n*-octyl amine and 2*M* nitric acid are 90, 0.04, and 1.8 for the (IV), (III), and (VI) oxidation states, respectively. Distribution coefficients for other systems of this type have been compiled.[196]

(c) *Ion Exchange.* Plutonium is absorbed on either cation- or anion-exchange resins, depending upon the oxidation state and concentration of the acid and also of the complex-forming substances in the influent solution. Several separation methods are based on these properties. Because separations from a wider variety of metal ions are possible using anion-exchange resins, their use is more prevalent, but many specific applications of cation-exchange resin separations also exist. For example, elution with 13.3*M* hydrochloric acid separates the actinide elements as a group from the lanthanides, a separation based on the fact that the former elements more readily form anionic chloride complexes and are eluted first from cation-exchange resins.[209] Plutonium is separated from stainless-steel decladding solutions of fuel elements using Dowex-50 cation-exchange resin with sulfuric acid solutions.[166] Uranium(VI) is eluted rapidly from silica gel columns by 30 per cent TBP, which leaves Pu(III) on the column.[210]

In the separation of plutonium from stainless-steel decladding solutions on a laboratory scale,[211] the plutonium is adsorbed on Dowex-50 cation-exchange resin following dilution of the decladding solution to 0.5*M* sulfate-ion concentration. Elution with 6*M* nitric acid provides a product solution containing 99 per cent of the plutonium and 4 per cent of the stainless steel. The uranium in the plutonium-free decladding solution is oxidized with Fe(III) and adsorbed on a Dowex-1 anion-exchange resin column. Elution with nitric acid recovers greater than 99 per cent of the uranium, which contains less than 0.01 per cent of the stainless-steel components. The behavior of fission products was determined by carrying trace amounts of gross fission products [3.7×10^4 (beta) and 5.3×10^4 (gamma) counts/min/ml] in a stainless-steel solution 0.7*M* in sulfate through the separation process. Greater than 70 per cent of the fission products followed the plutonium, and 18 per cent appeared in the first feed effluent and scrub solutions. Following the anion-exchange separation, the uranium-product solution contained about 1 per cent of the fission products, indicating the greater separation efficiency by anion exchange for samples of this type. For separations in which the purification of plutonium is the main objective, anion-exchange resins are more frequently used.

Because the relative orders of absorption on cation-exchange resins among the oxidation states of plutonium are (IV) > (III) > (VI) > (V), selective separations can be made by changing the oxidation state. In high concentrations of mineral acids, especially nitric and hydrochloric acids, plutonium forms anionic complexes, which are not held by cation-exchange resins. Therefore, influent solutions are generally weakly acid, and eluants are strongly acid or contain

complexing agents. The absorption of plutonium as a function of acidity is shown in Table 2.22. Complexing agents that serve as eluants include citrate, lactate, tartrate, ethylenediaminetetraacetate, and fluoride.

The anion complexes of plutonium with strong nitric and hydrochloric acid are absorbed quantitatively by anion-exchange resins. The order of absorption among the plutonium oxidation states is (IV) > (VI) > (III).

Although the absorption of plutonium and other metal ions is highly dependent upon oxidation state and acid concentration, separations based upon selective reduction or oxidation of plutonium, or upon a change in the acidity to destroy the anion complex, are commonly employed. For the nitrate system, a typical separation consists of absorption of Pu(IV), and Pu(VI) if present, on a strongly basic anion-exchange resin from 7*M* to 10*M* nitric acid and elution of the plutonium with dilute acid, or a solution of a reductant or a complexing agent. Appropriate reductants are hydroxylamine-nitrate or ferrous sulfamate. Dilute fluoride ion, as well as organics such as EDTA, citrate, or tartrate, have also been used as complexing eluants. If hydrochloric acid systems are employed, the best separations result when the influent solution is 12*M* in hydrochloric acid and the eluant is 12*M* hydrochloric acid containing 0.25*M* hydriodic acid, which selectively reduces plutonium to the (III) oxidation state.[212, 213] Dilute hydrochloric acid, solutions of complexing agents, or other eluants also remove plutonium from the anion-exchange resin, but the separation is not as selective. The absorption behaviors of several metals on the anion-exchange resin Dowex-1 as a function of acid concentration are given in Table 2.23.

Table 2.22—RELATIVE ELUTION RATES OF PLUTONIUM FROM CATION-EXCHANGE RESINS [187]

Resin	Influent solution	Volume of eluant,* ml		
		Pu(III)	Pu(IV)	Pu(VI)
Dowex-50	3.6*M* H_2SO_4	3.7	----------	----------
	0.25*M* H_2SO_4	>1000	----------	----------
Duolite C-65	0.5*M* H_2SO_4	5.3	35	----------
Dowex-50	3.2*M* HCl	102	>1000	8.2
	6.2*M* HCl	27	70	2.8
	9.3*M* HCl	20	7	2.0
	12.2*M* HCl	12	7	2.0

*Relative volume required for complete elution.

Table 2.23—ABSORPTION BEHAVIOR OF ELEMENTS ON DOWEX-1 ANION-EXCHANGE RESIN [41, 189, 221]

Acid	Elements not absorbed	Acid conc., moles/liter	Elements partially absorbed	Acid conc., moles/liter	Elements completely absorbed	Acid conc., moles/liter
HCl	Ac, Al, Am(III), Be, Ca, Ce, Cs, Eu, Fr, K, La, Li, Mg, Mn(II), Na, Ni, *Pu*(III), Ra, Rb, Re(III), Sr, Th, Y.	0.1 to 12	Fe(III), Mo, *Pu*(IV)	0.1 to 3	Ag, Nb	1 to 8.
			Ge	1 to 12	Cu(I), Tc(VII)	2 to 10.
			Pa, Np(IV)	1 to 5	Cu(II), Fe(III), Ga, In, Mo(VI), Os, Pd, *Pu*(IV), Re(VII), Rh, Ru(IV), Zn.	3 to 12.
			U	2 to 12		
			Zr	3 to 8		
			Cd, Co	5 to 12		
			Ca, Cr(III), Mn(IV), Pb, Sc(III), Ti(III), V(IV).	12	Np(IV), Pa, Ta	5 to 12.
					Fe(II), Zr	8 to 12.
					Cr(VI), Hf, Sb, Sn, Te(IV), Ti(IV).	10 to 12.
					Cd, Co, U	12.
HNO_3	Al, Am(III), B, Ba, Be, Ca, Cm(III), Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, *Pu*(III), Rb, Rh, Ru, Sc, Sm, Sr, Tb, Te, Ti, Tm, V, Y, Yb.	0.1 to 15	*Pu*(IV)	1 to 3	Ag	1 to 2.
			As	1 to 5	Re	1 to 3.
			Nb, Pt, Sn, Tl, Zn, Zr.	1 to 14	Hg	1 to 4.
			Np(IV)	2 to 4	Pd	1 to 8.
			Ag	2 to 14	Bi	1 to 11.
			Re, Th	3 to 4	Au	1 to 14.
			Ce	4 to 8	*Pu*(IV)	3 to 14.
			Hg, U	4 to 14	Np(IV), Th(IV)	4 to 14.
			Pd	8 to 14		
			Bi	11 to 14		

Sequential separations of several elements and plutonium are possible using anion-exchange resins and various eluants. In the radiochemical determination of the fission-product elements and plutonium in irradiated uranium fuel, zirconium is eluted first from Dowex-2×8 anion-exchange resin with 12*M* hydrochloric–0.06*M* hydrofluoric acid, niobium and plutonium elute together with 6.0*M* hydrochloric–0.06*M* hydrofluoric acid, and uranium and tellurium (IV) are eluted with 0.1*M* hydrochloric–0.06*M* hydrofluoric acid. Finally, molybdenum is eluted with 12*M* nitric acid.[214] Additional separations are possible by including phosphoric acid solutions as eluants in this sequential separation method.[215] Americium, thorium, plutonium, and neptunium are separated by successive elution from Dowex-1 anion-exchange resin with 8*M* nitric acid, 12*M* hydrochloric acid, 12*M* hydrochloric acid–0.1*M* ammonium iodide, and 4*M* hydrochloric acid, respectively.[216]

Other applications of anion-exchange methods include separations of plutonium from americium,[217, 218] fission-product elements,[82, 219] irradiated uranium,[40] and from trace impurities which are then determined spectrographically.[40, 42]

2–3.3 Determination of Plutonium in Uranium Fuels

(a) *Isotopic Dilution–Mass Spectrometer Method.* This new method, which promises to be one of the most versatile for determining plutonium in dissolver solutions, has been applied in this capacity only to a limited extent, mostly by the British.[220] Modifications of the basic method are being actively investigated now, and the method will undoubtedly attain greater importance in the future. The method has the advantages of: (1) requiring only a very small sample (10^{-6} to 10^{-8} g of plutonium), which permits removal of the samples from hot-cell facilities following initial separations; (2) simultaneous determination of both the plutonium concentration and isotopic population; (3) quantitative separations are not required; and (4) good precision is obtainable (coefficient of variation as low as 0.2 per cent in determining 0.1 μg is routinely possible). Disadvantages include the high cost of the mass spectrometer and the need for the Pu^{242} isotope of good (98 per cent) purity. This isotope is prepared by prolonged irradiation of Pu^{239} in a high-flux reactor. The amount of Pu^{242} produced in several years of irradiation is only about 2 percent of the original Pu^{239} target. Although the yield is poor, the need is not great because only 0.1 μg of the tracer is used per analysis.

Procedure. An aliquot of the dissolver solution is diluted with 3*M* nitric acid to a volume in which the plutonium concentration is about 0.1 μg/g. A 2-g aliquot of the dilute solution and a 2-g aliquot of a

solution containing 0.1 μg of the Pu^{242} tracer per gram are weighed into a polyethylene bottle. After the solution has been thoroughly mixed, one-half the solution is taken for analysis; the remainder is reserved for future analysis if required. At this point the concentrations of the fission-product elements are sufficiently dilute that the sample may be removed from shielded facilities without causing a radiation hazard. Nitric acid is then added to the sample solution until the acidity is 8*M*, and the solution is passed through an anion-exchange resin column to absorb the plutonium. Uranium and fission-product elements are washed from the resin with seven column volumes of 8*M* nitric acid. Then the plutonium is eluted with 0.1 per cent hydroxylamine hydrochloride in 1*M* hydrochloric acid. Plutonium recoveries are usually greater than 90 per cent, and contamination by uranium and fission products is reduced to less than 0.01 per cent and 1.0 per cent, respectively. Thus the plutonium fraction should consist approximately of 0.1 μg each of Pu^{239} and Pu^{242}, 0.01 to 0.03 μg of uranium, and 0.1 to 0.2 microcurie of fission-product gamma activity, depending on the starting concentrations.

The plutonium fraction from the column is evaporated to small volume and then transferred dropwise to an indented microscope slide treated with silicone. Each drop is evaporated to dryness under an infrared heater before the next drop is added. Hydroxylamine in the residue is destroyed by nitric acid, and the plutonium is transferred to the sample filament of a mass spectrometer source unit. A multiple-filament source unit with electron multiplication is recommended for the mass spectrometer measurements.

If the concentration of the Pu^{242} in the sample solution is either unknown or high, it must be determined by analyzing an aliquot to which no Pu^{242} tracer has been added. With this analysis as a basis, the mass spectrometer results are then corrected.

The yield from the separation process, as determined from the recovery of the added Pu^{242}, and the measured isotopic populations are sufficient data to permit calculation of the chemical atomic weight and the concentration of the plutonium in the original sample, using the following equation:

$$W = YD(R_M - R_T)(239/242)(100/P)(\text{mass tracer/mass dilute sample})$$

where:

W = concentration of total plutonium in the original solution
D = dilution factor
P = the mass percentage of Pu^{239} in the sample
Y = the concentration of the Pu^{242} tracer
R_M = the Pu^{239}/Pu^{242} ratio for the mixture of sample and tracer
R_T = the Pu^{239}/Pu^{242} ratio for the tracer.

In addition to the anion-exchange resin separation of the plutonium, other methods or combinations of methods are applicable. Frequently the anion-exchange resin method is followed by a TTA

extraction separation to effect a cleaner separation. Extraction of the plutonium from an acid-deficient solution of the uranium fuel into hexone using aluminum nitrate as a salting agent has also been employed to obtain a clean sample.

More recently, the mass spectrometer method was applied to the simultaneous determination of plutonium and uranium in simulated dissolver solutions.[220a] The uranium and plutonium are separated by batch liquid–liquid extraction to provide a uranium–plutonium fraction free of fuel cladding components, americium, and curium. The method also provides chemical control of the uranium to plutonium atom ratio; therefore both elements can be determined with a single loading of the mass spectrometer filament. The coefficient of variation in measuring either plutonium or uranium is about 1 per cent.

Procedure. Following the addition of known quantities of U^{233} and Pu^{242} isotopes, uranium and plutonium in the sample are oxidized by permanganate to their (VI) oxidation states, in which form they are selectively extracted as the tetrapropylammonium complexes into methyl isobutyl ketone. The organic phase is separated, tetrahexylammonium iodide is added to it, and the uranium and plutonium are stripped into hydrochloric acid. By the careful selection of the concentration of the hydrochloric acid solution, the uranium to plutonium atom ratio can be chemically controlled. For example, if the ratio in the original solution is 250 to 1, a final ratio of 12.6 to 1 is obtained by this separation process when 4*N* hydrochloric acid is used. To the aqueous phase are then added a few drops of hydrogen peroxide and nitric acid, and the solution is evaporated to fumes. The uranium and plutonium are determined by multiple-filament mass spectrometry in which the singly charged metal ions are measured.

(b) *Thenoyltrifluoroacetone Extraction–Alpha-counting Method.* Direct alpha counting, in which an aliquot of the dissolver solution is evaporated to dryness on a counting disk and the total alpha radiation is counted, is frequently employed for estimating the plutonium concentration in the dissolver solution. It is obvious from the compositions of the dissolver solutions given in Table 2.14 that the total alpha-counting method suffers from several possible errors caused by the high salt concentrations and the presence of other highly radioactive isotopes. Therefore, a separation of the plutonium is to be recommended for more accurate analyses. Extractions into TTA are generally favored for this separation.

In a typical determination (Refs. 46, 58, 222–225), the higher oxidation states of plutonium are reduced with hydroxylamine to Pu(III), which is then oxidized with nitrite ion to Pu(IV) and extracted from 0.7*M* to 0.8*M* free nitric acid into TTA in xylene. An aliquot of the extract may be evaporated on a counting disk, ignited, and alpha counted; or the plutonium may be back extracted

into 10*M* nitric acid, and an aliquot of this aqueous phase taken for counting. Under the conditions of this extraction, plutonium is quantitatively recovered, but americium, curium, neptunium, and most of the uranium and thorium remain in the first aqueous phase. Addition of aluminum nitrate eliminates the interference caused by anions such as sulfate, phosphate, fluoride, and oxalate. Zirconium and niobium interfere and should be removed from the aqueous phase by extraction into TTA-xylene. To prevent the coextraction of the plutonium, it is oxidized to the (VI) oxidation state with Cr(VI). The plutonium that remains in the aqueous phase is then reduced and extracted as described above. The method applies specifically to the determination of plutonium in dissolver solutions, uranium-product solutions, and waste streams having high salt concentrations. The coefficient of variation of a single determination of plutonium in a dissolver solution is 0.8 to 1.0 per cent.

Procedure. A 0.100-ml aliquot of the dissolver solution is diluted to 10 ml with 1*M* nitric acid, and a 0.500-ml aliquot of the diluted solution is transferred to a 10-ml vial containing 1 ml of 2*M* nitric acid. Following the addition of 0.20 ml each of 5*M* hydroxylamine hydrochloride and 0.1*M* Fe(III) nitrate solutions, the solution is warmed at 80°C for 15 to 20 min to reduce the plutonium and to destroy any plutonium polymers that may be present. (If fluorides, phosphates, sulfates, or oxalates are known to be present, 0.25 ml of 2*M* aluminum nitrate is added.) The solution is cooled, and 1 ml of 1.5*M* sodium nitrite is added. After the solution has been stirred for 5 to 10 min, 1 ml of 0.5*M* TTA-xylene is added to the vial, and the mixture is stirred for 15 min before the organic phase is transferred to a second 10-ml vial. (In an alternate method, an aliquot of appropriate size is taken from the 1-ml organic phase, is transferred to a counting plate, evaporated, ignited, and alpha counted.) The aqueous phase is washed successively with three 0.50-ml volumes of 0.5*M* TTA-xylene, and these washes are combined with the original organic phase. The combined organic phase is washed with 1 ml of 1*M* nitric acid, and the wash is discarded. The organic phase is then scrubbed with 1 ml of 10*M* nitric acid for 15 min, and the aqueous phase is transferred to a 10-ml volumetric flask. The organic phase is washed with 0.50 ml of 10*M* nitric acid for 30 sec, the washings are added to the volumetric flask, and the solution is diluted to 10 ml with water. A 0.100-ml aliquot of this solution is evaporated on a 22-mm stainless-steel disk which is flamed, and the alpha activity is counted. Using the observed count rate, the factors for counter geometry, the specific activity of plutonium, and the dilution of the sample, the plutonium content is then calculated.

An analysis by mass spectrometer techniques is recommended to obtain the isotopic composition of the plutonium which is required in the above calculations. Because it is necessary to provide a pure sample for the determination of the isotopic population, the sample

should be taken following the separation of the plutonium. This is conveniently done by taking an aliquot of the dilute nitric acid solution into which the plutonium is back extracted in the final step of the above separation method. In the alternate separation procedure, the sample is taken from the organic extract of the plutonium. The aliquot should be treated in accordance with the specifications provided by the mass spectrometer section and submitted to them for analysis. The determination of isotopic populations using the mass spectrometer is discussed in Chap. 13.

(c) *Hexone–Thenoyltrifluoroacetone Extraction–Alpha-counting Method.* Recently, an alternate method [226] for the determination of plutonium in uranium–fission-product mixtures was developed in which the TTA extraction is coupled with an extraction of Pu(VI) into methyl isobutyl ketone to effect cleaner separation of the plutonium before it is alpha counted. The plutonium is oxidized with Mn(VII) and extracted from an acid-deficient aluminum nitrate solution into hexone as a tetra alkyl ammonium trinitrate complex. Following reduction and back-extraction into a hydroxylamine-Fe (II) solution, the plutonium is oxidized to the (IV) oxidation state with nitrite, extracted into TTA-xylene, and determined by a method similar to the method described above. The average recovery of plutonium is 98.8 per cent with a coefficient of variation of 0.8 per cent, and fission-product decontamination is greater than 1×10^4. Carry-through of uranium is less than 0.05 per cent.

Procedure. A salting solution is prepared by dissolving 1050 g of aluminum nitrate nonohydrate by warming in a final volume of 800 ml of water. Then 135 ml of 14.8*M* ammonium hydroxide is added, and the solution is stirred and cooled to less than 50°C. Fifty milliliters of 10 per cent tetrapropylammonium hydroxide reagent are added before the solution is diluted to 1 liter with water.

Six milliliters of the salting solution, 0.1 ml of 0.05*M* potassium permanganate solution, 1 ml or less of the sample, and 3 ml of hexone are added to a 15- × 125-mm test tube, which is then stoppered with a polyethylene stopper. The two phases are mixed vigorously for 5 min to effect extraction and then centrifuged to separate the phases. Two milliliters of the organic phase is transferred to a second test tube, and 3 ml of 3.125*M* nitric acid and 2 ml of 1.25*M* hydroxylamine hydrochloride solution are added. The tube is stoppered, and the two phases are mixed for 10 min. After centrifuging to separate the phases, 2 ml of the aqueous phase is transferred to a 50-ml centrifuge cone, and 0.1 ml of freshly prepared 0.2*M* Fe(II) sulfate solution is added. After 5 min, 3 ml of freshly prepared 0.22*M* sodium nitrite solution is added, and gas evolution is then allowed to subside. Five milliliters of 0.5*M* TTA-xylene is added, and the mixture is stirred vigorously for 20 min. An aliquot of the organic phase is transferred to a counting disk, dried, ignited, and alpha counted.

(d) *Ion-exchange Resin Separation–Alpha-counting Method.*[226a] A highly selective method for determining plutonium in dissolver solutions combines an anion-exchange resin separation of plutonium from uranium and fission-product elements with a cation-exchange resin cleanup of the separated plutonium. The method was tested using synthetic dissolver solution samples containing between 2 and 200 mg of uranium and having not greater than 4500 disintegration per min of Pu^{239}. A plutonium recovery of 92 per cent, which was not affected by quantities of uranium of 200 mg or less, was obtained.[226a]

Procedure. The plutonium in the (IV) oxidation state, in a 7*M* nitric acid solution of the irradiated uranium, is adsorbed on a Dowex-1 anion-exchange resin column, and the uranium and fission product elements are washed out of the column with additional 7*M* nitric acid. The plutonium is eluted with a 5 percent hydroxylamine solution, and this eluate is passed through a Dowex-50 cation-exchange resin column. The hydroxylamine is washed from the column with 0.3*M* nitric acid, and the plutonium is eluted with 7*M* nitric acid. An aliquot of the final eluate is evaporated on a suitable counting plate, and the plutonium is measured by alpha counting.

In addition to the radiochemical determinations involving extraction or ion-exchange separations of plutonium from dissolver solutions, there are several applications of coprecipitation separations, generally with lanthanum trifluoride, to reactor fuel reprocessing solutions.[226b, 226c] The precipitate is mounted directly on stainless steel counting plates and the alpha activity determined using scintillation counting equipment. However, other alpha emitters interfere in this simple method; thus one of the previously described methods probably is better.

(e) *Anion-exchange Resin Separation–Spectrophotometric Method.*[226d] Plutonium is determined in uranium fuels that have undergone a long irradiation by the separation of the plutonium using anion-exchange resin and measuring the absorbance of Pu(III) at a wave length of 602 mμ. This method reportedly has a negative bias of about 0.2 per cent and a coefficient of variation of 0.7 per cent in the determination of 1.5 to 4 mg of plutonium. The method is readily adaptable to remote operation.

Procedure. An aliquot of dissolver solution containing between 1.5 and 4 mg of plutonium is adjusted to 8*M* in nitric acid and passed through a 2-ml column of Dowex-1, 250 to 350 mesh, anion-exchange resin in the nitrate form. The column is washed with five 2-ml portions of 10*M* nitric acid followed by one column volume of 1*M* nitric acid. The plutonium is eluted with 5 ml of 10 per cent hydroxylamine nitrate. The eluate is centrifuged, transferred to a 5-cm cell, and the absorbance is measured at a wave length of 602 mμ. The plutonium concentration is obtained from a calibration curve prepared from data obtained for known plutonium solutions.

The extraction separation–indirect EDTA titration method,[77a] as described in Sec. 2–2.5(b)(2), has been applied to irradiated uranium reactor fuels. This extraction separation is highly selective for plutonium; the two-stage extraction cycle results in a decontamination factor of approximately 10^5 from fission products and 10^2 from plutonium.

The plutonium content of irradiated natural uranium may also be determined using an alpha spectrometer.[226c] The irradiated sample is dissolved in acid, and an aliquot is evaporated in a thin film on a stainless-steel counting plate. The amount of Pu^{239} is determined from the alpha spectra with the U^{234} and U^{238} peaks being used as interna standards. The method is efficient for Pu^{239} to U^{234} atom ratios between 0.1 and 1.0.

Promising results have been obtained in applying a controlled-potential coulometric method to the determination of plutonium in Purex dissolver solutions of uranium-aluminum and uranium-aluminum-nickel fuels and Sulflex dissolver solutions of uranium–stainless-steel fuel.[58] A preliminary separation is required in which Pu(IV) is absorbed on anion-exchange resin, such as Dowex-1, from $8M$ nitric acid solution. After the column has been washed with $8M$ nitric acid, the plutonium is eluted with $0.5M$ nitric acid–$0.02M$ hydroxylamine, the eluate is evaporated, and the plutonium is finally determined by coulometric titration. A coefficient of variation of about 1 per cent has been reported for this determination.[58] Other preliminary work in applying the controlled-potential coulometric titration technique to similar samples without separation of the plutonium is also being undertaken.[227] For dissolver solutions of fuels having less than 1000 Mwd exposure, the coefficient of variation for a single determination is 1 per cent, provided the iron/plutonium concentration ratio does not exceed 10. Routine application of this method has not been made.

2–3.4 Analysis of Experimental Plutonium Fuel Materials

Although several alloys, ceramics, and cermets containing plutonium possess properties that make them attractive as possible reactor fuels, only a few of these materials have been developed sufficiently to be used as fuels in experimental reactors. These materials include alloys of plutonium with aluminum, iron, uranium and molybdenum, or uranium and fission-product elements and ceramics composed of plutonium dioxide or plutonium–uranium dioxide.[227a] The use of some of these materials is so recent that methods for their analysis have not appeared in the literature. The few analytical methods that are published generally were developed by combining existing methods for determining plutonium (see Sec. 2–2.5) with methods for determining the other constituents. Therefore, all that is

required here, with few exceptions, is to indicate the applicable methods and any modifications or separations required.

For the spectrochemical determinations of trace impurities, modifications to the methods for analyzing high-purity plutonium are required because the alloying elements change the characteristics of the sample matrix and affect its burning. In carrier-distillation methods standards with compositions similar to the samples are required. In the methods in which the impurities are concentrated prior to their determination, the separation methods, such as cupferron extraction or ion exchange, must be tested or modified for use with the alloy in question. For example, in the carrier-distillation determination of trace impurities in the plutonium oxide–uranium oxide mixtures, standards containing the appropriate concentrations of the two oxides are necessary. In the analysis of plutonium-aluminum alloy, aluminum would not be removed as the cupferrate, and a modification in the cupferron extraction–copper-spark method is necessary. The separation methods employed in the spectrochemical determinations of impurities in aluminum should be referred to in selecting a separation method to be used with this alloy.

(a) *Plutonium–Aluminum Alloy.* Most of the methods for determining plutonium should apply to plutonium-aluminum alloys. Aluminum, even at high concentrations, does not interfere with the potentiometric titration of plutonium using Ce(IV) solutions as titrants or with the controlled-potential coulometric titration, and these methods are recommended for precise determinations. For alloys containing low concentrations of plutonium, direct alpha counting is a rapid method, but absorption of the alpha particles by the aluminum reduces the accuracy of the method. Following separation of the plutonium by an appropriate method, such as extraction into TTA-xylene, alpha-counting methods are applicable to most samples without serious errors. X-ray absorption, spectrophotometric determination as the chloride or nitrate and volumetric titrations are among the other methods that should apply to the determination of the plutonium over a wide range of alloy compositions. For low concentrations of plutonium, a preliminary separation may be advisable. Because aluminum is not absorbed from nitric acid or hydrochloric acid systems onto anion-exchange resin under conditions which ensure quantitative absorption of plutonium, this separation method may be used to permit the subsequent application of any of the methods for determining plutonium.

Several methods are also available for determining the aluminum. Spectrophotometric methods are generally used to determine low concentrations of aluminum after the plutonium has been removed

either by anion exchange, precipitation, or extraction. In one anion-exchange method,[228] the plutonium in the (IV) oxidation state is absorbed from 8*M* nitric acid on strongly basic anion-exchange resin, the effluent is evaporated to fumes with perchloric acid, and any iron impurity is extracted at pH 9.2 into chloroform as the 8-hydroxyquinaldinate. Aluminum, as the oxinate, is then extracted into chloroform and measured spectrophotometrically at a wave length of 390 mμ. In a spectrophotometric method in which aluminon is used as the color reagent,[229] plutonium is first removed by precipitation as the iodate, and iron is removed by electrolysis. In still another method, plutonium is separated as the cupferrate by extraction into chloroform, and the aluminum, which remains in the aqueous phase, is determined spectrophotometrically as the oxinate.[230]

Gravimetric and titrimetric methods are also available for determining aluminum, and these methods are favored for determining greater than trace concentrations of the element. In a recently developed method reportedly applicable to remote-control operations, aluminum is determined gravimetrically as the oxinate or titrimetrically using oxine or ethylenediaminetetraacetic acid (EDTA) as the titrant.[231] To a solution containing about 5 mg of aluminum in 2 ml of 8*M* hydrochloric acid is added 2 ml of concentrated nitric acid to oxidize the plutonium to the (IV) oxidation state; the solution is then transferred to a strongly basic anion-exchange resin column (Dowex 1 X 4, 50 to 100 mesh), 35 cm long and 2.2 cm in diameter, which has been washed with 8*M* hydrochloric acid. The aluminum is washed from the column with 60 ml of 8*M* hydrochloric acid at a flow rate of 2 ml/min and is determined by one of the following methods.

(1) *Gravimetric.* The eluate is neutralized with ammonium hydroxide to the yellow-blue color change of bromphenol blue indicator, and then hydrochloric acid is added to the blue-yellow color change. In a modification of a procedure described by Kolthoff and Sandell,[232] aluminum is precipitated by adding oxine in 8*M* hydrochloric acid and heating the solution almost to boiling. Then the precipitate is filtered. In determining 5 mg of aluminum, an average recovery of 5.03 mg and a coefficient of variation of 2.2 per cent were reported.

(2) *Titrimetric.* The titration of aluminum in the eluate with oxine is similar to the procedure of Kolthoff and Sandell.[232] In the titration with EDTA, 5.0 ml of 0.1*M* EDTA is added, and the eluate is neutralized by adding sodium hydroxide to the bromcresol green end point. The solution is buffered with sodium acetate-acetic acid

buffer, and the excess EDTA is titrated with standard zinc acetate solution.

Nickel and chromium(III) interfere in these determinations, but the interference caused by nickel is eliminated by adding dimethylglyoxime or cyanide. Chromium is oxidized to the (VI) oxidation state, which does not interfere. The oxine titrimetric and the EDTA titrimetric method each showed an average recovery of 4.98 mg from 5-mg samples. Coefficients of variation of 1.9 and 0.6 per cent were reported for the respective methods.

(b) *Plutonium–Iron Alloy.* Because of the interference caused by iron, most of the methods for determining plutonium are not applicable to plutonium–iron alloys. For iron concentrations greater than 0.5 per cent, a separation is required before plutonium can be determined by titration of Pu(III) with Ce(IV). This separation is accomplished by electrolysis of the iron using a mercury cathode cell. Iron does not interfere in the potentiometric or the amperometric titration methods in which Pu(VI) is titrated with Fe(II) solution, and therefore they are recommended for the precise determination of plutonium [see Sec. 2–2.5(a)]. Controlled-potential coulometric titration or radiochemical methods also are applicable. The comments concerning the radiochemical determination of plutonium in plutonium–aluminum alloys apply to plutonium–iron alloys. However, because the plutonium–iron fuels considered to date contain greater than 95 per cent plutonium, direct alpha-counting methods are frequently used. Iron in these plutonium-rich alloys is determined spectrophotometrically as the *o*-phenanthrolate without separation from the plutonium. However, the iron is readily separated by extraction as Fe(III) chloride or by anion-exchange methods [see Sec. 2–3.2(c)]. Then any of the usual methods for determining iron can be used.

(c) *Plutonium–Uranium–Molybdenum Alloy.* The alloy is dissolved in hydrochloric and nitric acids, and the final nitric acid concentration is adjusted to 8*M*. The Pu(IV) is absorbed on anion-exchange resin (De-Acidite FF), and the molybdenum and uranium are eluted with 8*M* nitric acid. An aliquot of the eluate is evaporated to fumes with sulfuric acid, and the molybdenum is determined spectrophotometrically as the thiocyanate. Uranium is determined [242] in a second aliquot of the eluate by evaporation to fumes with sulfuric acid and measurement of the absorbance of the uranyl sulfate at a wave length of 430 mμ. The plutonium is then eluted from the column with hydroxylamine hydrochloride, and the absorbance of the Pu(III) chloride is measured at a wave length of 565 mμ. This method is applicable to a wide range of concentrations

of the three constituents. However, ratios of uranium to molybdenum concentrations greater than 100 cause errors in the determination of molybdenum. Coefficients of variation of approximately 1 per cent in determining plutonium or molybdenum and of 0.3 per cent in determining uranium in alloys containing between 50 and 90 per cent uranium, between 5 and 30 per cent molybdenum, and between 5 and 20 per cent plutonium have been reported.[233]

Several other methods are applicable for determining the three constituents of this alloy. Molybdenum is separated and determined using the dithiol or chloranilic acid spectrophotometric procedures described in Sec. 2–2.6(b). Molybdenum, if not separated, interferes in the titration of plutonium. However, following the ion-exchange separation described above, plutonium can be determined by any of the methods given in Sec. 2–2.5. Uranium, following its separation from plutonium, can also be determined by titration with Ce(IV) or spectrophotometrically as the Arsenazo complex.

(d) *Plutonium–Uranium–Fission-element Alloys.*[232a] Reprocessing of plutonium–uranium fuels by melting in a refractory oxide crucible and recasting leads to a fuel alloy containing percentage quantities of several fission product elements. Analysis of this alloy requires separation procedures which permit application of established methods of analysis. The alloy is dissolved in acids, preferably in hydrochloric acid followed by dropwise addition of hydrogen peroxide, and an aliquot is converted to 2*M* hydrochloric acid medium. Group VIII elements are reduced by magnesium metal and separated by filtration. Then uranium is extracted into carbon tetrachloride containing 30 volume per cent of tributylphosphate (TBP) and back-extracted into 0.2*M* hydrochloric acid. The aqueous phase is converted to nitrate solution, and the uranium is determined by the X-ray spectrometry method[109] described in Sec. 2–2.5(g)(2). Other methods for determining uranium should apply equally well to the separated uranium fraction.

To the aqueous raffinate, from which uranium is extracted, is added nitrite to oxidize the plutonium, and the Pu(IV) is extracted into 30 volume per cent of TBP in Amsco–140. The plutonium is back-extracted into 0.2*M* hydrochloric acid and reduced with hydroxylamine. The Pu(III) is precipitated as the hydroxide which is washed and dissolved in 16*M* nitric acid. The solution is heated to boiling to destroy plutonium polymers, then cooled and diluted. The absorbance of the Pu(IV) nitrate complex is measured at a wave length of 475 mμ. The plutonium concentration is obtained from a calibration curve prepared from data obtained for known solutions. The absorbance of the Pu(IV) is independent of nitric acid concentration

in the range between 2.3*M* and 3.5*M*. This method is applicable to plutonium having considerable variation in isotopic composition which would make simple radiochemical methods impractical. Other methods for determining plutonium also would apply.

In an alternate separation scheme for the determination of only the plutonium, Pu(III) is coprecipitated from a solution containing hydroxylamine by adding hydrofluoric acid. The precipitate is washed, dissolved in nitric acid–zirconium nitrate solution, and the plutonium is measured spectrophotometrically as before.

Coefficients of variation of 0.5 per cent for determining uranium and 0.8 per cent for determining plutonium by the extraction separation method were ascertained by analyses of solutions representing dissolved alloys containing 75 per cent uranium, 20 per cent plutonium, and 0.2 to 2.5 per cent each of molybdenum, palladium, rhodium, and ruthenium. A negative bias of 0.5 per cent for the plutonium analysis probably is attributable to incomplete reduction of the plutonium prior to the extraction of the uranium. A coefficient of variation of 0.7 per cent was obtained in determining plutonium by the coprecipitation separation–spectrophotometric method. No bias was reported.

(e) *Plutonium Dioxide–Uranium Dioxide Mixtures.* The main problem involved in the analysis of these oxide mixtures lies in dissolution. High-fired oxides require strenuous dissolution techniques, but low-fired oxides, especially if the plutonium content is low, can be dissolved in hot nitric acid or mixtures of nitric, hydrofluoric, and sulfuric acids. Several methods for dissolving oxides are given in Sec. 2–3.1. Several of the methods given in Sec. 2–2.5 are applicable for determining the plutonium without separation from uranium. Depending on the concentration involved, controlled-potential coulometric titration of radio-chemical determination is favored. There are several methods for separating plutonium and uranium. In one method [233] Pu(IV) is absorbed from 8*M* nitric acid onto an anion-exchange resin column, and the uranium in the effluent is determined spectrophotometrically as a uranyl sulfate complex in sulfuric acid. Plutonium, following its elution with hydroxylamine hydrochloride, is determined spectrophotometrically as Pu(III). In an alternate method applied to plutonium–uranium carbides and oxides, plutonium is separated by cation exchange resin techniques.[233a] Then the Pu(III) is absorbed from 0.3*M* nitric acid–0.05*M* hydroxylamine sulfate onto a Dowex-50 X 10, 200 to 400 mesh, resin column, uranium is washed from the column with 0.3*M* sulfuric acid–0.05*M* hydroxylamine, and the plutonium is eluted with 6*M* nitric acid–0.05*M* sulfamic acid. The separated plutonium is determined by

potentiometric titration [see Sec. 2–2.5(a)(6)]. It is obvious that, following separation of the two elements, uranium may be determined by any established method, such as titration with Ce(IV) or spectrophotometrically as the thiocyanate or Arsenazo complexes. Plutonium can be determined by any method described in Sec. 2–2.5.

Gamma spectrometry has been applied to the nondestructive determination of plutonium in ceramic fuel elements.[233b] The most energetic gamma ray of Pu^{239}, which has an energy of 384 kev, is counted in a gamma spectrometer using a sodium iodide scintillation crystal. A coefficient of variation of 0.3 per cent was obtained in determining plutonium in uranium dioxide pellets containing 10 per cent plutonium dioxide. The method has been used for fuel elements containing 0.2 per cent or greater of plutonium dioxide by weight.

2–3.5 Analysis of "Simulated Plutonium Fuels"

(a) *Plutonium Fissium.* Materials representing simulated plutonium-rich spent reactor fuels containing 2 to 10 per cent of iron, cerium, cobalt, or combinations of these elements as alloying constituents, as well as the important fission-product elements, have been investigated. Relative concentrations of the fission-product elements are indicated by a typical analysis of a plutonium-iron fissium corresponding to 10 per cent burn-up after 130 days of fast fission (Table 2.24). Complete dissolution of alloys representing a significant percentage burn-up is difficult, and the rigorous methods described in Sec. 2–3.1 must be used. Aliquots of the dissolver solutions are then taken for analysis.

Table 2.24—COMPOSITION OF PLUTONIUM-IRON-FISSIUM ALLOY REPRESENTING 10 PER CENT BURN-UP [234]

Element	Concentration, wt. %
Pu	92. 3
Fe	2. 76
Ce	0. 74
La*	1. 31
Mo	0. 74
Nb	0. 03
Ru	1. 28
Zr	0. 82

*Excess lanthanum added as a stand-in for all rare-earth fission products except cerium.

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Because all the elements in the fissium alloys are nonradioactive except plutonium, which is the major constituent, determination of the latter by radiochemical methods is rapidly and reliably accomplished by direct alpha counting. Under these favorable conditions, the coefficient of variation of the plutonium determination is less than 1 per cent.

(1) *Cerium.* Either of two methods is used for determining cerium. It can be determined either spectrophotometrically as Ce(IV) following separation from Pu(VI) by precipitation as Ce(IV) fluoride [see Sec. 2–2.6(b)] or spectrochemically by the europium carrier–copper-spark method [see Sec. 2–2.6(a)].

(2) *Cobalt.* This element is usually determined spectrophotometrically as cobalt chloride in hydrochloric acid–acetone medium.[235, 236] An aliquot of the plutonium fissium solution containing 3 to 18 mg of cobalt is evaporated to incipient dryness with 70 per cent perchloric acid. The residue is dissolved in 4 ml of 25 per cent hydroxylamine hydrochloride solution, and the plutonium is reduced upon warming the solution. Five milliliters of 12*M* hydrochloric acid is added, and the solution is diluted to 25 ml with acetone. The absorbance of the Co(II) chloride complex is measured at 665 mμ, and a correction for the absorbance of the Pu(III) at this wave length is obtained by measuring the absorbance of the solution at a wave length of 785 mμ. The molar absorptivity of Pu(III) is about 14.5 at each of the two wave lengths, but Co(II) does not absorb at the higher wave length. For cobalt concentrations of 0.5, 1.0, and 3.0 per cent relative to the plutonium, coefficients of variation of 1.4, 1.2, and 0.3 per cent, respectively, are obtained. Because of the low molar absorptivity of 565 for Co(II) at 665 mμ, this method is not applicable for determining trace concentrations of cobalt, and a method in which the absorbance of the cobalt–Nitroso-R complex is measured is preferred.[237]

(3) *Iron.* Because of the relatively high concentration of iron in plutonium-iron fissium, the spectrophotometric determination of iron as Fe(II) orthophenanthrolate is applicable [see Sec. 2–2.6(b)] without separation of the plutonium. For low concentrations of iron in the other plutonium-fuel alloys, one of the methods described in Sec. 2–2.6(b) is recommended, i.e., the one in which the plutonium is separated prior to the iron determination.

(4) *Lanthanum.* This element is determined spectrochemically using the europium carrier–copper-spark method described in Sec. 2–2.6(a).

(5) *Molybdenum.* The method described in Sec. 2–2.6(b) is used for fissium samples. The molybdenum is extracted from hydro-

chloric-hydrofluoric acid into hexone and determined spectrophotometrically as the chloranilate.

(6) *Niobium.* This element is separated by extraction from 6.3*M* sulfuric–1.6*M* hydrofluoric acid solution into hexone. Following neutralization, the organic phase is evaporated to fumes with sulfuric acid, and a second extraction of the niobium into hexone is performed to ensure complete separation. Following neutralization and evaporation of this second extract, niobium is determined spectrophotometrically at a wave length of 410 mμ as the hydroquinone complex in concentrated (18*M*) sulfuric acid.[238] An absorbance of 5.5 per milligram of niobium in 10 ml is obtained, and the coefficient of variation of the method is about 2 per cent, provided the measured absorbance is greater than 0.100. Tantalum interferes in this determination. For niobium concentrations greater than 0.1 per cent in plutonium, only one extraction is required.

(7) *Ruthenium.* As mentioned in Sec. 2–3.1, the method generally used to dissolve plutonium fissium consists in treating the sample with hydrochloric and perchloric acids, followed by evaporation to fumes of perchloric acid. Ruthenium distills as the tetroxide and is absorbed in 3*M* sodium hydroxide, thus effecting quantitative separation. An aliquot of the basic solution containing between 25 and 400 μg of ruthenium is acidified with 10 ml of 12*M* hydrochloric acid, heated in a steam bath for 20 min, and cooled. The absorbance of the ruthenium chloro complex is measured at a wave length of 485 mμ. The coefficient of variation of the method is 0.9 per cent.[235, 236] No known interferences exist, and the method is insensitive to small variations in the concentration of 3*M* sodium hydroxide or 12*M* hydrochloric acid.

(8) *Zirconium.* As described in Sec. 2–2.6(b), this element is separated by precipitation as the *p*-bromomandelate and determined spectrophotometrically as the chloranilate.

(b) *Radiochemical Determinations of Major Fission-product Elements in Irradiated Plutonium.* Although no plutonium-rich fuels are available, methods for determining most of the major fission-product elements have been developed using irradiated plutonium as a stand-in for spent fuel.[113] In these methods alpha activity decontamination factors of between 10^5 and 10^9 are achieved, and the separated fission-product activities are gamma counted by scintillation methods if possible. Between 10 and 50 mg of a stable isotope of the fission-product element is used as a carrier in all cases. Because hydrochloric acid is a good solvent for most plutonium alloys, the irradiated plutonium is dissolved in this acid.

(1) *Barium.* In a modification of a method described by Kleinberg,[158] barium is separated by making three successive precipitations of barium chloride from a 4:1 mixture of hydrochloric acid and ether. To ensure good alpha decontamination, each precipitation is followed by a ferric or lanthanum hydroxide scavenging precipitation. The barium is then precipitated as the sulfate, which is dried, weighed, and gamma counted. Yields of between 60 and 70 per cent, with a coefficient of variation of 3 per cent, are obtained. Alpha-activity decontamination factors of 10^6 are normal.

(2) *Cadmium.* Following the addition of cadmium carrier, ammonium hydroxide is added to the solution to precipitate plutonium as the hydroxide. The supernatant solution is saturated with hydrogen sulfide to precipitate cadmium sulfide, which is dissolved in aqua regia. Cadmium is then precipitated as the hydroxide and dissolved in hydrochloric acid. Lanthanum carrier and hydroxylamine are added, and lanthanum hydroxide is precipitated from the heated solution by adding excess ammonia. The cadmium sulfide, cadmium hydroxide, and lanthanum hydroxide precipitation cycle is repeated. Then cadmium ammonium phosphate is precipitated, weighed, and beta counted. The yield is between 80 and 90 per cent, and the alpha decontamination factor is 10^6.

(3) *Cerium.* The hydrochloric acid solution of the sample is evaporated repeatedly with nitric acid to eliminate chloride, and plutonium in the (IV) oxidation state is absorbed from 8 to 10*M* nitric acid on strongly basic anion-exchange resin. The cerium is eluted from the column with 10*M* nitric acid. Following its oxidation with sodium bromate, cerium is extracted into hexone (4-methyl-2-pentanone). Back-extraction into dilute hydrogen peroxide solution and two precipitations as the oxalate completes the separation. The cerium oxalate is washed, vacuum dried, and gamma counted. An alpha-activity decontamination of 10^6 is obtained. The yield usually varies between 70 and 80 per cent. The coefficient of variation is 3 per cent.

(4) *Cesium.* Cesium is precipitated as the silico-tungstate, which is then decomposed in sodium hydroxide. Silica and tungstic acid from the cesium silico–tungstate are precipitated by acidifying the solution, and cesium is precipitated as the perchlorate. Following several cycles of perchlorate precipitations and iron hydroxide scavengings, the final cesium perchlorate precipitate is dried, weighed, and gamma counted. Again, yields are about 70 per cent, and alpha decontamination is 10^6. A coefficient of variation of 2 per cent is reported.[113]

(5) *Iodine.* After iodide carrier has been added, exchange with the various oxidation states of iodine is accomplished by oxidation

of the iodide to periodate with sodium hypochlorite in basic solution, reduction of the periodate with hydroxylamine, and oxidation of the iodide to iodine. The iodine is extracted into carbon tetrachloride, back-extracted into water, and the oxidation and extraction cycle is repeated using sodium bisulfite to reduce iodine and sodium nitrite to oxidize the iodide. Finally, the iodide is precipitated as silver iodide and is beta counted. The yield is usually between 80 and 95 per cent, and the alpha-activity decontamination is 10^6. The coefficient of variation is about 3 per cent.

(6) *Molybdenum.* The $6M$ hydrochloric acid solution of the sample is passed through a strongly basic anion-exchange resin column, which is then washed with hydrochloric acid, dilute hydrofluoric acid, water, and ammonium hydroxide. Molybdenum remains on the column and is finally eluted with ammonium acetate. The eluate is scavenged with Fe(III) hydroxide, and lead molybdate is precipitated, dried, and weighed. After Tc^{99} has grown into transient equilibrium with Mo^{99}, the sample is gamma counted. Alpha decontamination is 10^7.

(7) *Neodymium and Praseodymium.* Plutonium(III) and americium(III) are first removed by being absorbed on strongly basic anion-exchange resin from $5M$ ammonium thiocyanate. Neodymium and praseodymium in the effluent are precipitated once as the hydroxides, twice as fluorides, and twice again as hydroxides. The final precipitate is dissolved in perchloric acid and loaded on a cation-exchange resin column conditioned with $1M$ lactic acid at pH 3.15. This reagent is used to chromatographically elute the two rare earths. Each element is precipitated twice as the oxalate, and then washed, dried, and weighed. Neodymium-147 is gamma counted; praseodymium-143 is beta counted. The coefficient of variation of a single determination of neodymium is 5 per cent, and of praseodymium, 3 per cent. Yields are usually between 40 and 50 per cent. The alpha-activity decontamination is usually 10^6.

(8) *Niobium.* One milliliter of niobium carrier, containing 10 mg of the element in $0.5M$ oxalic acid, is added to the aliquot of the sample solution. Nitric acid and sodium bromate are added to destroy the oxalic acid and precipitate the niobium as niobic acid. The precipitate is dissolved in saturated oxalic acid, copper and tellurium carriers are added, and copper sulfide is precipitated from hot $1M$ hydrochloric acid solution. Then tellurium is reduced with sulfur dioxide and precipitated from $3M$ hydrochloric acid. Following these two scavenging precipitations, niobium is precipitated as niobic acid, which is dissolved in sulfuric and hydrofluoric acids. Niobium is extracted from this solution into 100 per cent tributyl

phosphate, back-extracted into ammonium hydroxide, and precipitated as niobic acid, which is ignited at 800°C, weighed, and gamma counted. Average yields are between 60 and 65 per cent. The alpha-activity decontamination factor is 10^6.

(9) *Palladium.* The addition of a slight excess of sodium iodide to the $1M$ hydrochloric acid solution of the sample precipitates palladium iodide, which is then dissolved in fuming perchloric acid. The solution is scavenged by precipitation of zirconium hydroxide, and then palladium dimethylglyoximate is precipitated. The precipitate is dissolved in aqua regia, the solution is scavenged with Fe(III) hydroxide, and palladium is again precipitated as the dimethylglyoximate, which is weighed and gamma counted. The yield is between 80 and 90 per cent, and the alpha-activity decontamination factor is 10^6.

(10) *Rhodium.* Ruthenium, palladium, and rhodium carriers are added to the $1M$ to $3M$ hydrochloric acid solution of the sample, and the solution is boiled to achieve good exchange. Palladium iodide is precipitated from the cooled solution upon addition of a slight excess of sodium iodide, then rhodium is precipitated as the iodide from boiling $6M$ hydrochloric acid containing a large excess of sodium iodide. Perchloric acid is added to the precipitate, which is heated to fumes to eliminate ruthenium and iodine. Nitric acid and water are added to give a final perchloric acid concentration of $1M$ and rhodium is adsorbed on a cation-exchange resin column. The column is washed with water, and rhodium is eluted with hot $3M$ hydrochloric acid and precipitated twice as potassium rhodium nitrite. The final precipitate is weighed and gamma counted. The average yield is between 65 and 70 per cent, and the alpha-activity decontamination is 10^6.

(11) *Ruthenium.* The sample solution is neutralized with sodium hydroxide to prevent loss of ruthenium as the tetroxide, and the ruthenium is oxidized at room temperature by adding sodium hypochlorite. Hydrochloric acid is slowly added to decrease the pH to 4. The ruthenium tetroxide is extracted into carbon tetrachloride, and then ruthenium hydroxide is precipitated from ethanol–sodium hydroxide solution. After it has dried, the precipitate is gamma counted. Alpha-activity decontamination is about 10^5 in this quantitative separation. The coefficient of variation of the method is 2 per cent.

(12) *Strontium.* This element is precipitated as the nitrate from fuming nitric acid, the precipitate is dissolved, and the solution is scavenged repeatedly by Fe(III) hydroxide precipitations. Finally, strontium oxalate is precipitated, dried, and weighed, and Sr^{89} is

beta counted. Yields of about 70 per cent, an alpha-activity decontamination of 10^7, and a coefficient of variation of 4 per cent are reported.[113]

(13) *Tellurium.* Reduction and precipitation of tellurium from hydrobromic acid solution by the addition of sulfur dioxide yields a precipitate contaminated with rhodium. The latter is scavenged with Fe(III) hydroxide following dissolution of the tellurium precipitate in nitric acid. This cycle is repeated, and tellurium is finally precipitated as the metal; it is dried, weighed, and gamma counted after I^{132} has grown into transient equilibrium. Alpha decontamination is 10^7, and the coefficient of variation of a single determination is 2 per cent.

(14) *Zirconium.* Following two cycles of precipitation as the *p*-bromomandelate and the hydroxide, zirconium is precipitated as the *p*-bromomandelate; it is dried and weighed, and Zr^{95} is gamma counted. Yields of between 60 and 70 per cent, an alpha-activity decontamination of 10^8, and a coefficient of variation of 3 per cent for a single determination are obtained.

2–3.6 Plutonium Alloys

The possibility (see Sec. 2–1) of utilizing more of the potential energy of the world's supply of uranium by using Pu^{239} as the fissionable material in a reactor destines plutonium to an important role in future reactors. As a result, some reactors, which are still in the planning stages, are being designed to utilize plutonium as the fissionable material. Of the several plutonium alloys being considered, the properties and possible processing schemes of some have been investigated, at least to a limited extent; others have not yet reached this stage of development. The analysis of a few of these alloys is described briefly below. It should be emphasized that the alloys included here do not necessarily represent the materials that may eventually be used.

In developing analytical methods for analyzing these alloys, existing methods were combined and modified wherever necessary, and no entirely new methods were devised. Therefore, details are not included in pointing out the applicable methods. As described previously, the spectrochemical methods for determining impurity elements also require modification for some alloys. For example, in the carrier-distillation determination of trace impurities in plutonium–2.5 per cent iron alloys, standards containing the appropriate concentrations of plutonium and iron are necessary. However, no modification in the cupferron extraction–copper-spark method is required because the iron follows the plutonium in this separation. The

separation methods employed in the spectrochemical determinations of impurities are dependent upon the alloying element as well as the plutonium, and separations used in the spectrochemical determination of impurities in the alloying element should be consulted in selecting the separation method to be used with the alloy.

(a) *Plutonium–Cobalt Alloy.* The only plutonium-cobalt alloys that have been investigated are plutonium-rich alloys containing greater than 95 per cent plutonium. A precise determination is accomplished using controlled-potential coulometric or Ce(IV) titration methods, which do not require separation of the plutonium from cobalt. At this high concentration, the plutonium is also reliably and rapidly determined by direct alpha counting. Most of the methods given in Sec. 2–2.5 should be applicable.

Several methods for determining cobalt exist. Of these, the spectrophotometric determination as Co(II) chloride in a hydrochloric acid–acetone medium was developed specifically for plutonium-cobalt alloys and plutonium-cobalt fissium.[235] This method is described in Sec. 2–3.5(a). In another method, plutonium is removed from 8*M* nitric acid solution by absorption on strongly basic anion-exchange resin, and cobalt is determined spectrophotometrically using Nitroso-R–salt for the color reagent.[239] Cobalt is also determined gravimetrically following electrodeposition from 0.25*M* sulfuric acid into a mercury cathode using a platinum anode.[240] In this method a solution of the sample containing 10 to 20 mg of cobalt is evaporated to fumes with sulfuric acid and transferred to a weighed mercury-cathode cell. The alloying metal is deposited using a current of 0.1 amp for 30 min, 0.4 amp for 10 min, and finally 0.01 to 0.02 amp for 5 min. The plutonium solution is removed, and the cell and cathode are rinsed with water and acetone. After being air dried to remove acetone, the cell is weighed. A preliminary precipitation of plutonium as the peroxide is often incorporated into this procedure. The coefficient of variation in determining 20 mg of cobalt deposited in 3 to 10 g of mercury is about 0.4 per cent. Those elements interfere which codeposit on a mercury cathode under these conditions.

(b) *Plutonium–Cerium–Cobalt Alloys.* Cerium is one of the metals that serves as an effective diluent for plutonium-rich alloy fuels. Therefore, addition of cerium to any of the alloy fuels is possible. Alloys of plutonium-cobalt, plutonium-iron, plutonium-nickel, and plutonium-copper containing various concentrations of cerium have been prepared. Of these, the first two alloys are now being considered as reactor fuels. The presence of cerium does not affect the choice of a method for the determination of plutonium.

The titrimetric, spectrophotometric, and radiochemical methods used with the binary alloys apply to the ternary alloys as well. For alloys having high cerium concentrations, separation of the plutonium by TTA extraction or anion-exchange techniques is necessary before its radiochemical determination.

In one method,[239] Pu(IV) is absorbed from $7M$ to $10M$ nitric acid on strongly basic anion-exchange resin, and cerium in the effluent is determined by titration with a permanganate standard solution in a pyrophosphate solution. Cobalt is determined spectrophotometrically using Nitroso-R-salt. The plutonium is eluted from the column with hydroxylamine hydrochloride solution and determined spectrophotometrically as Pu(III). Any of the methods for determining plutonium apply following the anion-exchange separation (see Sec. 2–2.5).

Other methods for determining cobalt are given in (b) of this section, and methods for determining cerium appear in Sec. 2–3.5(a).

(c) *Plutonium–Osmium Alloy.* As in the determination of ruthenium in plutonium [Sec. 2–3.5(a)], the alloy is dissolved, and the osmium is separated by treating the sample in an all-glass still with hydrochloric and perchloric acids and evaporating to fumes of perchloric acid. Osmium tetroxide distills and is trapped in $2M$ sulfuric acid–5 per cent thiourea solution. The absorbance of the red osmium-thiourea complex is measured spectrophotometrically at a wave length of either 480 or 540 mμ, as described by Sandell.[241] If ruthenium is present, a sodium hydroxide trap absorbs the ruthenium and osmium tetroxides, which are then separated by distilling only the osmium tetroxide from $9M$ sulfuric acid. Following the separation of osmium, any of the methods for determining plutonium are applicable.

(d) *Plutonium–Nickel Alloy.* The methods discussed in Sec. 2–2.6(b) for the separation and determination of nickel in plutonium are applicable to the alloy, and no further details are necessary here. For the determination of plutonium following its separation by cation-exchange resin techniques or by precipitation as the iodate, any of the methods given in Sec. 2–2.5 are applicable. For alloys of low nickel concentrations, many of the methods for determining plutonium are applicable without separation of the nickel. For example, small quantities of nickel do not interfere in the titration of plutonium with Ce(IV), in the direct alpha-counting methods, or in the controlled-potential coulometric titration.

(e) *Plutonium–Uranium–Niobium Alloys.* Uranium alloyed with 20 per cent plutonium and 10 to 60 per cent niobium is being investigated as possible reactor fuel, but no methods for accurate chemical

analysis of these alloys have appeared in the literature. The determination of trace impurities in the three main components is reported.[239a]

Several other alloys including plutonium–thorium, plutonium–zirconium, plutonium–niobium, plutonium–silicon, and ternary alloys of plutonium and cerium with a third metal are under investigation. Plutonium carbides, nitrides, and silicides also are of interest. However, no analytical methods for these materials have appeared. The methods mentioned previously for determining plutonium and various elements in plutonium should apply to these materials. The publication of analytical methods naturally lags behind the initial production and testing of experimental materials. This is especially true for reactor materials because the ever-increasing interest in power reactors and the wide range of materials attracting attention create a real challenge to the ingenuity of the analytical chemist.

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CHAPTER 3

THORIUM

By Robert Z. Bachman and Charles V. Banks*

3–1 INTRODUCTION

The isolation of thorium from the mineral now called thorite and the preparation of the metal were first reported by Berzelius in 1829.[1] The name is derived from that of Thor, the god of war in Scandinavian mythology.

The principal thorium-containing minerals are thorite and monazite. Thorite, a thorium silicate, may contain from 25 to 63 per cent thorium and as much as 10 per cent uranium. It is the principal thorium-bearing mineral in the vein deposits of New Mexico, Colorado, Wyoming, Montana, and Idaho. Monazite is a complex phosphate of the rare-earth metals and thorium. Its thorium content usually ranges from a few per cent up to 10 or 11 per cent. Monazite, commercially the most important source of thorium, is found in the United States in Idaho and the southeastern states; it is also found in India and Brazil.

The first large commercial use of thorium was in the production of incandescent gas mantles. Other uses for thorium oxide include controlling the grain size of tungsten filaments, serving as electron-emitting cathodes, and acting as a catalyst in the Fischer-Tropsch reaction. Thorium sulfide has been used for the preparation of crucibles. The present interest in thorium is based on its ability to serve as a breeder material in the production of U^{233} by the capture of neutrons.

The currently accepted atomic weight for thorium is 232.05, which is slightly less than the weight of 232.12 that was adopted in 1928 and used for many years.

The only oxidation state shown by thorium in aqueous solution is +4, its chemical properties being quite similar to those of zirconium and cerium(IV). This fact and the fact that thorium ions in solution are colorless are the reasons for many of the difficulties encountered in the determination of thorium. Thorium is very electropositive with potentials of +1.77 and +1.90 volts being estimated for the Th/Th^{+44} couple.

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Solid salts of thorium with inorganic anions commonly show between 4 and 12 molecules of water of hydration per atom of thorium, although some lower hydrates are known. Thorium forms complexes with such anions as fluoride, iodate, bromate, nitrate, chlorate, chloride, formate, acetate, sulfate, sulfite, carbonate, oxalate tartrate, malate, citrate, salicylate, and sulfosalicylate. It also forms complexes with ethylenediaminetetraacetate and thenoyltrifluoroacetone, which are of analytical importance. The complexes with fluoride, sulfate, and phosphate are strong enough to cause interference with many methods for the determination of thorium. Thorium also forms insoluble compounds with fluoride, sulfate, oxalate, and iodate; these will be discussed in the appropriate sections. Thorium hydrolyzes with the precipitation of thorium hydroxide from solutions of pH 3.6 or above.

Thorium metal is silver white in color when it has a fresh surface, but it turns very dark grey on continued exposure to air. The massive metal is stable in air, but, when finely divided, it is pyrophoric.

Thorium forms alloys with a large number of metals. The constitution of at least 37 binary thorium systems have been reported, and constitutional diagrams are available for 18 of these systems.[2]

A more detailed discussion of the geology of thorium [3] and the inorganic chemistry of thorium [4, 5] can be found in the literature.

3–2 LITERATURE

As interest in the chemistry of thorium has grown, the literature pertaining to it has been the subject of a number of reviews and bibliographies. The early literature on the analysis of thorium was summarized [6] in 1923. A comprehensive survey [7] of the analytical methods containing 277 references was published in 1948. The second chapter of the book, *Analytical Chemistry of the Manhattan Project*,[8] published in 1950, gives a very complete and detailed discussion of the analytical procedures for thorium used up to that time and lists 105 references. In 1953 a bibliography [9] was published that contained 211 annotated abstracts pertaining to the analytical chemistry of thorium which had appeared in *Chemical Abstracts* from 1947 through September 1953. The literature that appeared in *Chemical Abstracts* from 1907 through 1952 has been compiled with annotated abstracts and subject and author indexes.[10] A bibliography containing 828 annotated references to the chemical literature published from 1951 to 1955 and a subject index has also been published.[11] A review [12] with 48 references on the analysis of uranium and thorium raw materials was published in 1955. The preceding references adequately cover the thorium literature through

1955. A review [13] with 152 references to developments in various aspects of the analytical chemistry of thorium from 1955 through September of 1957 was published in 1958. An annotated bibliography covering papers and reports dealing with thorium from 1957 through April 1958, with a subject index included, has also been published.[14] A comprehensive review [15] covering the detection, separation, and determination of thorium with 319 references was published in 1959. Collections of methods, with detailed procedures, on the analysis of uranium and thorium have also been published.[16, 17]

3–3 SOLUTION OF THORIUM AND THORIUM COMPOUNDS

3–3.1 Thorium Ores

Monazite sands, the principal ore of thorium, can be dissolved by digestion with concentrated sulfuric acid [18–20] or perchloric acid [21] or by fusion with potassium hydrogen fluoride.[17, 22] Thorite when very finely pulverized can be dissolved by digestion with concentrated hydrochloric acid. If a residue remains, it should be fused with potassium pyrosulfate. The melt is taken up in 6*M* hydrochloric acid and added to the main solution.[18] Black sands can also be decomposed by fusion with potassium hydrogen fluoride.[23]

3–3.2 Thorium Metal

Thorium metal can be most easily dissolved in 8*M* to 16*M* nitric acid containing a small amount of fluoride, frequently added as fluosilicic acid. If the surface area of the sample is large, the acid must be added slowly to prevent the reaction from becoming too vigorous. Dilute hydrochloric acid with fluoride has also been used for the dissolution of thorium metal. When hydrochloric acid is used without a fluoride, a black residue remains which turns white on long digestion. As the result of the study of the action of several acids on four metals, it has been stated that thorium dissolves very slowly in HF, HCl, and H_2SO_4 but that it dissolves more rapidly in aqua regia.[24]

The effect of small amounts of fluoride on the dissolution of thorium metal in nitric acid has been studied.[25] It was found that for a constant nitric acid concentration and sample weight, the dissolution rate is approximately proportional to the hydrofluoric acid concentration. It was also pointed out that the hydrofluoric acid acts as a catalyst rather than forming a permanent complex with all the dissolved thorium because the increased dissolution rate is observed when the ratio of fluoride ion to thorium ion is about 0.03 to 1.

Fuming phosphoric and perchloric acids will attack thorium metal very slowly.

3–3.3 Thorium Alloys

In general, thorium alloys can be dissolved in the same manner as thorium metal. Alloys of thorium and niobium have been dissolved by fusing them with potassium hydrogen fluoride and then dissolving the fluorides in concentrated sulfuric acid. Thorium-zinc alloys react very vigorously when attacked by hydrochloric acid; therefore, the acid must be added carefully. If thorium-zirconium alloys are dissolved in nitric acid, a pyrophoric residue may result unless hydrofluoric acid is also present.

3–3.4 Thorium Dioxide

Thorium dioxide that has not been heated to over 550 or 600°C will dissolve readily in $8M$ to $16M$ nitric acid with a small amount of fluoride present. As the ignition temperature is increased, the oxide becomes increasingly difficult to dissolve. If the oxide has been ignited at over 1000°C, it will be necessary to use concentrated nitric acid which is $0.03M$ in fluoride and a temperature of 100°C. Even under these conditions the reaction will proceed slowly.

Thorium dioxide can be converted to the sulfate by digestion in fuming sulfuric acid or by fusion with sodium acid sulfate or pyrosulfate. The sulfate can then be dissolved in water. Hydrochloric acid, even in the presence of fluoride, is ineffective toward high-burned thorium dioxide.

3–3.5 Thorium Fluoride

Thorium fluoride can be dissolved by fuming with sulfuric or perchloric acid. However, the reaction proceeds slowly. A mixture of boric and nitric acids will also dissolve thorium fluoride, as will a mixture of aluminum nitrate and nitric acid. Alkali oxalates have also been used to dissolve thorium fluoride through complex formation. Thorium fluoride can be easily converted to the oxide by pyrohydrolysis;[26] the oxide can then be dissolved in the usual way. This method can also be used for the determination of fluoride in thorium fluoride.

Procedure. The apparatus used is shown in Fig. 3.1. The steam rate should be about 2.5 g/min, and the reaction tube temperature should be about 1000°C. The thorium fluoride is spread evenly in a small platinum boat. The boat is then pushed into the central portion of the reaction tube with a stiff wire. The receiver is placed so that, when the tube is in the furnace, the tip of the condenser is barely above the bottom. Enough water is added to immerse the tip. This is necessary to prevent loss of fluoride from the first few drops of condensate. The reaction tube is placed in the furnace and fitted snugly to the superheater. It is necessary to press the silica to plati-

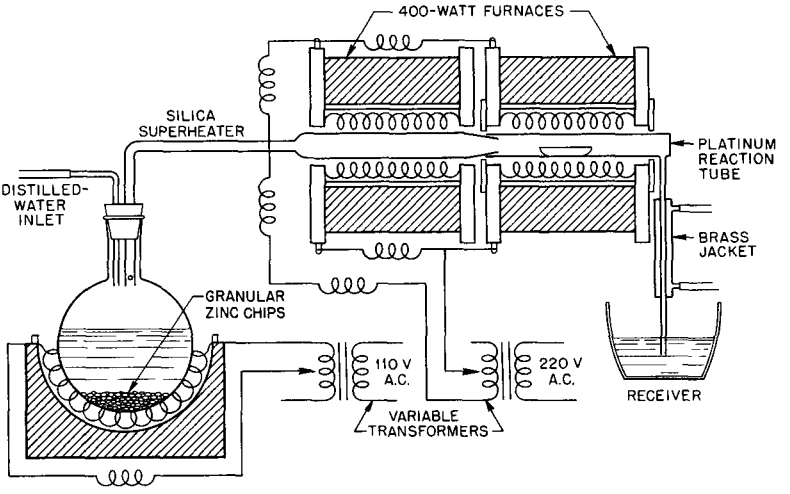


Fig. 3.1—Pyrohydrolysis apparatus, macro scale.

num joint together slightly more during the period of temperature rise because of the greater expansion of the metal. This may be done by hand or with a spring brass arm attached to the furnace so that it maintains a constant pressure against the end of the reaction tube. After 4 or 5 min, the reaction tube is removed from the furnace and allowed to cool below redness. The boat containing the thorium dioxide may now be removed from the tube, ignited in air, and weighed as thorium dioxide. If the fluoride is to be determined, it can be titrated with 0.1*N* sodium hydroxide to the phenolphthalein end point.

3–3.6 Thorium Oxalate

Thorium oxalate is nearly insoluble in water and in 3*N* to 4*N* acids. It will, however, dissolve in ammonium or potassium oxalate.

The oxalate can be ignited to the oxide at temperatures of 610°C or above;[27] the oxide is then dissolved by the usual methods.

3–3.7 Thorium Sulfate

Thorium sulfate tetrahydrate is more soluble in cold water than in hot. The salts with six, eight, and nine waters of hydration are more soluble in warm solutions than in cold. Thorium sulfate can be dissolved in hydrochloric or nitric acids.[5]

3–4 QUALITATIVE DETECTION

In the usual procedures for qualitative analysis, thorium is precipitated along with aluminum in the ammonium hydroxide group. Unless care is exercised in the case of mineral or ore analysis, the thorium may remain undissolved and be counted as insoluble residue.

A method for the detection of thorium involving separation as the oxalate and iodate has been used.[19, 28] In this method, the thorium is first separated as the oxalate along with scandium, yttrium, and the rare earths from zirconium, titanium, and the more common members of the ammonium hydroxide group. The thorium can then be separated from scandium, yttrium, and the rare earths by an iodate precipitation. If there is any doubt as to the prior removal of zirconium, the iodate precipitate may then be converted to the oxalate. A white precipitate at this time indicates the presence of thorium. Detailed procedures for the oxalate and iodate precipitations are given in Sec. 3–5.3.

A number of other qualitative tests for thorium based on emission spectra, fluorescence, and color reactions have also been proposed. The selectivity of such tests can be improved by combining them with a separation technique, such as paper chromatography, or by using selective sequestering agents. The lower limit of detection by spectral analysis is about 35 ppm and by flame photometry, about 100 ppm.[29]

Table 3.1—RECENT QUALITATIVE DETECTIONS FOR THORIUM (PAPER CHROMATOGRAPHY)

Solvent	Developer	Colors	Comments	Ref.
iso-BuOH-HCl	Alizarin			34
MeOH-Py-$PhCH_3$, MeOH-Py-dioxane, *n*-BuOH-Py-dioxane, MeOH-$CHCl_3$-$PhCH_3$, or Py-$CHCl_3$-$PhCH_3$.	Alizarin Red S.	Th, pink-violet; U, blue.		35
	Quinalizarin	Th, blue; U, green		
	Quinalizarin–$K_4Fe(CN)_6$.	Th, blue; U, brown		
EtOH-$CHCl_3$-$PhCH_3$.	Morin	Fluorescence under uv; 0.25 μg Th in 0.1 ml.	Ti, Zr, Th sepd.	30
	Quercetin	Th, yellow	Poor selectivity.	36
	Rubeanic acid–$Na_3[Fe(CN)_5NH_3]$.	Th, Zr, Hf, red-purple; U, Ti, Bi, Mo, brown; RE, Mn, Ni, blue.		31
	Pyrocatechol violet.	Th, Al, Fe, Sb, Bi, Zr, V, Cr, Mo, W, blue-purple; M(I), RE, alk. earths, none.		32

A paper chromatographic separation of thorium using an ethanol–hydrochloric acid–water mixture as the solvent has been used. This was then followed by the production of a fluorescence with morin. In this way, thorium, titanium, and zirconium are separated.[30]

A method that distinguishes thorium from the rare earths but does not differentiate between thorium and zirconium has been developed using rubeanic acid and trisodium pentacyanoamminoferrate(II) to give a red-purple color.[31]

Pyrocatechol violet has been used as a developer following a paper chromatographic separation of multivalent metals. Thorium yields a blue-purple color; no color is produced by the rare earths.[32]

The violet color formed by thorium with 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid (arsenazo) has been used for the detection of thorium. This test is sensitive to 4 ppm.[33]

Procedure.[33] A small excess of ethylenediaminetetraacetic acid (EDTA) is added over that amount required to react with the cations in the solution; the pH is adjusted to 7.5 to 8; and then arsenazo is added. If a violet color appears, a positive test is indicated. Of thirty-nine cations studied, the only three that were found to interfere were Cr(III), Be(II), and U(VI). The U(VI) interference is conveniently eliminated by a prior extraction of uranyl diethyldithiocarbamate by a mixture of benzene and isoamyl alcohol.

Table 3.1 summarizes some of the recently proposed qualitative tests for thorium using paper chromatographic separations and chromogenic reagents, and Table 3.2 lists recently proposed color reactions for thorium.[13]

Table 3.2—RECENT QUALITATIVE DETECTIONS FOR THORIUM (COLOR REACTIONS)

Reagent	Colors	Selectivity	Ref.
Morin	Green fluorescence	Th, Al, Be, Ga, In, Ge, Sn, Sb, Zr, react.	37
Iodoxine	Th, Pd, orange-yellow; Zr, cream-yellow; Ti, pink-yellow; Cu, green-yellow; V(V), Pb, yellow; Fe, green-gray; Ni, red-brown; Co, chocolate.	Poor	38
Arsenazo	Violet	Excellent for as little as 4 ppm Th; excess EDTA added, pH 7.5–8.5, then arsenazo. Only Cr (III), Be(II), U(VI) interfere at 100-ppm level.	33

3–5 METHODS OF SEPARATION

Before thorium became of interest in the field of atomic energy, the principal separations were those from the other elements that occur with thorium in ores. Most of these separations were by precipitation of the thorium as the hydroxide or fluoride or by the use of various organic reagents. The increased interest in thorium has prompted the investigation of other techniques, such as extraction, ion exchange, and adsorption, for the separation of thorium from other elements.

3–5.1 Extraction Separations

(a) *Thenoyltrifluoroacetone.* The preparation of thenoyltrifluoroacetone (TTA) was first reported about 1944. The rate and equilibrium constants for the tautomeric equilibrium of this and of other fluorinated β-diketones have been studied.[39] The trifluoromethyl group serves to increase the acidity of the enol form, making it possible to carry out extractions from solutions of very low pH. The thenoyl group decreases the solubility of the reagent in the aqueous phase. TTA has been widely used for the extraction of a number of elements in connection with radiochemical determinations, for which it is particularly suited because of the ease of adapting the procedures to remote-handling techniques. It has also been used for separations preceding spectrophotometric determinations. In addition, it has been used in the determination of the stability constants for some thorium complexes.[40] The early workers used benzene as the solvent for the TTA, but later workers have used xylene and carbon tetrachloride with success. The conditions for the extraction of a number of elements have been summarized in tabular [41] and graphical [42] form. These show that, by selection of a suitable acid concentration, thorium can be separated from zirconium by extraction of the zirconium and from bismuth, thallium, indium, rare earths, yttrium, lead, vanadium, and calcium by extraction of the thorium. The separation of thorium from uranium [43] and from titanium, aluminum, nickel, and chromium (III)[44] have also been studied in detail. There is some evidence that the presence of acetic acid enhances the extraction of thorium into TTA in carbon tetrachloride and methyl isobutyl ketone (hexone).[45] This may make possible separations of thorium from other elements that extract at about the same pH.

Procedure.[44] Take a sample containing 10 to 150 μg of thorium. Add 3 ml of perchloric acid, and fume until about 1 ml remains. Dilute the solution to 20 ml, and then adjust the pH to 2.0 with 10 per cent sodium acetate. Add 5 mg of disodium–1,2–dihydroxybenzene–3,5–disulfonate

(Tiron) if titanium is present. Extract for 2 min with 10 ml of a 0.5*M* solution of TTA in carbon tetrachloride. Drain the organic phase into a second separatory funnel, and extract with an additional 10-ml portion of the TTA solution. Combine the organic phases and re-extract the thorium for 2 min into 10 ml of 6*M* hydrochloric acid. Repeat the re-extraction with an additional 10-ml portion of 6*M* hydrochloric acid. Combine the acid phases, and wash them with 10 ml of carbon tetrachloride. The thorium can then be determined spectrophotometrically. If phosphate is present, it must be separated prior to the extraction of thorium.

(b) *Mesityl Oxide.* Mesityl oxide has been studied as an extractant for thorium from a nitrate solution.[46] It was found that 0.4 to 100 mg of thorium could be quantitatively extracted under the conditions used.

This extraction has also been applied by other workers to the determination of thorium in monazite sands[22] and black sands.[23] The samples were decomposed by a potassium bifluoride fusion; the thorium was separated by extraction with mesityl oxide and determined spectrophotometrically with 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (Thorin).[47] Under the conditions used, uranium extracts quantitatively; zirconium extracts about 70 per cent; vanadium, 9 per cent; platinum, 8 per cent; iron(III), 4 per cent; and indium, 4 per cent. The rare earths, yttrium, calcium, beryllium, magnesium, aluminum, titanium, manganese(II), cobalt, copper(II), zinc, nickel, molybdenum, tin(II), barium, and lead all extract less than 1 per cent. Phosphate does not interfere appreciably up to a mole ratio of P_2O_5 to ThO_2 of 40 to 1.

Procedure.[46] Evaporate the thorium-containing sample to dryness. Then dissolve it in 10 ml of (15+85) nitric acid. Add 19 g of aluminum nitrate 9-hydrate, and warm to dissolve the crystals. After the solution has cooled, pour it into a 60-ml separatory funnel. Add 20 ml of mesityl oxide to the beaker containing the original solution. Agitate the solution gently, and pour the solvent into the separatory funnel containing the nitric acid solution of the sample. Shake the funnel for 20 sec, and then allow the layers to separate. Draw off the aqueous layer into a second separatory funnel. Save the organic layer. Repeat the extraction with 10 ml of mesityl oxide, and combine the organic layers. Discard the aqueous layer. Strip the extracted rare earths from the mesityl oxide by equilibrating the organic phase for 20 sec with three 20-ml portions of an aluminum nitrate scrub solution [9.5 g of aluminum nitrate 9-hydrate to 5 ml of (15+85) nitric acid]. Discard the wash solutions. Strip the thorium from the mesityl oxide with two 20-ml portions of water.

(c) *Methyl Isobutyl Ketone and Tri-*n*-butyl Phosphate.* A mixture of methyl isobutyl ketone (hexone) and tri-*n*-butyl phosphate (TBP) will extract 1 mg of thorium dioxide from an aluminum nitrate–nitric acid solution.[48] Mesotartaric acid is added to prevent

the extraction of zirconium. The thorium loss has been shown to be about 0.4 per cent in the extraction step and 0.003 per cent in the stripping step.

Procedure. Take 10 ml aliquots (containing 0.8 to 1.6 mg of ThO_2 and 15 per cent in nitric acid) of the thorium-containing samples. Add 19 g of aluminum nitrate 9-hydrate and 0.2 g of mesotartaric acid. Warm to dissolve the solid reagents and then cool. Add by pipet, 20 ml of the extraction mixture. This mixture is prepared by mixing 1 volume of TBP (which has been purified by washing with a 1 per cent sodium carbonate solution and then with water) and 9 volumes of methyl isobutyl ketone. Shake the mixture for 1 min and set it aside for 1 hr. Transfer a 10-ml aliquot of the organic phase to a separatory funnel, and strip the thorium with two 20-ml and one 10-ml portions of water. Combine the aqueous phases containing the thorium. A reagent blank and a standard thorium solution should be carried along with each set of thorium samples.

If the amount of zirconium is large, the mesotartaric acid should be added as 1 ml of a 20 per cent solution just before the addition of the extraction mixture. In this way, the precipitation of the zirconium is delayed until after the thorium has been extracted.

(d) *Tri-*n*-octylphosphine Oxide.* Tri-*n*-octylphosphine oxide (TOPO) has been used for the extraction of thorium.[49, 50] Greater than 99 per cent of 10 mg of thorium can be extracted from 1*M* to 3*M* nitric acid or 4.5*M* to 7*M* hydrochloric acid with a single 10-min equilibration. The extraction also takes place to greater than 99 per cent from 7*M* perchloric acid, but, in general, it is not suitable because of the frequent appearance of a third phase. The extraction from sulfate or phosphate solutions is slight. As much as 48 mg of thorium can be extracted into 1 millimole of TOPO from 1*M* nitric acid. The phase ratio of aqueous to organic can be varied from 1 to 20 without affecting the extraction. When the hydrochloric or nitric acid concentrations are maintained at 1*M* and the anion concentration is increased by the addition of neutral salts, the extraction coefficients are higher than if the anion concentration is achieved by the addition of acid alone. For the nitric acid system, the extraction coefficient reaches a maximum of 3800 for 1*M* nitric acid and 1*M* sodium nitrate, the extraction being essentially complete for nitrate concentrations of from 1*M* to 9*M*. Complete extraction is observed from solutions from 4*M* to 8*M* in chloride. In this case, aluminum chloride is used to obtain the desired chloride concentration. Small amounts of sulfate and phosphate do not interfere with the extraction if the proper nitrate concentrations are used. Up to 0.8*M* sulfuric acid, 0.3*M* phosphoric acid, or a combination of 0.5*M* sulfuric acid with 0.3*M* phosphoric acid do not prevent complete extraction from a solution 0.5*M* in nitric acid and 4*M* in sodium nitrate. When this extraction is applied to sulfuric acid leach liquors from monazite

sands, the rare earths quantitatively remain in the aqueous phase. Chromium (VI), uranium, and zirconium will extract, but chromium (III) will not. The zirconium remains in the TOPO rather than back-extracting with the thorium. The U(IV) back-extracts, but if it is oxidized to U(VI), the interference in the spectrophotometric-thorin method for thorium is reduced.

Procedure.[50] Transfer an aliquot containing less than 20 mg of thorium to an extraction apparatus[51] or to a separatory funnel. Dilute with 1*M* nitric acid until the concentration of sulfate and phosphate are less than 0.1*M*. The final volume should not be more than 50 ml. Make the solution approximately 1*M* in sodium nitrate by dissolving the salt. Add 5 ml of a 0.1*M* solution of TOPO in cyclohexane, and extract for 10 min. Allow the phases to separate. The aqueous phase is free of thorium and can be used for the determination of the rare earths. Transfer an aliquot of the organic phase to a second extraction apparatus and add 15 ml of a 0.3*M* sulfuric acid solution. Equilibrate for 10 min, and allow the phases to separate. An aliquot of the aqueous phase can be taken for the thorium determination. No change in volume occurs during extractions with TOPO in cyclohexane.

(e) *Tri-n-butyl Phosphate.* Tri-*n*-butyl phosphate and other trialkyl phosphates and dialkylalkyl phosphonates have been studied as extractants for thorium.[52] Under the conditions used (1.09*M* extractant in *n*-dodecane at 30°C), the dialkylalkyl phosphonates showed higher extraction coefficients for thorium and better separation from zirconium than did the trialkyl phosphates for nitric acid cencentrations from about 0.5*M* to 5*M*. Among the trialkyl phosphates both triisoamyl phosphate and tricyclohexyl phosphate had higher extraction coefficients than did tri-*n*-butyl phosphate. The phosphonates investigated gave distribution coefficients in the following order: di-*n*-amyl-*n*-amyl > di-*n*-hexyl-*n*-hexyl > di-*n*-butyl-*n*-butyl > di-*n*-butyl-cyclohexyl > bis(2-ethylhexyl). The extraction coefficient for di-*n*-amyl-*n*-amyl phosphonate is about 11 times that for tri-*n*-butyl phosphate. Quantitative extraction of thorium by TBP has been achieved by using 100 per cent TBP and nitric acid concentrations of 6*M* or greater.[53] An extraction coefficient of 96 has been reported for 48 per cent TBP in kerosene from 15.4*M* nitric acid.[54] The observation was also made that higher extraction coefficients could be obtained from acidified sodium nitrate than from nitric acid of the same nitrate concentration.

(f) *Bis(di-n-hexylphosphinyl)methane.* Bis(di-*n*-hexylphosphinyl)methane, HDPM, is one of a family of β-diphosphine dioxides of the form $R_2P(O)CH_2P(O)R_2$ which can be used as metal extractants.[55] It is soluble in common organic solvents and nearly insoluble in water. A solution of HDPM in 1,2-dichloro-

benzene will quantitatively extract thorium from hydrochloric or nitric acid solutions if the acid concentration is 1*M* or greater and from perchloric acid solution if the acid concentration is 2*M* or greater. Other elements quantitatively extracted from 1*M* nitric acid solution are gold(III), bismuth(III), uranium(VI), and zirconium. Elements only partially extracted are mercury(II), iron (III), samarium, yttrium, and molybdenum(VI). Elements not extracted are aluminum, calcium, copper, gallium, lead, magnesium, nickel, vanadium(V), and zinc. The elements that are quantitatively extracted from 1*M* hydrochloric acid solution are the same as those extracted from 1*M* nitric acid solution along with mercury (II) and molybdenum(VI). Zirconium and iron(III) are partially extracted. The elements that are not extracted are iron(II), samarium, yttrium, and those elements that are not extracted from 1*M* nitric acid solution. In addition to thorium, the elements that are quantitatively extracted from 2*M* perchloric acid solution are uranium, yttrium, scandium, and the rare earths. Aluminum is not extracted if the perchloric acid concentration is between 1*M* and 8*M*.

(g) *Salicylate.* The extraction of thorium salicylate has been used to separate thorium from rare earths.[56] A 99.9 per cent extraction of 0.1 g of thorium has been achieved with a 79 per cent recovery of 1.0 g of yttrium, and a 99.0 per cent extraction of thorium is possible with a 94 per cent recovery of yttrium.

Procedure. To 0.1 g of thorium as the nitrate in a separatory funnel are added 5 ml of a 10 per cent ammonium acetate–10 per cent acetic acid buffer and 5 ml of a 20 per cent ammonium salicylate solution. Add 10 drops of concentrated nitric acid, and extract with 5 ml of a 65 per cent chloroform–35 per cent ethyl acetate solution. Perform two more extraction steps by adding 5 ml of the salicylate solution and 7 to 10 drops of nitric acid, and extract with 5 ml of the solvent. Extract once more, adding only nitric acid and 5 ml of the solvent. This procedure should extract 99.9 per cent of the thorium; however, some of the rare earths are carried along also. If it is desirable to leave a larger percentage of the rare earths in the aqueous phase, the procedure should be modified as follows: Do not add the nitric acid before each extraction. After the final wash, collect all portions of the organic phase in a second separatory funnel, and back-extract with 3 ml of the salicylate solution, 3 ml of the buffer solution, and 5 drops of nitric acid. The separated wash solution is then acidified with 5 drops of nitric acid and extracted with 5 ml of solvent. The initial aqueous phase and the wash solution are then combined.

(h) *Cupferron.* The extraction of the cupferrates has been used to separate a number of the M(III) and M(IV) (including thorium) ions from M(II) ions.[57] The extraction also has been used to sep-

arate thorium from uranium [58] in which case ethyl acetate was used as the solvent. In the separation from M(II) cations, a number of solvents were studied, and a mixture of equal volumes of benzene and isoamyl alcohol was selected as the most satisfactory. Iron, bismuth, zirconium, titanium, and tin are extracted along with the thorium; zinc, lead, manganese, magnesium, cobalt, nickel, calcium, and cadmium will remain in the aqueous phase. Aluminum and the rare earths do not extract completely.

Procedure. Place an aliquot of the sample containing 0.1 to 0.5 millimole of thorium in a separatory funnel. Adjust the pH to 0.3 to 0.8 with 6*M* hydrochloric acid. Add 15 ml of the solvent mixture (equal volumes of benzene and isoamyl alcohol) for each 0.25 millimole of extractable metal (15 ml minimum). Add 4 ml of a 0.3*M* solution of cupferron in water. Shake for 45 sec; then allow the phases to separate, and wash the organic portion two or three times with 10-ml portions of water. Combine the original aqueous phase and the washings if the M(II) ions are to be determined.

3–5.2 Ion-Exchange and Chromatographic Separations

Both cation-exchange resins and anion-exchange resins are used for separating thorium from elements that interfere in the determination of thorium. Thorium forms negatively charged complexes with some anions, such as nitrate and sulfate, but not with chloride. This fact has been used in many separations in which the anion and the conditions have been so selected that thorium would not be adsorbed while other metals would be retained by the column. Ion-exchange separations of thorium are used successfully both on the tracer level and for milligram amounts.

(a) *Separation Using Anion-exchange Resins.* Distribution coefficients have been measured for a number of elements using Dowex–2–X8 resin and hydrochloric, nitric, and sulfuric acids [59] (see table 3.3). It was found that thorium along with strontium, yttrium, cerium (III), and americium were not adsorbed from hydrochloric acid solution. Uranium shows maximum adsorption from hydrochloric acid when the concentration is approximately 8*M*. Thorium, protactinium, and uranium can be separated, in that order, by placing the sample on the column and eluting the thorium with concentrated hydrochloric acid, then eluting the protactinium with 4*M* to 5*M* hydrochloric acid, and, finally eluting the uranium with 0.1*M* hydrochloric acid. Zirconium shows increasing adsorption as the acid concentration is increased.

In the case of nitric acid, thorium, zirconium, and uranium show maximum adsorption when the acid concentration is near 8*M*. Strontium, yttrium, cerium, and americium show no adsorption.

Table 3.3.—ANION-EXCHANGE SEPARATIONS

Elements separated	Resin	Anion and concentration	Anion used to elute thorium	Ref.
Pa, U(IV), U(VI)	Dowex-1	10*M* HCl	10*M* HCl	60
Ce(IV), Cr(VI), Hf, Fe(III), U(IV), U(VI), Zr.	Dowex-1	9*M* HCl	9*M* HCl	64
Pa, U	Dowex-2	Conc. HCl	Conc. HCl	59
Fe, U, Zr, Co, Sn, V(V)	Dowex-2	10*M* HCl	10*M* HCl	44
U(VI)	Amberlite IRA-400.	6*M* HCl	6*M* HCl	62
Bi	De-Acidite FF.	10% HCl	10% HCl	61
Pb	De-Acidite FF.	2*M* HBr	2*M* HBr	63
Rare-earth elements, U	Dowex-1	0.1*M* H_2SO_4	0.4*M* H_2SO_4	71
La	Dowex-1	0.02*M* H_2SO_4	1*M* H_2SO_4	72
Monazite solutions	Amberlite IRA-400.	SO_4^{-2}, pH=2.3	2*M* HCl	73
Sr, Y, Ce, Am	Dowex-2	9*M* H_2SO_4	1 to 2*M* H_2SO_4	59
Rare-earth elements, Y	Dowex-1	7*M* HNO_3	2.4*M* HCl	65
Am, Pu, Np, Pa, U	Dowex-1	8*M* HNO_3	12*M* HCl	67
Sr, Y, Ce, Am, Nb, Zr, U.	Dowex-2	8*M* HNO_3	8*M* HNO_3	59
U(VI)	De-Acidite FF.	6*M* HNO_3	H_2O	69
Silicate materials	Dowex-1	0.7*N* HNO_3 in 80% EtOH.	0.1*N* HNO_3 sat. with Et_2O.	70
U	Amberlite IR-1.	$NH_2OH \cdot HCl$	1.25*M* $NaHSO_4$.	74

When sulfuric acid is used, thorium shows a minimum adsorption at 1*M* and a maximum near 9*M*. Thorium can be eluted from the column with 1*M* to 2*M* sulfuric acid. Strontium, yttrium, cerium, and americium show no adsorption.

(1) *Separations Using Hydrochloric Acid Solutions.* Thorium shows no adsorption on Dowex-1-X10 from hydrochloric acid in the concentration range of 0.1*M* to 12*M* acid, permitting the separation of thorium from protactinium and the separation of thorium, protactinium, and uranium.[60] For the separation of thorium from protactinium, the sample is placed on the column in concentrated hydrochloric acid. The thorium is then eluted with 7*M* or greater hydrochloric acid. For the separation of thorium, protactinium, and uranium, the sample is placed on the column in 10*M* hydrochloric

acid, and the thorium is eluted with the same acid. The elution order for a number of elements placed on the column in concentrated hydrochloric acid and then eluted with successively decreasing concentrations of acid is thorium, vanadium(IV), titanium(IV), hafnium, zirconium, uranium(IV), germanium, and tin(IV). The tin (IV) is not readily elutable.

Dowex-2-X10 has been used in the separation of thorium from iron, uranium, zirconium, cobalt, tin, and vanadium(V), using 10*M* hydrochloric acid.[44]

A 10 per cent hydrochloric acid solution and De-Acidite FF resin have been used for the separation of thorium from bismuth.[61]

Amberlite IRA-400 has been used to separate thorium from uranium(VI) in a 6*M* hydrochloric acid solution.[62]

Lead can be adsorbed on a De-Acidite FF column from 2*M* hydrobromic acid and in this way can be separated from thorium, which is not adsorbed.[63]

The resin Dowex-1-X4 has also been used for the separation of cerium(IV), chromium(VI), hafnium, iron, uranium(IV), uranium(VI), and zirconium from a 9*M* hydrochloric acid solution.[64] Yttrium, the trivalent rare earths, and titanium are not separated from thorium.

Procedure.[64] **Transfer an aliquot of the sample containing 0.3 to 1.5 mg of thorium to a beaker of suitable size and evaporate to dryness. Add approximately 25 ml of 9*M* hydrochloric acid, and warm to dissolve the salts. Allow the solution to cool, and pass it through a column 1 cm in diameter containing 15 ml of Dowex-1 resin in 9*M* hydrochloric acid. The flow rate should be about 1 ml/min. Wash out the beaker with several small portions of 9*M* hydrochloric acid. Pass these washings over the column, and wash the resin column with 60 ml of 9*M* hydrochloric acid. Collect the effluent in a 250-ml beaker. Evaporate the hydrochloric acid solution to dryness, add 10 ml of nitric acid and 1 or 2 ml of perchloric acid, and evaporate to dryness. The thorium can now be determined spectrophotometrically.**

(2) *Adsorption From Nitric Acid Solution.* Thorium is adsorbed from nitric acid solutions on anion-exchange resins. This has formed the basis of a method for separating thorium from the rare earths.[65] The resin used was Dowex-1-X8; the rare earths studied were lanthanum, samarium, neodymium, europium, and yttrium. It was found that they could be readily eluted with 5*M* to 8*M* nitric acid and that the thorium would be retained. The thorium can then be removed with dilute or concentrated hydrochloric acid. Amberlite IRA-410 will also adsorb thorium from approximately 7*M* nitric acid.[66] The behavior of several actinide elements in 8*M* nitric acid has also been studied.[67] Americium is not adsorbed on Dowex-1-X4 from 8*M* nitric acid; thorium, plutonium, and neptunium

are. The thorium can be eluted with 12*M* hydrochloric acid; the plutonium, with 12*M* hydrochloric plus 0.1*M* ammonium iodide, and the neptunium, with 4*M* hydrochloric acid.

Procedure.[67] The resin used is analytical-grade Dowex-1-X4 (100 to 200 mesh) which is converted to the nitrate form by washing with 8*M* nitric acid just prior to use. The columns used are 3 mm by 4 cm. The samples, containing trace quantities of Am^{241}, Th^{234}, Pu^{239}, and Np^{239} in 8*M* nitric acid, are first made 0.03*M* in ferrous sulfamate and then 0.1*M* in sodium nitrate. The samples are then passed through the column at the rate of 3 to 5 drops per minute. The column is then washed with 10 ml of 8*M* nitric acid to remove the americium. The thorium is eluted with 5 ml of 12*M* hydrochloric acid–0.1*M* ammonium iodide solution, and the neptunium is eluted with 5 ml of 4*M* hydrochloric acid.

It has also been found[68] that the adsorption of thorium on De-Acidite FF increases with increasing nitric acid concentration from 2 to 8*M*. The order of adsorption from greater than 4*M* nitric acid is Np(IV), Pu(IV), >thorium >protactinium >U(VI), Np(VI), and Np(V).

Uranium has been separated from thorium using De-Acidite FF and nitric acid at elevated temperatures.[69] The uranium is eluted with 4*M* nitric acid, and the thorium is then eluted with water. The separation is not good at room temperature but is satisfactory at 77°C.

Thorium is also adsorbed on Dowex-1 from a solution 0.7*M* in nitric acid and 80 per cent in ethanol. The thorium can then be eluted with 0.1*M* aqueous nitric acid saturated with diethyl ether.[70]

(3) *Adsorption From Sulfuric Acid Solution.* The distribution coefficients of thorium and uranium in sulfuric acid and ammonium sulfate solution using Dowex-1 have been studied, and a method has been proposed for the separation of rare earths, thorium, and uranium.[71] At 50°C, the rare earths can be eluted with 0.1*M* sulfuric acid; thorium, with 0.4*M* sulfuric acid; and U(VI), with 1.5*M* sulfuric acid. At room temperature the bands tend to tail, but at elevated temperatures this difficulty is eliminated.

The anionic complex formed by thorium in dilute sulfate solution has been used to separate thorium from lanthanum[72] using Dowex-1-X8 and from cerium or monazite solution[73] using Amberlite IRA-400. The pH of the sulfate solution should be about 2.3, and the sulfate concentration should be about 0.05*M* for the adsorption of thorium. Beryllium, magnesium, zinc, aluminum, copper, nickel, and cobalt are not adsorbed. The rare earths may be adsorbed slightly but are eluted with dilute sulfuric acid, pH 1 to 2. Iron and uranium stay with the thorium. The thorium can be eluted with 1*M* sulfuric acid or 2*M* hydrochloric acid.

Procedure.[73] Convert the 36- to 50-mesh Amberlite IRA-400 resin to the sulfate form by passing a 5 per cent (w/v) solution of sodium sulfate through a column packed with the resin. Rinse the resin with distilled water until the effluent is free of sulfate. Use columns of 15 mm internal diameter containing a resin bed 20 cm in length. Place the sample of thorium in a beaker, or in a platinum dish if the sample consists of thorium and rare-earth fluorides, add 5 to 6 ml of concentrated sulfuric acid, and heat until fumes are evolved. When sufficient acid remains to keep the sulfates in the form of a thick paste, cool, and extract with about 100 ml of ice-cold water containing a few milliliters of 5 per cent sulfurous acid to reduce any oxidized cerium. If the solution is not clear after 1 to 2 hr, filter and ignite the residue to a dull red heat. Add a few drops of sulfuric acid, heat until fumes are evolved, dissolve the sulfates as previously described, and combine the sulfate solutions. Adjust the pH of the sulfate solution to 2.0 by careful addition of concentrated sodium hydroxide solution. If the solution is yellow, oxidized cerium is present; this can be reduced by adding a few milligrams of sodium nitrite. Pass the sample solution through the column at a rate of 2.5 ml/min. Rinse the column with 250 ml of distilled water that has been adjusted to pH 2 with sulfuric acid. The flow rate should be 5 ml/min. The effluent from the sample solution and washings contain the rare earths. Elute the thorium from the column with 200 ml of 2*M* hydrochloric acid at a rate of 2.5 ml/min.

The elements that can be separated from thorium by this procedure are rare earths, beryllium, magnesium, zinc, aluminum, copper, nickel, and cobalt. Uranium and iron are not separated from thorium.

(4) *Adsorption With Hydroxylammonium Chloride Present.*[74] A method has been developed for the separation of thorium from uranium in uranium-thorium alloys which uses hydroxylammonium chloride as a complexing agent and Amberlite IR-1. After the solution containing uranium and thorium with hydroxylammonium chloride has been passed through the column, the uranium can be eluted with 0.5*M* hydrochloric acid. The thorium can then be eluted with 1.25*M* sodium bisulfate, followed by water.

(b) *Separation Using Cation-exchange Resins.* Cation-exchange resins have also been widely used for the separation of thorium from other elements. Thorium does not form anionic chloride complexes to any great extent and is therefore strongly adsorbed on cation-exchange resins from hydrochloric acid solutions.[75] This fact has been used to prepare carrier-free Th^{234} (UX_1)[76] and for the separation of thorium from the rare earths and other cations.[77, 78]

A summary of cation-exchange separations is given in Table 3.4.

(1) *Adsorption From Hydrochloric Acid Solution.* In the preparation of UX_1, the resins used were Wofatit KS and Amberlite

Table 3.4—CATION-EXCHANGE SEPARATIONS

Elements separated	Resin	Anion and concentration	Anion used to elute thorium	Ref.
U, Fe, probably Al, Ca, Mg, Cu.	Wofatit KS or Amberlite IR-100.	0.1*M* HCl	0.5*M* oxalic acid.	76
Cd, Bi, Co, Ni, Mn, Pb, Zn, Cr, Mg, Cu, Fe, Al, Ca, U, V, rare earths.	Dowex-50	4*M* HCl	4*M* H_2SO_4	77
Zr, rare earths	Dowex-50 (AG 50W).	4*M* HCl	Resin ignited	78
Pa	Dowex-50	HNO_3		79
Rare earths	Amberlite IR-100.	Dilute NO_3^-	6*N* H_2SO_4	80
Ce	Dowex-50	Dilute NO_3^-	0.015*M* Pb-EDTA.	81
Y, La	Dowex-50	EDTA, pH 2.1.	EDTA	82
La, U(VI), Ca, Sr, Mg, Ba.	Dowex-50	0.05*M* EDTA, pH 2.1.	0.05*M* EDTA	83
Zr, Ti	Dowex-50	0.0520*M* citric acid, ph 1.75.	0.0520*M* diammonium citrate.	84
Co, Cr, Cu, Fe, Mo, Ni, V, U, Ti.	Dowex-50	1.0*M* H_2SO_4	3.0*M* H_2SO_4	64
Cu, Zn, Ni, Cd	Dowex-50	Sulfosalicylic acid.	Sulfosalicylic acid.	85

IR-100. Most of the uranium was first removed by the extraction of solid uranyl nitrate crystals with ether. The remaining uranium and thorium were then dissolved in 0.1*M* hydrochloric acid and passed through the column. The uranium and iron were eluted with 2*M* hydrochloric acid. Aluminum, calcium, magnesium, and copper were probably separated also. The thorium was eluted with 0.5*M* oxalic acid. It was found that the oxalic acid solution would not strip thorium from Dowex-50 as readily as it did from the resins used. In one procedure using Dowex-50, the resin was removed from the column and ignited, the thorium being weighed as thorium dioxide.[78] The sample was placed on the column, and the rare earths and zirconium were eluted with 4*M* hydrochloric acid. It was found, however, that thorium could not be eluted with either 10*M* hydrochloric acid or 8*M* nitric acid; therefore, the ignition was used.

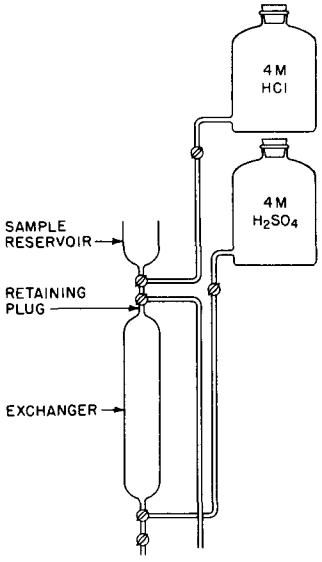


Fig. 3.2—Cation-exchange separation of thorium.

Another method for removing the thorium from Dowex-50 is to back-wash the column with 4*M* sulfuric acid after eluting the rare earths and other elements with 4*M* hydrochloric acid.[77] Cadmium, bismuth, cobalt, nickel, manganese(II), lead, zinc, chromium(III), magnesium, copper, iron(III), aluminum, calcium, uranium(VI), yttrium, and the rare earths can be separated from thorium in this way.

Procedure.[77] A positive pressure is applied to the top of the resin bed by placing the hydrochloric acid reservoirs 2.5 ft above the column, and a negative pressure is applied to the bottom of the bed by extending the take-off tubing 3.7 ft below the column (Fig. 3.2). The column is 1.5 ft long. With this arrangement, a downflow of 1.0 liter/hr can be obtained. The sulfuric acid reservoir is placed 1.0 ft above the top of the resin bed to obtain a flow rate of 0.39 liter/hr. Add 110±10 ml of a 4*M* hydrochloric acid solution containing 10 g of thorium to the sample reservoir. After washing the sample container and sample reservoir with 10-ml portions of 4*M* hydrochloric acid, allow 2 liters of 4*M* hydrochloric acid to flow through the column. This fraction contains the elements other than rare earths. Now change the receiver and collect 4.3 liters more of the effluent containing the rare earths. The thorium is now removed from the column by back-washing with about 4.8 liters of 4*M* sulfuric acid. Before introducing the next sample, pass 200 ml of 4*M* hydrochloric acid through the column to remove the sulfuric acid.

(2) *Adsorption From Nitric Acid Solution.* Thorium forms an anionic nitrate complex in solutions greater than 4*M* in nitric acid

but is adsorbed on cation-exchange resins from 1*M* nitric acid.[68] The order of adsorption on Zeokarb 225 from 1*M* nitric acid is thorium>Pu(IV)>Pu(III)>U(VI), Np(VI), Pa(V). This behavior of thorium has been used to separate thorium from protactinium,[79] lanthanum,[80] and cerium.[81]

In the case of protactinium, the resin used was Dowex-50, and the protactinium was eluted with 2*M* nitric acid. For the separation of thorium from lanthanum, the elements were placed on Amberlite IR-100 from aqueous solutions of the nitrates, the lanthanum was eluted with a 10 per cent citric acid solution adjusted to pH 2 with ammonium hydroxide, and the thorium was finally eluted with 3*M* sulfuric acid.

For the separation of thorium from cerium, an aqueous solution of the nitrates was passed over Dowex-50. The thorium was eluted first using a solution of lead-ethylenediaminetetraacetic acid complex at pH 3.0. The cerium was eluted after the thorium using 3*M* hydrochloric acid. Lead ions are present in both effluents but can be removed as lead sulfate.

(3) *Adsorption from Ethylenediaminetetraacetic Acid (EDTA) Solution.* The thorium–EDTA complex can be used with Dowex-50 resin for reducing the amount of rare-earth impurities in thorium.[82] An amount of EDTA exactly equal to the amount of thorium present is added to the sample. The pH is adjusted to 2.1, and the sample is passed over a column of Dowex-50-X8 which has been carefully conditioned with ammonium formate buffer. The major portion of the rare earths and some of the thorium remain on the column. The effluent contains 93 to 97 per cent of the thorium and up to 1.4 per cent of the rare earths initially present.

The fact that the adsorption of thorium on Dowex-50 from an EDTA solution is quite sensitive to pH has been used for the separation of thorium from several metals.[83] It was found that thorium was completely retained on the column at pH 0.9 and that only 0.1 per cent was retained at pH 2.1. Quantitative separation of thorium and lanthanum were reported at pH 2.2. It was also found that uranium(VI), calcium, strontium, magnesium, and barium were completely retained on the column at pH values above that at which thorium was completely eluted. Iron(III) and bismuth(III) were not retained at pH values at which thorium was completely retained. Dowex-50-X4 was satisfactory, but some tailing occurred with Dowex-50-X16.

Procedure. Before it is used the first time, the Dowex-50-X4 resin should be eluted with sodium citrate to remove any impurities, then washed with ethanol and acetone and air dried. The buffer solutions used are prepared by pouring the appropriate acid solution (0.2*M*

glycine for pH 1.0 to 3.6, 0.2*M* formic acid for pH 2.7 to 4.2, or mineral acid for pH less than 1.0) into a 1-liter beaker to within 2.5 cm of the top, adding 50 ml of 0.05*M* EDTA, and adjusting the pH with hydrochloric acid, nitric acid, or ammonium hydroxide to the desired value using a pH meter. The columns are prepared as follows: Add 5 g of air-dried resin to each column (20 mm in diameter and 7 cm long). Pass the appropriate buffer solution through the column at a rate of 10 to 15 ml/min until the pH of the effluent is within 0.1 pH unit of the desired value.

To 10 ml of solution containing 0.5 millimoles of the ion to be adsorbed, add 30 ml of buffer and 15 ml of 0.05*M* EDTA. Adjust the pH of the sample to the proper value using the appropriate acid or ammonium hydroxide. Pass the sample through the column at the rate of 8 to 11 ml/min. Rinse the column three times using 30 to 40 ml of the buffer solution each time. When the element retained on the column is of interest, it may be eluted by passing 90 ml of 4*M* hydrochloric acid through the column at a rate of 1.5 to 2 ml/min.

At pH 2.0 the rare earths through samarium can be separated from thorium, and at pH 4.4 calcium, strontium, barium, and magnesium are completely adsorbed by the resin.

(4) *Adsorption from Citric Acid Solution.* Thorium, zirconium, and titanium can be separated using Dowex-50 and citric acid.[84] The solutions are equilibrated with a small amount of the resin and then added to the top of the column. The zirconium and titanium are eluted with 0.0520*M* citric acid at a pH of 1.75. The zirconium is eluted by the first liter of citric acid, and the titanium is present in the effluent from 1.75 to 2.7 liters. The eluant is then changed to diammonium citrate to elute the thorium.

(5) *Adsorption from Sulfuric Acid Solution.* Amberlite IR-120 will adsorb thorium from a 1.0*M* sulfuric acid solution.[64] The thorium is placed on the resin from sulfuric acid, and the column is washed with 2*M* hydrochloric acid. The thorium can then be eluted with 3*M* sulfuric acid. Separation of thorium is achieved from Co(II), Cr(VI), Cu(II), Fe(III), Mo(VI), Ni(II), V(IV), and U(VI). Zirconium is not separated from thorium in this way.

Procedure. Pass an aliquot of the sample, which contains 0.3 to 1.5 mg of thorium in no more than 25 ml of 1*M* sulfuric acid, over 15 ml of wet-settled Amberlite IR-120 resin in the hydrogen form at a rate of 2 ml/min. Wash the resin with 150 ml of 2*M* hydrochloric acid. Elute the thorium with 300 ml of 3*M* sulfuric acid. Collect the eluate in a 600-ml beaker. Evaporate the eluate to dryness, add 10 ml of nitric acid and 1 to 2 ml of perchloric acid, and evaporate to dryness again to destroy any organic matter from the resin. Rinse down the sides of the beaker with 5 ml of 5*M* hydrochloric acid, and warm the acid to dissolve the thorium salt. Wash down the sides of the beaker, and dilute the solution to 20 ml with deionized water. The thorium can now be determined with thorin.

(6) *Adsorption from Sulfosalicylic Acid Solution.* The negatively charged complex formed between thorium and sulfosalicyclic acid has also been used for the separation of thorium.[85] Ethylenediamine is used to form positive complexes with copper, zinc, nickel, and cadmium. The solution, of pH 8 to 10, is then passed through a column containing Dowex-50-X12, which retains the positively charged complexes and allows the negatively charged thorium complex to pass through. Iron, uranium, aluminum, zirconium, and yttrium also form negatively charged complexes with sulfosalicylic acid.

(c) *Separation Using Cellulose Columns or Strips.* Cellulose columns can be used both for the separation of thorium from other elements prior to the determination of thorium and for the separation of rare earths from thorium in order to determine the rare earths. The behavior of thorium toward a cellulose column has been used for the separation of thorium prior to the determination of uranium.[86] Thorium is completely retained on a cellulose column from a 3 per cent nitric acid–ether mixture but is eluted to some extent by a 5 per cent nitric acid–ether mixture. Complete separation of thorium from uranium is achieved. Similar conditions are used for the separation of thorium from monazites and the separation of thorium from uranium and the other cations found in urano-thorianite ore.[87] In the case of urano-thorianite ore, the uranium is first eluted from the column with a 3 per cent nitric acid–ether solution, and then the thorium is eluted with a 12.5 per cent nitric acid–ether solution. Calcium, tin, lead, iron, cobalt, nickel, copper, titanium, Ce(III), and yttrium remain at or near the top of the column. Zirconium will move through the column, but tartaric acid will hold it back. Cerium(IV) moves with the thorium, and scandium moves nearly as fast as thorium. Phosphate, sulfate, and oxalate interfere and must be removed before the sample is placed on the column. The interference from phosphate can be eliminated by the use of a compound column consisting of a cellulose section preceded by an alumina section that separates thorium from phosphate.[88, 89] In this case, uranium is eluted ahead of the thorium with a 1 per cent nitric acid–ether mixture. This method is reported to work well for the separation of thorium from zirconium, yttrium, and the rare earths. Amounts of thorium up to 25 g have been separated from rare earths by means of a cellulose column and a 12.5 per cent nitric acid–ether mixture in connection with spectrographic rare-earth determinations.[90] A batch separation has also been used for the removal of thorium in order to determine the rare earths.[91] In this work, a 11.1 per cent nitric acid–ether mixture is used. It was found

that di-*n*-propyl ether can be used in place of diethyl ether. After the sample solution is adsorbed on the cellulose, the thorium is separated by washing with successive portions of the nitric acid–ether mixture and filtering off each portion before the next is added. Thenoyltrifluoroacetone is used to remove the last traces of thorium.

Procedure.[88] Add about 40 ml of concentrated nitric acid to a solution of the sample and evaporate until the residue is just moist. Add 20 ml of 4*M* nitric acid and heat gently for 5 min. Then add 2 ml of 20 per cent hydrogen peroxide and heat for 10 min to reduce cerium. Add 8 g of ferric nitrate and heat for 15 min; then add 1.4 g of disodium hydrogen phosphate and heat again for 15 min. The ferric nitrate must be added before the sodium phosphate or the results will be low. With monazite sands or other samples low in zirconium, the sodium phosphate can be omitted or the amount reduced, and the amount of ferric nitrate can be reduced to 4 g. The column should be about 2.7 cm in diameter and 30 cm long. The inside of the column is made water repellent by coating with silicone. The column contains 5 cm of activated cellulose and 6 cm of activated alumina. Add approximately 50 g of alumina to the sample solution and stir thoroughly. Then transfer the alumina to the column. Rinse the beaker with small portions of the nitric acid–ether mixtures. Elute the thorium and uranium with 500 ml of the solvent. The solvent should not be allowed to fall below the top of the alumina. Add 20 ml of water and 50 ml of ammonium hydroxide, and heat the mixture on a steam bath to remove the ether. If uranium is to be separated from thorium, elute the uranium first using 400 ml of a 1 per cent nitric acid–ether mixture, then elute the thorium with 400 ml of a 12.5 per cent nitric acid–ether solution.

Attempts to use the 12.5 per cent nitric acid–ether mixture for paper strip chromatography produced an elongated and sometimes discontinuous thorium band extending from the top line to the bottom line.[92] Increasing the amount of water and acid in the ether causes the thorium band to become much more compact. The best mixture results from equilibrating the ether with an equal volume of 8*M* nitric acid and then eluting the thorium with the ether-rich phase. It was also shown that, if the same solvent were used for eluting the thorium from a cellulose column, the volume necessary for complete elution would be greatly reduced.

A dioxane–antipyrene solvent mixture has also been used for the chromatographic separation of uranium and thorium from solutions of monazite sands.[93] Thorium has an R_F value of 0.78, and uranium has a value of 0.81; thus uranium and thorium are not separated. The maximum R_F values for other elements in this solvent, however, are never over 0.41.

Procedure.[93] The apparatus consists of a glass trough supported in a glass tank (50 by 25 by 15 cm), which is tightly covered with a glass

plate. In the trough is placed the freshly prepared solvent mixture, which consists of 100 ml of dioxane, 1 ml of concentrated nitric acid, 1 g of antipyrine (phenazone), and 2.5 ml of distilled water. A little of the solvent is also placed at the bottom of the tank to keep the inside atmosphere saturated. Filter-paper sheets are cut into strips 18 by 52 cm, and these are penciled into six vertical strips 3 cm wide. Place 0.01 ml of the thorium-containing sample in 50 per cent nitric acid on four of the six strips 8 to 10 cm from the top and allow the spots to dry. Fold the paper between the top edge and the row of spots into a V-shape and hang the strip over the edge of the trough so that the short fold is in contact with the solvent. The strips are allowed to stand in the tank until the solvent front is about 5 cm from the lower edge of the paper (about 10 hr). The chromatograms are removed from the tank and dried in a stream of hot air. Two of the strips are cut from the sheet and sprayed with kojic acid–oxine spray (1 g of kojic acid and 5 g of 8-quinolinol in 1 liter of 60 per cent alcohol). The strips are allowed to dry and are viewed under ultraviolet light while being held over concentrated ammonium hydroxide in a beaker. The thorium appears as a greenish-yellow faintly fluorescent spot; uranium appears as a black spot. The position of the thorium-uranium zone is marked with a pencil. The strips are placed beside the remainder of the chromatogram, and the positions of the thorium-uranium zones marked. The loaded and blank spots are then cut out and used for the determination of thorium. The thorium can be dissolved in excess EDTA solution, and the excess EDTA can be titrated.

3–5.3 Precipitation Separations

The separation of thorium by ion-exchange and solvent-extraction methods has become popular in recent years; whereas many of the precipitation separations date back many years. There is still an active interest, however, in the separation of thorium by precipitation. Many new reagents are being studied, and new studies are being made of many of the older reagents. Many precipitation separations have the advantage that the precipitate can be ignited to thorium dioxide and weighed without further treatment. Many of the older procedures will be mentioned only briefly here, and references to the literature will be given.

(a) *Oxalate.* Oxalic acid is widely used for the precipitation of thorium, and a number of procedures using this reagent have appeared in various periodicals as well as in many text and reference books. However, it has been found that thorium oxalate is slightly soluble in dilute mineral acid solutions.[94, 95] The pH, volume of the solution, and the concentration of ammonium salts all have definite effects on the solubility of the thorium oxalate, and a large excess of oxalate also increases the solubility loss. If the proper conditions are selected, the solubility can be reduced to 0.1 to 0.2 mg of thorium dioxide, making the error relatively small if the sample is sufficiently

large. It has been found that the presence of rare earths reduces the amount of thorium in the filtrate following the oxalic acid precipitation. The solubility loss can also be reduced by the use of filter-paper pulp. The following procedures are the ones that are claimed to have the smallest solubility loss of thorium.

Thorium oxalate precipitates as $Th(C_2O_4)_2$ with a varying amount of water. Rare earth and uranium(IV) oxalates precipitate along with thorium and must be separated by some other method. The oxalates of certain metals such as calcium, strontium, barium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, and bismuth may contaminate the thorium oxalate precipitate if present in large amounts. Zirconium oxalate also tends to precipitate, but an excess of oxalate will prevent this. Uranium(VI) and Fe(III) form complexes with oxalate, and an excess must be added if these ions are present.

Procedure of Ewing and Banks.[96] A solution containing perchloric acid and 200 to 300 mg of thorium is evaporated to a volume of about 5 ml. The solution is then diluted to a volume of about 300 ml and heated to boiling. Five milliliters of a thick slurry of filter pulp and five grams of oxalic acid are added; and, after a 15-min digestion period, the mixture is cooled, and the thorium oxalate is filtered, washed with a solution containing 25 g of oxalic acid dihydrate and 20 ml of concentrated hydrochloric acid per liter, and ignited to the oxide at 1000°C.

Procedure of Kall and Gordon.[96] The above procedure is used except that the precipitation is made with 1 g of dimethyl oxalate followed by 4 g of oxalic acid dihydrate.

Procedure of the Bureau of Standards.[97] Evaporate a solution containing hydrochloric acid and thorium to dryness, and add 20 to 25 ml of a 10 per cent solution of oxalic acid to the residue. Stir and then dilute to 100 ml. Cover the beaker and boil the solution gently for a few minutes. Readjust the volume to 100 ml, and let the sample stand at room temperature overnight. Filter through fine-porosity filter paper (Whatman No. 42), wash with a 1 to 2 per cent oxalic acid solution, and ignite to thorium dioxide at 1000 to 1100°C.

(b) *Iodate.* The precipitation of thorium as thorium iodate $[Th(IO_3)_4]$ has been widely used for the separation of thorium from rare earths in the analysis of ores and minerals. Lead, mercury, tin, niobium, tantalum, tungsten, cerium(IV), uranium(IV), zirconium, titanium, silver, and, to a smaller extent, scandium, bismuth, and iron(III) also form insoluble iodates, making other separations necessary in ore analysis. In the classical procedure, the rare earth iodates coprecipitate with the thorium iodate necessitating at least a double iodate precipitation for complete separation. This procedure is discussed in many reference books, and it will be omitted from this discussion. However, the attempts that have been made to improve

the classical method by precipitation from a homogeneous solution [98] and by the use of masking agents [99] will be discussed.

(1) *Precipitation of Thorium Iodate from Homogeneous Solution.*[98, 100] Iodate can be synthesized by the reduction of periodate with ethylene glycol, which, in turn, is produced slowly by the hydrolysis of 2-hydroxyethyl acetate:

$$CH_3COOCH_2CH_2OH + H_2O \rightarrow HOCH_2CH_2OH + CH_3COOH$$

$$HOCH_2CH_2OH + IO_4^- \rightarrow 2HCHO + H_2O + IO_3^-$$

Ethylene diacetate can also be used to form the ethylene glycol. Precipitating the thorium iodate from a homogeneous solution results in a much more crystalline and more easily filterable precipitate with an appreciable reduction in the amount of coprecipitation of the rare earths. It was found that thorium iodate is slightly soluble in the 7*M* nitric acid solution that was usually recommended for the classical precipitation, but this solubility is partially compensated for by the entrapment of silica in the gelatinous precipitate.

As the conditions were varied to increase the percentage of thorium precipitated from homogeneous solution from 99.8 to 99.98, the amount of coprecipitated rare earths increased rapidly. In one series of experiments it was found that the extent of coprecipitation by rare earths did not change when the amount of rare earths present was varied from slightly more than the amount of thorium to much less than the amount of thorium. There also appears to be a general relationship between decreasing ionic radius and decreasing extent of coprecipitation.

Procedure.[98] Concentrate the solution containing 2 to 150 mg of thorium as perchlorate, sulfate, or nitrate to about 50 ml. This solution should not contain more than 36 milliequivalents of mineral acid. The total acidity of the final solution must be between 2.5*M* and 3*M* in hydrogen ion.

Add 40 ml of concentrated nitric acid, and then add a filtered solution containing 14 g of sodium metaperiodate in 100 ml of water. Dilute the solution to 230 ml and cool to room temperature. Employ mechanical stirring throughout the entire period of precipitation. Add 2 ml of distilled β-hydroxyethyl acetate. Precipitation will begin in about 10 min when 50 to 100 mg of thorium is present.

Thirty minutes after precipitation begins, add 6 ml of β-hydroxyethyl acetate. If more than 100 mg of thorium is present, it is better to add 3 ml of the reagent and another 3 ml about 30 min later. One and one-half hours after the first addition, add a solution containing 2 g of potassium iodate, 9 ml of nitric acid, and 50 ml of water. Thirty minutes following this, stop the stirring and allow the precipitate to settle.

Decant the supernatant liquid through a medium-porosity filter paper (Whatman No. 40). Wash the precipitate by decantation 10 times with

a potassium iodate—nitric acid solution (8 g of potassium iodate, 100 ml of concentrated nitric acid, and 900 ml of water). Dissolve the small amount of precipitate from the filter with a 10 per cent hydrochloric acid solution saturated with sulfur dioxide, and collect the filtrate in the original precipitation beaker containing the bulk of the thorium iodate. The latter operation also dissolves any of the precipitate that may adhere tenaciously to the beaker walls.

Evaporate the solution to dryness on a low-temperature hot plate, and bake at 110°C for 1 hr. Dissolve the salts in 50 ml of 10 per cent hydrochloric acid, and filter off any dehydrated silica. Wash well with hot (1+20) hydrochloric acid solution.

The determination may now be concluded by any desired method. However, if the original quantity of rare earths and phosphate was large, as in monazite sands, it may be necessary first to reprecipitate the thorium by the iodate method.

(2) *Precipitation of Thorium Iodate from a Tartaric Acid–Hydrogen Peroxide Solution.*[99] The precipitation of thorium iodate from a nitric acid medium containing hydrogen peroxide, *d*-tartaric acid, and 8 quinolinol can be used in conjunction with the thorin–mesotartaric acid spectrophotometric procedure for the separation and determination of thorium in silicate rocks, black sands, monazite sands, thorite, thorianite, euxenite, and zircon. The tartaric acid minimizes the coprecipitation of zirconium, tungsten, scandium, and bismuth. Hydrogen peroxide minimizes the precipitation of titanium, niobium, and tantalum. The purpose of the 8-quinolinol is to prevent the catalytic decomposition of the hydrogen peroxide. Iron and mercury are added as carriers for the precipitation of the thorium. The mixed carrier was found to be more effective than mercury alone for small amounts of thorium.

The concentrations of nitric acid and iodate are selected to allow complete precipitation of the thorium but to minimize the coprecipitation of foreign ions. At the 500-μg level of thorium dioxide, an increase of 1 ml of nitric acid or a decrease of 2 ml of 6 per cent potassium iodate results in a 7 per cent loss of thorium. The amount of mercury added must not be greater than recommended or increased coprecipitation will result. Halides prevent the precipitation of mercury. A large excess of hydrogen peroxide over the amount necessary to complex the titanium, niobium, and tantalum will cause the precipitation of the peroxy complex of zirconium. The concentration of 8-quinolinol is less critical than that of any of the other reagents. The *d*-tartaric acid delays the precipitation of thorium, but a 50 per cent excess will not affect the thorium recovery.

Procedure. To the sample solution containing 2 to 150 μg of thorium add 1 ml of a solution containing 0.875 g of ferric nitrate 6-hydrate in 100 ml of (1+99) nitric acid. Add 1 or 2 drops of 30 per cent hydrogen peroxide and then a 50 per cent solution of potassium hydroxide to

neutrality. Add 5 ml excess for each 50 ml of solution. Digest on the steam bath for about 15 min. Filter on a fast paper, and wash the precipitate several times with a dilute solution of potassium hydroxide (2 ml of 50 per cent solution diluted to 500 ml with water). Drain the precipitate thoroughly by placing the palm of the hand over the funnel and pressing down.

Pipet 5 ml of water and 1 ml of 8-quinolinol solution [0.5 g in 100 ml of (1+99) nitric acid] into a 100-ml beaker and place it under the funnel. Dissolve the precipitated hydroxide as follows: Add 1 ml of 3 per cent hydrogen peroxide over the precipitate, being careful to cause the peroxide to come in contact with all portions of the precipitate. After the hydrogen peroxide has drained, add 2 ml of hot (1+1) nitric acid slowly dropwise to allow the acid to dissolve as much of the precipitate as possible. After the acid drains, add 5 ml of hot water, playing the water over all surfaces of the filter paper. Repeat the sequence of peroxide, acid, and water twice more. Drain the funnel. Add all reagents and water with pipets to ensure proper concentrations for the iodate precipitation. To the beaker add 0.1 ml of a filtered potassium iodate solution (6 per cent aqueous) and 6 ml of a filtered *d*-tartaric acid solution (600 g per liter of solution).

Add slowly from pipets, first 10 ml of potassium iodate and then 5 ml of the mercury carrier solution [1.58 g of mercuric nitrate 1-hydrate, dissolved in 10 ml of (1+1) nitric acid, and diluted with water to 1 liter], stirring the solution during each addition. Place the beaker in an ice bath and allow to stand for 45 min.

Stir in a small amount of paper pulp, and filter on a slow (No. 42 Whatman or equivalent) 7-cm filter paper. Wash the precipitate thoroughly six to eight times with 25- to 35-ml portions of ice-cold iodate wash solution (60 ml of nitric acid, 6 ml of 30 percent hydrogen peroxide, and 200 ml of 6 per cent potassium iodate solution diluted to 1 liter with water). Wash further if the sample is known to contain large amounts of titanium, niobium, or tantalum. Any cloudiness or small amount of precipitate forming in the filtrate is due to the post-precipitation of mercury and may be disregarded.

Drain the precipitate and stem of the filter funnel by pressing the funnel with the hand. Also drain the last drop from the beaker in which the precipitation was made. Place the beaker in which the precipitation was made under the funnel in place of the beaker containing the filtrate. Dissolve the precipitate from the filter with three alternate additions of 5 ml of hot (1+1) hydrochloric acid and 5 ml of hot water. Drain the paper and funnel stem.

Add 1 ml of perchloric acid and fume to dryness, being careful not to convert any zirconium that might be present to the insoluble form. Add 2 ml of (1+1) hydrocholoric acid and evaporate to dryness. A blank should be run by carrying water samples through the iodate separation. The sample is now ready for the determination of thorium by the thorin–mesotartaric acid procedure.

(c) *Urea–Formic Acid.* The hydrolysis of urea can be used to raise the pH of a thorium solution containing formic acid; this results in a dense, easily filterable precipitate.[21] By careful control of the conditions and a double precipitation, thorium can be separated from

the rare earths by this method. The Ce(IV) is reduced to Ce(III) with potassium iodide. Before the precipitate is weighed, the coprecipitated silica must be removed.

Procedure. To a sample containing about 0.1 g of thorium in 10 ml of perchloric acid, add 1 g of potassium iodide in 25 ml of water, followed by 150 ml of water containing 8 g of urea, 10 g of ammonium chloride, and 3 ml of formic acid (87 to 90 per cent). The solution containing the urea, ammonium chloride, and formic acid should be filtered before it is added to the thorium solution.

Dilute the solution to about 350 ml, adjust the pH to 4.45 ± 0.02 with silica-free ammonium hydroxide, then dilute the solution to approximately 450 ml.

Place in the solution a stirring rod with about a 1-mm indentation in one end. This indentation can be conveniently made with a carpet tack. Bring the solution to a boil, and adjust the heat so that a steady stream of bubbles just issues from the indentation on the stirring rod. Boil gently for 95 to 97 min after the appearance of the opalescence.

The final pH should be 5.4 to 6.2. If the pH is less than 5.4, incomplete precipitation occurs, and it will be necessary to boil the solution a little longer. If the pH is more than 6.2, some of the rare earths may precipitate, but this is not generally serious because they will be removed by the double precipitation. In most precipitations, the final pH will fall between 5.5 and 5.9.

Filter the precipitate and wash 10 times with a hot solution containing 20 g of ammonium nitrate and 8 ml of formic acid (87 to 90 per cent) per liter. The pH of the wash solution should be adjusted to 5.6 with ammonium hydroxide.

Remove most of the thorium precipitate remaining on the beaker walls with a single policeman treatment. Place the beaker with stirring rod under the funnel, and dissolve the precipitate from the filter with hot 2*M* hydrochloric acid. Wash the filter thoroughly with the acid wash.

Repeat the precipitation, filtering, and washing procedure. After most of the precipitate has been removed from the beaker walls by a policeman and transferred to the filter, add 5 ml of concentrated hydrochloric acid and 5 ml of water to the beaker, cover with a watch glass, and reflux gently for 10 min. Wash down the watch glass, beaker walls, and stirring rod with distilled water, and then add ammonium hydroxide dropwise until the solution turns purple to brom cresol purple indicator. Warm gently for 1 to 2 min, and transfer the gelationous precipitate to the filter containing the bulk of the precipitate. Wash five times with the ammonium nitrate-formic acid wash solution. Ignite in a platinum crucible for 2 hr at 950°C. Remove the silica by treatment with hydrofluoric and sulfuric acids; then ignite to the oxide at 950°C.

(d) *Hexamethylenetetramine.* Precipitation of thorium with hexamethylenetetramine (hexamine) is one of the simplest and most satisfactory methods for the separation of thorium from rare earths even though, in the case of monazite sands, three precipitations are required.[107] Hexamine is a weak base that serves to control the hydro-

gen-ion concentration of a solution by hydrolysis in the presence of hydrogen ions to form formaldehyde and ammonia. Elements that precipitate along with the thorium and, therefore, must be separated by some other method are iron, aluminum, titanium, chromium, uranium, and zirconium. Elements that do not precipitate if ammonium salts are present in the solution are zinc, manganese, nickel, cobalt, and magnesium. Rare-earth solutions develop a turbidity if ammonium salts are not present but show no turbidity in the presence of ammonium salts. Some coprecipitation of the rare earths does occur, especially if they are present in large amounts. Therefore two or three precipitations should be used to obtain a complete separation. Depending upon what other elements were originally present, the final hexamine precipitate may be ignited directly to the oxide, or the precipitate may be dissolved and the thorium precipitated as the oxalate.

Procedure.[17] Take a sample containing 20 to 100 mg of thorium in hydrochloric acid solution. Add (1+1) ammonium hydroxide until a faint turbidity is formed. Add a few drops of (1+1) hydrochloric acid, and dilute the solution to 200 ml. Add enough ammonium chloride to make a 5 per cent solution of the salt, and then add a few crystals of sodium metabisulfite to reduce any Ce(IV) to Ce(III). Stir the solution well and warm to about 70°C. Slowly add a hexamine solution (2 per cent aqueous) until the solution becomes turbid, then add 3 to 4 ml more. Stir well and heat to not over 75°C. After the precipitate has settled, add 1 ml more of hexamine solution and stir again. Allow the precipitate to settle and filter through a medium-porosity filter paper (Whatman No. 40). Wash the precipitate with a 5 per cent ammonium chloride solution. Test the filtrate for complete precipitation with 1 ml of hexamine solution. Dissolve the precipitate with hot (1+2) hydrochloric acid into a 250-ml beaker. Wash the paper with hot 5 per cent hydrochloric acid. Repeat the hexamine precipitation twice. Test the filtrate with 1 ml of hexamine solution; then test the filtrate with excess ammonium hydroxide. The precipitate can be dissolved in hot hydrochloric acid if further separations are necessary or ignited to the oxide at 950°C and weighed if no interfering elements are present.

(e) *Tetrachlorophthalic Acid.* Thorium can be separated from the rare earths by precipitation from a homogeneous solution with tetrachlorophthalic acid.[101] If the recommended procedure is used, the thorium will precipitate in a dense, crystalline, easily filterable form. However, if a hot solution of the reagent is added to a hot sample solution, the precipitate will be very gelatinous. At pH 2.0, cerium (III) will precipitate; at pH 1.0 the amount of coprecipitated rare earths from a mixture containing lanthanum, cerium (III), praseodymium, and yttrium is small. At pH 1.2 some of the rare earths will coprecipitate necessitating a double precipitation.

Procedure. Take a sample containing up to 0.1 g of thorium oxide in about 10 ml of perchloric acid solution. Add 200 ml of water and 1 g of sodium iodide; then adjust the pH to 1.5 to 1.6. Add 200 ml of a solution of tetrachlorophthalic acid containing 3 g per liter. This amount of acid represents 2.5 times the theoretical amount required to precipitate 0.1 g of thorium oxide. Adjust the pH to 1.0 to 1.1. Place the beaker on a temperature-controlled hot plate designed to reach 70 to 80°C. Employ rapid mechanical stirring. The precipitate will begin to form in approximately 20 min for amounts of thorium oxide in the range of 50 to 100 mg. Complete precipitation will be effected in 1.5 hr after the initial precipitate formation. If the amount of thorium is considerably less than 50 mg, the initial precipitate may not appear for 1 to 2 hr or longer.

Filter the hot solution; then wash with a cool 0.1 per cent tetrachlorophthalic acid solution adjusted to pH 1.5 with hydrochloric acid. Do not attempt to remove every trace of precipitate from the beaker walls. Next convert the thorium salt to insoluble hydrous thorium oxide by treating the precipitate with hot 2 per cent sodium hydroxide. Wash the stirring rod, beaker walls, and filter paper at least 10 times with this solution to remove the sodium tetrachlorophthalate.

Redissolve the hydrous thorium oxide with hot 2*N* hydrochloric acid, collecting the filtrate in the original precipitation beaker. Wash the stirring rod and beaker walls with the hot acid.

Reprecipitate the thorium with tetrachlorophthalic acid using the same procedure as for the original precipitation. Transfer the precipitate quantitatively to a previously ignited and weighed porcelain filtering crucible (Selas No. 3010). Wash thoroughly with a cool 0.1 per cent tetrachlorophthalic acid solution adjusted to pH 1.5.

Dry the crucible at 110°C; then place it in a cold muffle furnace and slowly raise the temperature to 350°C. Hold the temperature at 350°C for 45 min. This is necessary to prevent a loss of thorium through volatilization. Next slowly raise the temperature to 850°C and hold this temperature for 1 hr. Weigh the precipitate as ThO_2.

(f) *Benzoate.* Benzoic acid or ammonium benzoate has been found useful for the separation of thorium from the rare earths, calcium, strontium, and barium [102] by precipitation of thorium benzoate, $Th(C_6H_5COO)_4$. It was found that in the presence of acetic acid and thioglycollic acid thorium would precipitate from hydrochloric or nitric acid solutions at pH 2 but would not precipitate from a sulfuric acid solution until the pH was raised to 3.5. Zirconium, titanium, and aluminum also precipitate. The elements that do not form insoluble benzoates under these conditions are chromium(III), iron (II), iron(III), cerium(III), cerium(IV), bismuth, tin(II), tin (IV), uranium(IV), vanadium(IV), vanadium(V), cobalt(II), nickel, manganese(II), zinc, calcium, barium, strontium, magnesium, potassium, sodium, ammonium, lithium, cadmium, and mercury(II). This reagent has also been found useful for the separation of thorium from magnesium alloys that also contain the rare earths [103] and from solutions of monazite sands.[104]

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Procedure Using Benzoic Acid.[103] Take a sample containing 10 to 100 mg of thorium in hydrochloric acid solution. Adjust the volume to 100 ml. Add 2 drops of bromophenol blue indicator, and adjust with ammonium hydroxide (1+4) or hydrochloric acid (1+4) until the solution is just acid to bromophenol blue. Add 10 ml of freshly prepared sodium sulfite solution (dissolve 2 g of sodium sulfite in 98 ml of water and adjust to pH 2.4) to reduce any Ce(IV); then add 10 g of ammonium chloride. Heat to boiling on a hot plate. Pour in 100 ml of hot benzoic acid solution while stirring (dissolve 2 g of reagent grade benzoic acid in 98 ml of hot water), and continue to heat for 10 min. Set the solution aside until the precipitate settles; then filter through a coarse-porosity (Whatman No. 41H) paper. Police the beaker, and wash thoroughly with hot wash solution containing 0.25 g of reagent-grade benzoic acid in 100 ml of water. The precipitate can be ignited to constant weight and weighed as thorium dioxide.

Procedure Using Ammonium Benzoate in the Presence of Ammonium Acetate and Thioglycollic Acid.[102] Take a sample solution containing about 0.1 g of thorium dioxide and 10 ml of concentrated nitric acid in 150 ml of water. Heat almost to boiling, and add 20 ml each of 10 per cent ammonium benzoate and 10 per cent ammonium acetate and 3 ml of 90 per cent thioglycollic acid. Add a few drops of cresol red and then ammonium hydroxide dropwise until the indicator just turns yellow. Boil for 2 min, then allow the solution to stand on a steam bath for 15 min. The solution is now filtered using coarse-porosity (Whatman No. 41) paper and washed with a 1 per cent ammonium benzoate solution adjusted to the first yellow of cresol red with nitric acid or ammonium hydroxide. The precipitate can be ignited to constant weight and weighed as thorium dioxide.

(g) *Other Methods.* In addition to the methods covered in detail, there are many other excellent methods for the precipitation separation of thorium from other elements, principally those found with thorium in minerals and ores. These methods are covered in detail, with procedures included, in several reference books on analytical chemistry [8, 18, 19] and therefore will be discussed only briefly here.

Thorium hydroxide can be quantitatively precipitated from solution by the addition of ammonium hydroxide or alkali hydroxides. The precipitate starts to form at pH 3.5 to 3.6 and is not soluble in excess alkali. Carbonate and other anions that form strong complexes with thorium must be absent. When ammonium hydroxide is used, the precipitation should be made from a hot solution.

Potassium azide [105] and sodium thiosulfate [106] can be used to effect a separation from the rare earths by preferentially precipitating the thorium hydroxide. One or more reprecipitations are necessary to obtain a complete separation.

Hydrogen peroxide will precipitate complex thorium salts from ammoniacal, neutral, and acid solutions.[8, 19] The peroxides precipitated from ammoniacal or neutral solutions are gelatinous. However, from

hydrochloric or nitric acid solutions they are less gelatinous. Those formed from hot sulfuric acid solution are dense and crystalline. In neutral or acid solutions this method will separate thorium from the alkali metals, boron, beryllium, and magnesium.[108] Precipitation from acid solution has been used for the separation of thorium from solutions of monazite sands.[109] Thorium is not separated from zirconium and titanium. For precipitation from ammoniacal media, the solution is cooled to 0°C; whereas, for precipitation from neutral, acid, or sulfate media, the solution is heated to about 60°C.

Thorium is also precipitated from solution as thorium hypophosphate ($ThP_2O_6 \cdot 11H_2O$) and thorium pyrophosphate ($ThP_2O_7 \cdot 2H_2O$).[8, 18, 19] The pyrophosphate forms a granular, readily filterable precipitate. The hypophosphate forms a precipitate that tends to run through the filter and, therefore, is not used in quantitative procedures. Titanium, zirconium, hafnium, cerium(IV), and uranium(IV) also form pyrophosphate precipitates; however, separations from the rare earths can be made by multiple precipitations. The solution must be boiled after the pyrophosphate is added to effect complete precipitation of the thorium. If the acidity is too low, some thorium may fail to precipitate by forming the soluble double pyrophosphate [$Na_4Th(P_2O_7)_2 \cdot 2H_2O$]. Thorium pyrophosphate is also somewhat soluble in strong acid and in an excess of pyrophosphate. Thorium pyrophosphate is soluble in ammonium carbonate and oxalate and is converted to the hydroxide by boiling with sodium hydroxide.

Thorium fluoride (ThF_4) can be precipitated from aqueous solution by the addition of hydrofluoric acid.[8, 19] The precipitate formed in this manner is very gelatinous and must be centrifuged rather than filtered. This method can be used for the separation of thorium from zirconium, hafnium, niobium, tantalum, and tungsten. Elements that also form insoluble fluorides and precipitate along with thorium are uranium(IV), cerium(IV), the rare earths, and the alkaline earths. Potassium fluotitanate and fluozirconate are not very soluble and may precipitate if potassium is present. Mercurous chloride has been used as a carrier for the precipitation of small amounts of thorium.[110] The mercury is then separated from the thorium by careful volatilization of the mercurous chloride at a temperature below 500°C. A dense crystalline thorium fluoride is formed when monazite sands are fused with potassium bifluoride.[22] The bulk of the melt is readily soluble in water, and the insoluble thorium and rare earth fluorides are easily separated. Thorium fluoride can be dissolved in solutions of boric acid, ammonium oxalate, or aluminum nitrate.

Thorium molybdate [$Th(MoO_4)_2 \cdot xH_2O$] is precipitated from dilute acetic acid solutions by the addition of ammonium molybdate.[8] The

precipitate, which is readily dissolved in strong acids, is gelatinous and therefore must be filtered using filter pulp. Moderate amounts of calcium cause no interference; however, large amounts will precipitate with the thorium. Uranyl molybdate is difficultly soluble in dilute acetic acid, but the precipitation can be delayed for several hours by the addition of ammonium acetate. The precipitation of thorium molybdate has been used as the first step in a titrimetric determination of thorium.[111]

Thorium cupferrate [$Th(C_6H_5O_2N_2)_4$] is precipitated quantitatively from an acetic acid solution at a pH below 4, but free sulfuric acid must be absent.[8, 19] Thorium cupferrate can be extracted into chloroform, but again sulfuric acid prevents complete extraction. Uranium(VI) neither precipitates nor is extracted into chloroform under the conditions used.

Benzenearsonic acid and some of its derivatives, including *p*-dimethylaminoazobenzenearsonic acid, have been used for the precipitation of thorium.[8, 18, 19] A buffered acetate medium is required. Titanium, zirconium, and hafnium can be precipitated from strongly acid solutions; cerium(IV) and uranium(IV) are also precipitated. Less than 10 μg of thorium can be precipitated using *p*-dimethylaminoazobenzenearsonic acid.

A fair separation of thorium from the rare earths can be accomplished by a double precipitation with *m*-nitrobenzoic acid.[8] The precipitate [$Th(NO_2C_6H_4CO_2)_4$] formed in solutions free of excess mineral acid, settles rapidly and is easily filtered. The precipitate can be dried and weighed [112] or ignited to thorium dioxide. It is decomposed by both mineral acids and bases, and its formation is prevented by the presence of tartrates. Zirconium does not precipitate unless present in large amounts. Iron(III) and U(IV) form colored compounds with the reagent but do not precipitate.

A number of organic acids have recently been proposed for the precipitation separation of thorium. For the most part, they offer little advantage over the older methods either in selectivity or in a more favorable gravimetric factor. These methods are listed in Table 3.5.

3–6 METHODS OF DETERMINATION

3–6.1 Gravimetric Determination

Many thorium precipitates are suitable for the gravimetric determination of thorium. In most cases it is necessary to ignite the precipitate to thorium dioxide for weighing; however, a few precipitates can be successfully dried and weighed as the thorium compound.

(a) *Ignition to the Oxide.* Of the methods discussed in detail, the precipitates of thorium formed with oxalic, iodic, urea-formic,

Table 3.5—RECENT GRAVIMETRIC DETERMINATIONS OF THORIUM (ORGANIC ACIDS)

Reagent	Weighing form	Separations	Interferences	Ref.
β-Hydroxyamino-β-phenylpropionic acid.	ThO_2	Cerite earths, U, etc.	Hg, Fe, Zr	113
3'-Nitrophthalanilic acid.		Cerite earths	Zr	114
Diphenyl-2,2'-dicarboxylic acid.	Th salt or ThO_2.	PO_4^{-3}, AsO_4^{-3}, MoO_4^{-2}, alk. earths, Cu, Cd, Pb, Bi, Sn, Al, Cr, Ni, Co, Zn, Mn, Mg, Pd, cerite earths, U, Fe (II).	Zr, Hg, Ce(IV), Ag.	115 116 117 118
5-Nitrosalicylic acid		Zr, rare earths, etc.		119
3-Iodo-, 3,5-diiodo-, 2,3,5-triiodobenzoic acids.	ThO_2	Cerite earths, Ba, Sn, Ca, Mg, Zn, Ni, Co, Cr, Al, Mn.	Fe, Zr, Ti, Hg, V.	120
4-Aminosalicylic acid.	ThO_2	Cerite earths, U, Al, Cr, Ni, Co, Mn, Zn, Ca, Sr, Ba, Mg.		121
1-Hydroxy-, 1-hydroxy-4-bromo-, 1-hydroxy-4-nitro-2-naphthoic acids.		Cerite earths, Ba, Sr, Ca, Mg, Zn, Ti.	Zr	122
Rhodanine-*N*-salicylic acid.	ThO_2			123
Phytic acid	$Th(PO_3)_4$ or ThP_2O_7.	Rare earths	Zr, Ti, U, Fe.	124
trans-4-Hydroxycinnamic acid.	ThO_2	Rare earths	2% errors	125
2-(4-Sulfamoylphenylazo)-chromotropic acid.	ThO_2	Rare earths, Hg, Cu, Cd, Bi, Ca, Ba, Sr, Mg, Co, Ni, Au, U.	Zr, Pb, Hg (I), Fe, Al, Cr.	126
5,6-Benzoquinaldinic acid.	Th salt Th: R=1:4.	Rare earths, Ba, Sr, Ca, Mg.	Zr	127
2,4,5-Trichlorophenoxy-acetic acid.	Th salt or ThO_2.	Rare earths, Ba, Sr, Ca.	Zr, Fe	128
3-Nitrocinnamic acid.	Th salt Th: R=1:4.	Rare earths (double pptn. required).	Ti, Zr, Ce(IV).	129

tetrachlorophthalic, and benzoic acids can all be readily ignited to the oxide. Thorium hydroxide, peroxide, cupferrate, and *m*-nitrobenzoate can also be ignited to thorium dioxide. The gravimetric conversion factor for thorium dioxide to thorium is 0.87884.

It has been found [27] that thorium oxalate is completely converted to thorium dioxide at 610°C, although, in general, procedures in the literature call for ignition to 900 to 1000°C.

Thorium iodate can be converted [27] to thorium dioxide at any temperature above 674°C. The iodate is not generally ignited and weighed; this separation is rather followed by a different precipitation or the determination is finished titrimetrically or spectrophotometrically.

Basic thorium formate formed by the hydrolysis of urea in the presence of formic acid is readily ignited to thorium dioxide. The recommended [21] ignition temperature is 950°C. The precipitate has a tendency to carry down silica, and this must be removed by the usual treatment with hydrofluoric and sulfuric acids.

When thorium tetrachlorophthalate is ignited to thorium dioxide, care must be exercised to prevent the loss of thorium through volatilization.[101] The precipitate should first be dried at 110°C, then heated slowly to 350°C, and maintained at this temperature for 45 min. The temperature may then be increased slowly to 850°C, at which temperature it can be ignited to constant weight.

Thorium benzoate can be ignited to thorium dioxide at any temperature above 510°C and there is evidence [130] that it can be weighed as the benzoate [$Th(C_6H_5COO)_4$] if the temperature is held below 285°C. The gravimetric factor for converting thorium benzoate to thorium is 0.32387.

(b) *Weighing of the Thorium Salt.* The thorium salt of 8-quinolinol has been recommended in the literature as a weighing form for thorium. There appears to be little agreement among the various workers. One states [131] that the precipitate [$Th(C_9H_6NO)_4 \cdot C_6H_9NOH$] should be dried to constant weight at 130°C and that the extra molecule of oxine is slowly lost above 130 to 140°C. Another worker [132] states that the extra molecule of oxine is lost starting at 80°C and that the normal salt is stable from 250 to 310°C, with complete conversion to the oxide above 600°C. Other workers [27] have reported that there is no suitable weighing form at any temperature between 20 and 945°C. Therefore, the use of 8-quinolinol is not recommended for thorium.

(1) *Picrolonic Acid.* The precipitate formed by thorium with picrolonic acid [$Th(C_{10}H_7O_5N_4)_4$] can be weighed as the compound rather than as thorium dioxide.[27] The precipitate is voluminous, and few separations of thorium from other metals can be made be-

cause the rare earths and most heavy metals also precipitate. The method is suitable for the determination of milligram quantities of thorium.[131]

Procedure. The picrolonic acid solution is prepared by dissolving 2.6 g of the reagent in 1 liter of water. The sample should be 50 to 60 ml in volume, should contain no more than 10 mg of thorium, and should be free of ammonium salts. Any mineral acid present is just neutralized with dilute sodium hydroxide, and any precipitate thus formed is dissolved by adding glacial acetic acid and heating if necessary. Enough acetic acid is added to make the solution 2.5 per cent in acetic acid. Fifty milliliters of the picrolonic acid solution is added. The solution is stirred and allowed to stand 15 min or more. The precipitate can now be filtered, washed with water, and dried between 60 and 200°C. Care must be exercised because the precipitate has been known to explode at 268°C. The gravimetric conversion factor is 0.20779.

(2) *Ferron.* 7-Iodo-8-hydroxyquinoline-5-sulfonic acid (ferron) forms a precipitate with thorium which can either be weighed as the compound or ignited to thorium doxide.[27, 133] The yellow precipitate, which contains two ferron molecules per thorium atom [$Th(C_9H_4OSO_3NI)_2$], forms between pH 2.0 and 3.5 and is easily filtered. Separation from U(VI) can be made if the amount of uranium is not large. Sulfates interfere with precipitation, and many other elements are also precipitated.

Procedure.[133] A few drops of bromophenol blue are added to the mildly acid thorium solution. Ammonium acetate is then added until the indicator is blue. Dilute hydrochloric acid is then added until the color is yellow (pH 3). Heat the solution to 60 to 80°C, and add a 0.2 per cent ferron solution with stirring. The amount should be 4 ml of reagent for each milligram of thorium but not less than 40 ml. The precipitate is digested for half an hour, filtered, and washed with a 0.02 per cent ferron solution. The precipitate can now be dried between 110 and 216°C or ignited to thorium dioxide at a temperature greater than 570°C. The gravimetric conversion factor for thorium-ferron to thorium is 0.24944.

3–6.2 Titrimetric Determination

The titrimetric determinations of thorium have been developed more recently than the gravimetric determinations. Since thorium exhibits only one oxidation state in aqueous solution, the early titrimetric determinations were necessarily indirect and involved, with, in many cases, no advantages over gravimetric methods. With the growing interest in chelometric titrations, a large number of methods for the titration of thorium with ethylenediaminetetraacetic acid have appeared in the literature. These titrations are largely the same as far as the pH and interferences are concerned, the only real difference being in the way the end point is detected.

(a) *Molybdate.* The formation of insoluble thorium molybdate has been used as the basis for several methods for the titrimetric determination of thorium. In one procedure, the thorium is titrated directly with an ammonium molybdate solution, the end point being observed through a color change of diphenylcarbazide.[134] The method is rapid but not highly accurate because of the difficulty of observing the end point.

A variation on this procedure is to follow the titration potentiometrically with a 0.1*N* calomel reference electrode and a molybdenum-wire indicator electrode.[111] Calcium does not interfere with the determination of thorium by this method.

Another variation of the molybdate method is to precipitate thorium molybdate, wash the precipitate free of excess molybdate, dissolve the precipitate, and determine the molybdenum by reduction with an amalgamated zinc reductor and titration with Ce(IV) sulfate.[111]

$$Th^{+4}+2MoO_4^{-2}\rightarrow Th(MoO_4)_2$$

$$2MoO_4^{-2}+3Zn^0+16H^+\rightarrow 2Mo^{+3}+3Zn^{+2}+8H_2O$$

$$Mo^{+3}+3Fe^{+3}\rightarrow Mo^{+6}+3Fe^{+2}$$

$$Fe^{+2}+Ce^{+4}\rightarrow Fe^{+3}+Ce^{+3}$$

Calcium and uranium do not interfere, but the rare earths do.

The end point of the molybdate method has also been detected amperometrically using a manual polarograph.[135, 136] Rare earths do not interfere seriously, a relative error of about 1.5 per cent being obtained for the determination of thorium in the presence of rare earths. It was found that nitrate, sulfate, and perchlorate ions must be completely absent from the titration solution. It was also found that the molybdenum to thorium ratio in the precipitate increases as the amount of thorium increases. Therefore, it is necessary to prepare a standard curve relating "thorium taken" and "molybdenum required." For the determination of thorium in monazite sands, the thorium and rare earths are separated as the oxalates before the titration is undertaken. The results obtained using this method on monazite sands compared favorably with the results obtained using the urea and tetrachlorophthalate methods (see Sec. 3–6.1).

Procedure.[136] Evaporate the sample solution containing 50 to 150 mg of thorium oxide and up to 850 mg of rare earth oxides in hydrochloric acid to dryness on a low-temperature hot plate. Cool the residue, and add 125 ml of 5*M* sodium chloride solution and 17 ml of glacial acetic acid. Dilute to approximately 200 ml and then adjust the pH to 1.5 with a 20 per cent sodium acetate solution. Transfer the solution to a 250-ml volumetric flask, and dilute to volume. Pipet a 50-ml aliquot into the

titration cell (conventional H type), and pass nitrogen, freed of oxygen with vanadous sulfate,[137] through the solution for 15 min. Slowly add ammonium molybdate solution dropwise while stirring the solution with nitrogen gas. Titrate at an applied potential of −0.95 volt vs. a saturated calomel electrode. Bubble nitrogen gas through the solution for at least 2 min before obtaining the diffusion current. Prepare a standard curve by plotting "molybdenum required" against "thorium taken."

(b) *Iodate.* The titration of the iodine in the thorium iodate precipitate has been used as a titrimetric determination of thorium.[106, 138-140] Most published procedures are essentially the same in that they call for the addition of potassium iodide and the titration of the liberated iodine with a sodium thiosulfate solution.

$$Th^{+4} + 4IO_3^- \rightarrow Th(IO_3)_4$$

$$Th(IO_3)_4 + 20I^- + 24H^+ \rightarrow 12I_2 + 12H_2O + Th^{+4}$$

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^-$$

The major cause for error is the difficulty of washing the precipitate free of nitrate or excess iodate without decomposing or dissolving part of the precipitate. The procedures are rapid but not highly accurate. In a study of the determination of thorium by this method in the presence of rare earths,[139] it was found that the average recovery of thorium on synthetic samples was about 99 per cent. The results on actual monazite sands compared favorably with those obtained by the hexamine method, considering the difference in time required for analysis. In this study it was also found that the average iodate to thorium ratio was 4.02 to 1 under the conditions used.

Procedure.[139] Add 50 ml of concentrated nitric acid to a 100-ml sample containing 175 mg of thorium dioxide. If Ce(IV) is present, add a few drops of 30 per cent hydrogen peroxide and remove the excess by boiling. Cool the solution, and add 15 g of potassium iodate dissolved in 50 ml of concentrated nitric acid and 30 ml of water. The resulting suspension is allowed to stand for 0.5 hr with frequent stirring. The precipitate is then removed by filtration through a very fine qualitative filter paper (Whatman No. 50) and washed with 20 ml of a solution containing 2 g of potassium iodate in 25 ml of concentrated nitric acid and 225 ml of water.

The precipitate is then washed into the original precipitation beaker with hot water, the suspension is heated to boiling, and 30 ml of concentrated nitric acid is added with constant stirring to dissolve the precipitate. Allow the solution to cool to room temperature and reprecipitate the thorium by the addition of 4 g of potassium iodate dissolved in 7 ml of concentrated nitric acid and 20 ml of water. The precipitate is filtered onto the original paper and washed with no more than 100 ml of ice water added in small portions.

The filter paper and precipitate are transferred to a 500-ml Erlenmeyer flask, and the precipitate is dissolved in 100 ml of 4*N* sulfuric

acid. About 50 ml of water and 30 to 35 ml of a 10 per cent potassium iodide solution are added. The liberated iodine is titrated immediately with standard 0.2*N* sodium thiosulfate solution to the starch end point. The thorium is calculated on the basis of 4 moles of iodate to 1 mole of thorium.

(c) *Oxalate.* Oxalic acid has been reported in the literature as a titrant for thorium.[141-143] The results obtained are always low for a direct titration because the precipitate is deficient in oxalate, but satisfactory results can be obtained by a back-titration or by a reversal whereby the thorium solution is added to the oxalate. Various techniques have been used for detecting the end point. One worker [141] added thorium to excess oxalate, filtered the precipitate, and titrated the oxalate in the precipitate with permanganate or with an excess of Ce(IV) sulfate back-titrated with Fe(II) sulfate.

$$Th^{+4}+2C_2O_4^{-2}\rightarrow Th(C_2O_4)_2$$

$$5Th(C_2O_4)_2+4MnO_4^{-}+32H^{+}\rightarrow 20CO_2+4Mn^{+2}+5Th^{+4}+16H_2O$$

A high-frequency oscillator has also been used to detect the end point in this titration.[142] The direct titration yielded end points that were sharp and reproducible but about 1 per cent low. A back-titration, however, gave satisfactory results. The end point of a direct titration has been detected visually using 2,7-dinitroso-1, 8-dihydroxynaphthalene-3,6-disulphonic acid (dinitrosochromotropic acid).[143] The color of the thorium complex is pink-violet; that of the free indicator is red. Mercury(I), tin(II), lead, copper, iron (III), and zirconium interfere with the titration; but cadmium, barium, calcium, and aluminum do not interfere to a very large extent. The titration is most satisfactory when the amount of thorium is small because the precipitate obscures the end point. In general, the relative errors are rather large.

(d) m-*Nitrophenylarsonic Acid.* Thorium can be titrated amperometrically using *m*-nitrophenylarsonic acid.[144] Careful control of hydrochloric acid concentrations and neutral salts is necessary. Interferences were not studied.

(e) *Ethylenediaminetetraacetic Acid.* Ethylenediaminetetraacetic acid (EDTA) or, more properly, the disodium salt thereof has become very popular as a titrant for thorium. A recent review lists over 50 references to this titration.[145] The titration of thorium with EDTA is also discussed in at least two books dealing with EDTA titrations.[146, 147] Thorium forms a rather stable 1 to 1 complex with EDTA, the log of the stability constant being listed as 23.2. This complex is stable at rather low pH values, making titrations possible in the pH

range 2 to 3.5 where many other elements do not interfere by forming EDTA complexes. The end point of the titration is usually detected by the visible color change of an indicator. The indicators used form weaker complexes with thorium than does EDTA, the thorium indicator complex being a different color than the free indicator. The end point has also been detected potentiometrically, spectrophotometrically, amperometrically, and by means of a high-frequency oscillator. Both direct titrations and back-titrations have been used. No attempt will be made to discuss all the visual indicators that have been proposed for the titration. Three indicators that seem to be referred to most frequently in the literature are the sodium salt of 1,2-dihydroxyanthraquinone-3-sulfonic acid (Alizarin S, also known as Alizarin Red S and Alizarin Carmine), 3,3′-bis[*N*,*N*-di(carboxymethyl) aminomethyl]-*o*-cresol-sulfonphthalein (xylenol orange), and 3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid (pyrocatechol violet).

(1) *Alizarin S.* In a study of the direct titration of thorium using Alizarin S as the indicator,[148] it was found that the pH should be between 2.3 and 3.4. The ions that were found to interfere were titanium(IV), zirconium(IV), cerium(III), vanadium(IV), iron (III), nickel(II), copper(II), tin(II), tin(IV), lead, and bismuth (III). In addition, anions such as phosphate, fluoride, and oxalate interfere. Ions found not to interfere are lithium, sodium, potassium, magnesium, calcium, strontium, barium, lanthanum, chromium, manganese, cobalt, silver, zinc, cadmium, and uranium(VI). Thorium has also been titrated [149] in the presence of aluminum using Alizarin S as the indicator at pH 3.5. The thorium in thorium-tungsten alloys can also be titrated using Alizarin S as the indicator.[150] In this case the pH was 2.8, the tungsten was masked with peroxide, and a back-titration with standard thorium solution was performed, the end point being detected spectrophotometrically. The addition of a small amount of methylene blue to the Alizarin S is said to sharpen the end point. This has been used for the determination of thorium in thorium-aluminum alloys after separation of the aluminum [151] and in thorium-uranium alloys with the uranium present.[152]

Procedure.[148] Take a sample containing 6 to 50 mg of thorium and adjust the volume to about 25 ml. Add 4 drops of Alizarin S indicator (0.05 g dissolved in 100 ml of water), and adjust the acidity with dilute ammonia until a definite pink color appears (about pH 2.5). Titrate with standard 0.025*M* EDTA (dissolve 9.3 g of the disodium salt in water, dilute to 1 liter, and standardize against a thorium solution of known concentration) until the color begins to fade rapidly. Adjust the pH to 3.0 using a pH meter and continue the titration. The end point has been reached when the last trace of pink disappears, giving a clear yellow color. Magnetic stirring adds to the convenience of the titration.

(2) *Pyrocatechol Violet.* Pyrocatechol violet has also proved useful as an indicator for the EDTA titration of thorium. It has been found that lead(II), uranium(IV), copper(II), silver, cobalt(II), nickel(II), manganese(II), zinc, calcium, strontium, magnesium, sodium, potassium, ammonium, and the rare earths do not interfere.[153, 154] Interfering elements are iron(III), titanium(IV), zirconium, bismuth, tin(IV), antimony, molybdenum(VI), and tungsten (VI) as well as fluoride, phosphate, and other anions capable of forming stable complexes with thorium. The interference by Fe(III) can be avoided by the use of ascorbic acid.[155] The titration can also be performed as a back-titration,[156] and it has proved useful for titrations in the ultramicro range.[157] The direct titration has been applied to the determination of thorium in gas mantles and glass [158] and after separation in ores,[159] bismuth-thorium alloys,[61] and thorium-uranium-bismuth alloys.[160]

Procedure. Take a sample containing no more than 100 mg of thorium and dilute to 100 ml. Adjust the pH to 2.5 to 3.5 with nitric acid or ammonia, add 3 to 5 drops of pyrocatechol violet solution (0.1 g dissolved in 100 ml of water), and titrate with standard EDTA (standardized against a thorium solution of known concentration) until the red color changes to yellow.

Procedure (Iron Present).[155] Take a sample containing no more than 100 mg of thorium and dilute to 50 to 100 ml. Adjust the pH to 2.5 to 3.5 with nitric acid or ammonia. Then add 5 drops of a 2 per cent solution of sulfosalicylic acid, and, with stirring, add a freshly prepared 1 per cent solution of ascorbic acid dropwise until the red color disappears and 1 to 2 ml in excess. Add the pyrocatechol violet and titrate as in the absence of iron.

(3) *Xylenol Orange.* Another very useful indicator for the titration of thorium is xylenol orange.[161, 162] Elements that do not interfere are aluminum,[161] lithium, beryllium, uranium,[163] and magnesium.[164] Elements that definitely interfere are zirconium, iron,[161] and cerium.[163] A number of other elements may also interfere.

Procedure. Adjust the pH of the thorium solution to 3, and add a few drops of xylenol orange indicator solution (dissolve 0.1 g of xylenol orange in 10 ml of ethanol and dilute to 100 ml with water). The pH must be kept within the limits 2.5 to 3.5 because at lower pH values the results for thorium are low, whereas at higher pH values the color change becomes indistinct. Titrate with either 0.05*M* or 0.01*M* EDTA solution from a red to a lemon-yellow color. The EDTA should be standardized against a thorium solution of known concentration.

(4) *Other Visual Indicators.* Two other indicators that have been reported as suitable for the titration of thorium are 2′-sulfo-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid (eriochrome cyanine), which has been used for a photometric titration in the presence

of cerium [165] and after separation from uranium, titanium, and tungsten in alloys of thorium with these metals,[166] and 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid, trisodium salt (Arsenazo).[167]

(5) *Oscillometric End Point.* High-frequency oscillators have also been used to detect the end point of the titration of thorium with EDTA. A 5-Mc oscillator was used for the titration of 0.001*M* and 0.005*M* thorium solution with satisfactory results.[168] All electrolytes change the shape of the titration curve. Chloride, bromide, iodide, bromate, chlorate, thiocyanate, iodate, and sulfate do not interfere. Acetates, oxalates, and fluorides give serious interference. No interference other than the changing of the shape of the curve was observed from barium, strontium, silver, thallium(I), and the alkali metals. If a 250-Mc oscillator were used, the thorium concentration could be increased to 0.04*M*.[169]

(6) *Spectrophotometric End Point.* The titration of thorium with EDTA has also been carried out by means of an automatic spectrophotometric apparatus. Recording spectrophotometers are used in conjunction with constant-flow motor-driven burets. The wave length is held constant, and the volume of titrant is correlated with the number of scale divisions on the chart. In one case the absorbance of the Cu(II)-EDTA complex is measured at 290 mμ and plotted against milliliters of EDTA for a direct titration or against milliliters of Cu(II) solution in a back-titration.[170] For the direct titration, relative errors of 5 parts per thousand are claimed for amounts of thorium between 20 and 70 mg. In the back-titration, results precise to within 1 part per thousand were obtained. Lead, copper(II), nickel, bismuth(III), iron(III), zirconium, tin(II), tin(IV), and cerium(III) interfere. Another spectrophotometric method [171] for detecting the end point is to measure the decrease in the absorbance of the thorium-quercetin complex at 422 mμ. Two to thirty-three micrograms of thorium was determined by this method with a coefficient of variation of 1 per cent. Iron(III), titanium(IV), fluoride, phosphate, acetate, and sulfate must be absent. Relatively large amounts of calcium, cobalt(II), mercury(II), uranium(IV), aluminum, and chromium (III) can be tolerated. The presence of chloride, perchlorate, and nitrate has no effect on the titration.

(7) *Potentiometric End Point.* The end point of the titration of thorium with EDTA can also be detected potentiometrically using a mercury electrode with a small amount of Hg(II)-EDTA complex in solution.[172] The titration can be either a direct titration at pH 3.2 or a back-titration with Cu(II) in an acetate buffered solution at pH 4. The reference electrode is saturated calomel, and the indica-

tor electrode can be either liquid mercury or an amalgamated gold wire. The relative error found was about 0.5 per cent on 90 mg of thorium and 1 to 2 per cent on 18 mg of thorium.

3–6.3 Spectrophotometric Determination

The early methods for the spectrophotometric determination of thorium were indirect in that they called for the precipitation of thorium followed by dissolution of the precipitate and determination of the anion. More recently various colored complexes of thorium have been investigated. In these the color of the thorium compound is measured directly. Most of these methods are subject to the same interferences, and, unfortunately, several of these commonly occur with thorium in ores and minerals. Therefore, the spectrophotometric determination is nearly always preceded by a separation.

(a) *Thorin.* The most widely used reagent for the spectrophotometric determination of thorium is 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid. This compound has several trivial names: Thorin, Thoron, Thoronol, APANS, and Naphtharson. It will be referred to here as Thorin. This compound forms a moderately soluble red complex with thorium.[47] The reagent itself absorbs in the same region as does the thorium complex, the maximum difference being at 545 mμ. The amount of thorium taken for each determination can be from 5 μg to 2 mg, depending upon the conditions used. Many elements show some absorbance with thorin, the most serious interferences being zirconium, iron(III), uranium(IV), titanium, tantalum, tin, and niobium. Fluoride causes serious interference, and sulfate interferes slightly.

The interference of Fe(III) can be lessened by reduction with hydroxylammonium chloride, and that of uranium, by oxidation to U(VI).[47] Ascorbic acid can be used for the reduction of iron.[64] The interference by zirconium can be effectively reduced by the use of *meso*-tartaric acid as a masking agent.[173] Because of the frequent presence of interfering elements in materials in which thorium is to be determined, there are a number of papers in the literature presenting methods of separating thorium from the elements that interfere with the Thorin determination. A fluoride precipitation followed by a mesityl oxide extraction separates thorium from most interfering elements.[22, 23] Thorium has been separated from uranium by extraction with thenoyltrifluoroacetone.[174] Separations have been made using both cation- and anion-exchange resins.[61, 64] Chromatographic column separations have also been effective,[89] as has precipitation as the oxalate with a calcium carrier.[175]

Procedure.[22] Take a sample containing 0.5 to 1.5 mg of thorium and place it in a 250-ml beaker. Dilute to 140 ml and add, by pipet,

20 ml of a 0.1 per cent Thorin solution. Adjust the pH to 0.8 ± 0.1 with a pH meter using perchloric acid. Transfer to a 200-ml volumetric flask and dilute to volume with water. The solutions are ready for measurement immediately after dilution and mixing. Measure the absorbance within 2 hr against a reagent blank containing the same amount of Thorin at the same pH. The measurement is made at 545 mμ in 1-cm cuvets. The amount of thorium is read from a standard curve prepared by measuring the absorbance of known amounts of thorium and plotting absorbance vs. concentration.

Procedure Using meso-*Tartaric Acid as a Masking Agent.*[178] Take a sample containing 50 to 150 μg of thorium. Place it in a 100-ml beaker with 1 ml of perchloric acid; then transfer it to a sand bath and fume to dryness. Care must be exercised because heating too strongly may convert zirconium to an insoluble form which occludes thorium. Cool the beaker, and dissolve the residue in 1 ml of (1+1) hydrochloric acid. Rotate and tip the beaker so that the acid comes in contact with all parts of the residue. Allow the solution to stand 1 to 2 min; then add 4 ml of water. Cover the beaker and heat it on a steam bath for 5 min. Then add 1 ml of a 10 per cent hydroxylammonium chloride solution (10 per cent aqueous solution) and 0.2 ml of cupric chloride catalyst solution (0.538 g of cupric chloride dihydrate dissolved in 250 ml water). Heat the solution on a steam bath for 5 min more. Cool the solution. If the solution is clear, transfer it to a 25-ml volumetric flask. If the solution is not clear, add filter pulp and filter the solution into the flask using a very small, slow filter and wash. Add 4 ml of a 10 per cent *meso*-tartaric acid solution and mix. Add 3 ml of a 0.1 per cent Thorin solution and dilute to volume. Measure the absorbance at 545 mμ in 5-cm cells against a blank containing the same amounts of all the reagents. Make the measurements within 5 to 10 min after adding the *meso*-tartaric acid. Read the amount of thorium present from a standard curve prepared by measuring the absorbance of solutions containing known amounts of thorium.

(b) *Morin.* A colored complex formed between thorium and 3,5,7,2′,4′-pentahydroxyflavone (morin) is used as a very sensitive method for the determination of thorium.[176] As little as 0.1 μg of thorium can be detected in 50 ml of solution. Hydrochloric, nitric, and perchloric acids do not interfere, but sulfuric does. Zirconium and aluminum must be absent. Iron(III) is also a serious interference, but this can be decreased by the addition of hydroxylammonium chloride. Ytterbium, praseodymium, yttrium, uranium, and lead have been found to interfere to some extent; the interference from calcium and lanthanum is very slight and in most cases can be neglected. The ratio of thorium to morin has been found to be 1 to 2. The free morin does not adsorb at the wave length at which the absorbance of the complex is measured. This method has been

applied to the determination of thorium in urine following a fluoride precipitation with a lanthanum carrier and a thenoyltrifluoroacetone extraction.[177]

Procedure.[176] To a 50-ml volumetric flask add 1.0 ml of 0.63*N* hydrochloric acid and then the thorium solution containing no more than 60 μg of thorium and free from other ions. (This solution should be previously adjusted to pH 2.0). Now add 4 ml of a 10 per cent hydroxylammonium chloride solution, and dilute to about 20 ml with water. Mix the contents and then add 2.0 ml of morin solution (a 0.1 per cent solution of morin in 95 per cent of ethyl alcohol) and mix again. Dilute to volume, mix thoroughly, and after half an hour measure the absorbance at 410 mμ against water as a reference solution. The amount of thorium present is read from a standard curve prepared from solutions containing known amounts of thorium.

(c) *Quercetin.* 3,5,7,3′,4′-Pentahydroxyflavone (quercetin) is another reagent that has been used for the spectrophotometric determination of thorium.[44] A linear relationship between absorbance and concentration is obtained from 10 to 150 μg of thorium in a 25-ml volume. The ratio of thorium to quercetin has been found to be 1 to 2 with the absorbance maximum occurring at 422 mμ. The amount of various ions per microgram of thorium which cause a 10 per cent error are: nickel, 4 μg; iron(II), 0.08 μg; uranium(VI), 0.12 μg; and aluminum, 0.04 μg. Chloride and perchlorate cause no interference; nitrate causes erratic results; and sulfate, acetate, fluoride, and phosphate must be absent. The color development can be preceded by an ion-exchange separation and a thenoyltrifluoroacetone extraction to separate thorium from the interfering ions.

Procedure. Take a sample containing 10 to 150 μg of thorium in a volume of about 15 ml. Adjust the pH to 2.8 to 3.0 by the addition of a 10 per cent solution of sodium carbonate. Transfer the solution to a 25-ml volumetric flask. Add 4 ml of 95 per cent ethyl alcohol and 2 ml of quercetin solution (0.1 per cent in 95 per cent ethyl alcohol). Dilute to volume with water and allow to stand for 15 min. before reading. Read against a reagent blank at 422 mμ in 1-cm. cells. Prepare a standard curve using solutions of known thorium concentration.

(d) *Other Methods.* *p*-Dimethylaminoazo-phenylarsonic acid (pararsonic acid) has been used for the spectrophotometric determination of thorium.[178] The very insoluble thorium compound is precipitated, filtered, washed, and dissolved in ammonium or sodium hydroxide. The color of the resulting solution is then measured at 460 mμ.

Thorium iodate can be reduced with hypophosphorus acid in the presence of sulfuric acid.[179] The liberated iodine is then extracted into carbon tetrachloride, and the absorbance is measured at 520 mμ.

Various compounds with a chromotropic acid nucleus have been investigated as reagents for the spectrophotometric determination of thorium. Interference by zirconium, iron(III), phosphate, fluoride, and sulfate is common to all these reagents. These reagents are: 2,7-bis(4-sulfonaphthylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (di-SNADNS),[180] 2-(2-arsonophenylazo)chromotropic acid,[181, 182] 2,7 - dinitroso - 1,8 - dihydroxynaphthalene - 3,6 - disulfonic acid,[183] 2-(p-sulfophenylazo) - 1,8 - dihydroxy - 3,6 - naphthalenedisulfonic acid (SPADNS),[184] and 2-(4-carboxy-2-hydroxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid.[185]

2,4-Dichlorophenoxyacetic acid (2,4-D) has also been used for the spectrophotometric determination of thorium.[186] The thorium salt of 2,4-D is soluble in aqueous ammonium carbonate and shows a maximum absorbance at 230 mμ. The optimum concentration range is 2 to 14 μg of thorium per milliliter.

3–6.4 Other Methods of Determination.

Methods for the determination of thorium involving special analytical techniques such as spectrochemical, electrometric, X-ray spectroscopic, mass spectrometric, and radiochemical have been omitted from this chapter because it is felt that these methods should be discussed in the chapters of this book which describe these techniques.

A discussion of the determination of trace-element impurities is also omitted from this chapter. Because of the similarity of the methods used for impurity determinations in many metals, these methods, as they apply to many of the materials used in reactors, are discussed in Chap. 11.

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CHAPTER 4

BERYLLIUM

By C. J. Rodden*

The use of beryllium as a moderator and a reflector in reactors has drawn attention to the analytical chemistry of this metal. Although commercial beryllium metal is not so pure as many other reactor materials, the impurities are still rather low in concentration, and trace methods of analysis are employed to a large extent. As an indication of the range of impurities in commercial beryllium, the analysis given in Table 4.1 is typical of present vacuum-cast production material.

This chapter will deal with current methods of analysis of beryllium oxide and beryllium metal. The analysis of ores and compounds of beryllium has been adequately reviewed [1, 2] and will not be discussed. A rather extensive bibliography of the analytical chemistry of beryllium is given by Banks, McClure, and Meek,[3] and the analysis of metal is discussed by Rodden and Vinci.[5]

The reader is reminded of the health hazards in the handling and processing of beryllium and its compounds. A discussion of the health problems involved in the handling of beryllium is given by Eisenbud,[4] and the methods of sampling and analysis of air containing beryllium are discussed by Rodden and Vinci.[5]

4–1 METHODS OF SOLUTION

Beryllium metal is vigorously attacked by most of the common acids, with the exception of nitric acid. When the metal is dissolved by adding sulfuric acid (1+1) the reaction is so vigorous that the beaker containing the solution has to be kept in an ice bath. The same type of reaction occurs when beryllium metal is dissolved in hydrochloric acid (1+1). When perchloric acid (1+1) is used, the reaction starts out quite vigorously; but after the first addition of acid the reaction slows down, and the metal does not entirely dissolve even on warming. When beryllium metal is treated with nitric acid (1+1), no apparent reaction occurs even on warming. However, when 1 drop of 18*M* sulfuric acid is added, complete solution is obtained. Beryllium metal can be dissolved in nitric acid (1+1) by the addition of a few drops of 50 per cent fluoboric acid solution. The usual practice, however, is to employ sulfuric or hydrochloric acid.

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Table 4.1—ANALYSIS OF VACUUM-CAST BERYLLIUM METAL

Element	Concentration	
	Wt. %	Ppm
Total Be	99. 7	
BeO	0. 20	
Fe	0. 12	
Mg	0. 10	
Al	0. 06	
Total C	0. 06	
Si	0. 03	
Ni	0. 012	
Total N	0. 011	
Ca	<0. 010	
Cu	0. 008	
Mn	0. 008	
Cr	0. 006	
U		10.
Pb		5.
Co		2.
Mo		2.
Ag		1.
Cd		1.
Li		<1.
B		0.40.
Gd		0.07.
Dy		<0.07.
Eu		<0.07.
Zn		Not detected.

The alkalis react with beryllium metal with the evolution of hydrogen. Since beryllium hydroxide is amphoteric, it will dissolve in excess alkali. If the solution is dilute in alkali and is boiled, the beryllium may precipitate. This method of solution may be useful in some cases.

The solubility of beryllium oxide depends on the previous ignition treatment. After ignition to 1100°C the oxide dissolves in sulfuric acid (1+1) when heated on a hot plate at low temperature. The solubility of beryllium oxide when treated with hydrochloric acid will depend on the temperature of ignition. When ignited to 700°C and then treated with hydrochloric acid (1+1) for 30 min on a hot plate at low temperature, it is soluble. However, if it is ignited to 800°C and then treated with hydrochloric acid (1+1) as above, it is only somewhat soluble; when ignited to 900 and 1000°C, it is practically insoluble. With concentrated hydrochloric acid the ignition temperature can be increased by about 100°C, i.e., the beryllium oxide will be

soluble after ignition to 800°C and somewhat soluble after 900°C. High-fired (1600°C) beryllium oxide can be dissolved in concentrated hydrofluoric acid by heating overnight on a steam bath in a covered platinum dish; sulfuric acid (1+1) with a few drops of hydrofluoric acid can also be used.

4–2 METHODS OF SEPARATION

Since beryllium is usually determined by a gravimetric procedure, its separation from interfering elements is the main problem in its determination. The methods usually employed involve precipitation of the 8-hydroxyquinolates (oxinates) of interfering elements or the complexing of interfering elements with ethylenediaminetetraacetic acid (EDTA) in the precipitation of beryllium hydroxide with ammonium hydroxide. Since beryllium is not electrolyzed into mercury, the mercury-cathode electrolysis method of separation can also be quite useful. Unfortunately, however, the mercury-cathode electrolysis method does not separate beryllium from aluminum, one of its common impurities. Solvent-extraction methods have been used in radiochemical work and are occasionally employed in other separation and concentration procedures. Beryllium can be retained on the cation-exchange resin, Amberlite IR-120, when EDTA is present in the solution. The complexing action of this reagent prevents the retention of many interfering elements. This procedure is rather time consuming, however.

4–2.1 Precipitation

There are no specific precipitants for beryllium when it occurs in unknown mixtures. 8-Hydroxyquinoline (oxine) can be used to separate beryllium from aluminum and many other elements. 8-Hydroxyquinaldine can also be used to separate beryllium from many interfering elements. The use of the hydroxide precipitation of beryllium has been extended by employing ethylenediaminetetraacetic acid (EDTA) to complex many elements.

The separation by means of phosphate ion may be useful for reactor materials of zirconium and its alloys. Zirconium, hafnium, and titanium can be precipitated with monoammonium phosphate from a solution containing hydrochloric or sulfuric acid (1+9).

Although iron, titanium, vanadium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, tin, antimony, bismuth, polonium, palladium, and gallium can be separated by precipitation with cupferron in a hydrochloric or sulfuric acid solution (1+9), it is preferable to extract the cupferrates with chloroform as described in Sec. 4–2.3(d).

Small amounts of rare earths are separated from beryllium as oxalates or fluorides with thorium or yttrium as a carrier.[6, 6a] Details of these procedures are given in Sec. 4–4.9.

(a) *8-Hydroxyquinoline.* The usual method employed for the separation of beryllium from aluminum and most of the other members of the ammonium hydroxide group is by the use of 8-hydroxyquinoline (oxine) in acetic acid–acetate solution. There are indications that incomplete separations are made from the rare earths as well as from chromium.[7] In addition to separating beryllium from the interfering elements of the ammonium hydroxide group, oxine also separates it from molybdenum, tungsten, uranium, copper, nickel, cobalt, zinc, cadmium, mercury, and bismuth. The procedure is given below.[8]

In a series of articles by Motojima [9-11] a new approach to the separation and determination of beryllium by oxine, involving the precipitation of beryllium from weakly alkaline solution, is described. A beryllium hydroxide suspension, freshly precipitated with ammonium hydroxide and having a pH of about 9, is treated with a solution of oxine consisting of 2 g of oxine dissolved in 100 ml of acetic acid (1+19). The oxine precipitate[9] maintains a constant weight between 110 and 180°C with a composition of $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$.

In the work on this method at the New Brunswick Laboratory, the calculated amount of oxine plus 10 per cent excess was added. The pH of the solution was about 8.5. The pH was then adjusted to 8 ± 0.2 with solid ammonium chloride. The fine yellow precipitate that formed was allowed to digest at 40°C for 2 to 3 hr before filtration on a sintered-glass filter.

In the separation of beryllium from aluminum,[11] Motojima precipitates aluminum from an acetate buffer solution at a pH of 4.5 to 5.2. After the aluminum oxinate is filtered off, the excess of oxine, which interferes with the precipitation of beryllium, is removed by four or five extractions with 20 ml each of chloroform. The aqueous layer is treated with ammonium chloride and ammonium hydroxide to precipitate the beryllium hydroxide, which is then dissolved in 50 ml of 1*N* hydrochloric acid. The beryllium is then precipitated with oxine as described above.

Separation of Aluminum and Other Elements from Beryllium—8-Hydroxyquinoline.

Procedure.[8] A sulfuric acid solution of the metal containing about 0.1 g of beryllium is heated, and ammonium hydroxide is slowly added with constant stirring until the first permanent precipitate forms. A minimum of acetic acid is added to the warmed solution to dissolve the hydroxides completely and to preset the initial pH at 4.8 to 5.0. The solution temperature is adjusted to about 60°C, and an excess of oxine

solution (10 g dissolved in 20 ml of glacial acetic acid; the resulting solution diluted to 200 ml with water) is added. Ammonium acetate solution, 2*N* at pH 7, is next slowly added until the pH of the test solution is 5.7. After the solution has been heated to 60°C, it is allowed to stand for two or more hours and is then filtered. The insoluble oxinates are washed with 0.08*N* ammonium acetate at pH 5 7. Beryllium passes into the filtrate quantitatively.

(b) *8-Hydroxyquinaldine.* Although the literature [12] indicates that beryllium does not form a precipitate of definite composition in ammoniacal solution, Motojima [13] showed that, with amounts of beryllium ranging from 2 to 10 mg, beryllium is quantitatively precipitated at pH 8 to 9. The compound formed has the composition $Be(C_{10}H_8NO)_2$. Compounds of bismuth, cadmium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, silver, titanium, and zinc interfere, as they do in the case of the oxine. The use of a tartrate solution eliminates the interference of small amounts of aluminum (less than 0.5 mg). The precipitate obtained can be weighed or titrated by the usual bromate method. Motojima describes the following method of separation: iron and aluminum are separated by oxine in an acetic acid–acetate medium; excess oxine and the oxinates of the interfering elements are extracted with chloroform, and the beryllium is then precipitated with 8-hydroxyquinaldine.

(c) *Ammonium Hydroxide in the Presence of Ethylenediaminetetraacetic Acid.* Although beryllium does not form a stable complex with EDTA, practically all interfering elements, including aluminum, do form stable complexes; therefore, this reagent is quite useful in the separation of beryllium. After the removal of silica, the beryllium is separated as the hydroxide by the addition of ammonium hydroxide to a solution containing EDTA. This procedure is described in detail in Sec. 4–3.1(b).

4–2.2 Mercury-cathode Electrolysis

Mercury electrolysis in a 0.3*N* sulfuric acid solution can be used to separate beryllium from chromium, iron, cobalt, nickel, copper, zinc, gallium, germanium, rhodium, palladium, silver, cadmium, indium, tin, iridium, platinum, gold, mercury, thallium, bismuth, polonium, molybdenum, and rhenium. No separation is made from aluminum, however, and generally the mercury electrolysis has to be followed by the 8-hydroxyquinoline separation.

4–2.3 Solvent Extraction

In recent years attention has been given to the use of solvent extraction for the separation of beryllium from other elements.

(a) *Basic Acetate.* Although basic beryllium acetate is soluble in chloroform [14] and has been used for the preparation of pure beryllium compounds, little use has been made of this property in analytical chemistry.

(b) *Acetylacetone.* Bolomey and Broido [15] used acetylacetone to separate Be^7 from a lithium target bombarded with neutrons. The yield is about 96 per cent, and the chief impurities extracted are calcium, iron, and magnesium. Steinbach and Freiser [16] studied the extraction of beryllium acetylacetonate and found that from a sulfate solution at pH 3 beryllium is extracted with a yield of 97 per cent in one extraction. When a solution containing no acid (pH 5.5) is extracted, the same results are obtained. Alimarin and Gibalo,[17] in an extension of the work of Adam, Booth, and Strickland,[18] found that the acetylacetone complex of beryllium can be separated in the presence of ethylenediaminetetraacetic acid (EDTA) by extraction with carbon tetrachloride. They found that, from a mixture of the acetylacetone complexes of aluminum, chromium, cobalt, iron, nickel, manganese, zinc, cadmium, lead, copper, magnesium, and beryllium, none of the bivalent elements except beryllium is extracted and the tervalent elements are extracted only in a strongly ammoniacal solution. In their procedure for separating beryllium from aluminum, 10 to 15 ml of the solution at pH 4 to 5 is mixed in a separatory funnel with 12 to 15 ml of 0.05*M* EDTA (disodium salt), 5 ml of a solution of acetylacetone (15+85), and 2 drops of concentrated aqueous ammonia, and shaken with 8 ml of carbon tetrachloride for 5 to 7 min. The solvent layer is removed, and the extraction is carried out two more times with the addition of the same amounts of acetylacetone, aqueous ammonia, and carbon tetrachloride as before. The combined solvent layers are shaken with 20 ml of water and 15 ml of concentrated hydrochloric acid. The aqueous phase containing the beryllium is evaporated nearly to dryness, the residue is dissolved in 15 to 20 ml of water and 1 ml of concentrated hydrochloric acid, and the beryllium is precipitated by aqueous ammonia. A recovery of better than 99 per cent was obtained at the New Brunswick Laboratory when the above procedure was tested. This method may be quite useful in the separation of beryllium from impurities, not only for the purpose of determining beryllium itself, but also as a means of concentrating the impurities prior to chemical or spectrographic analysis.

(c) *Thenoyltrifluoroacetone.* Thenoyltrifluoroacetone (TTA) is used in a similar manner to acetylacetone,[19] but the chelate is difficult to decompose. Bolomey and Wish [20] favor the use of TTA because of the stronger complex which makes it more stable at low pH ranges. The time for back-extracting is excessive, however; aluminum, for instance, requires 6 hr.

(d) *Cupferron.* Cupferron is used extensively for the purification of uranium, prior to volumetric determination, by extraction of the cupferrates with chloroform.[21] The same type of separation is applicable to beryllium. Furman, Mason, and Pekola [22] studied the extraction of the cupferrates of a large number of elements. In a sulfuric acid solution (1+9), cupferrates of titanium, vanadium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, iron, palladium, gallium, tin, antimony(III), bismuth, and polonium are extracted by chloroform, leaving all the beryllium in solution. Aluminum, however, is not extracted, and a further separation is necessary. Solvents other than chloroform are given by Furman, Mason, and Pekola.[22]

(e) *8-Hydroxyquinoline.* 8-Hydroxyquinoline (oxine) is used for the separation of aluminum from beryllium by extraction with chloroform. In the presence of beryllium a large excess of oxine is needed; some of the beryllium also extracts. The method is used for the determination of aluminum after interfering elements have been removed by mercury electrolysis.[23]

(f) *Butyric Acid.* Beryllium is extracted with chloroform from a solution containing butyric acid.[24, 25] A chloride solution containing about 10 mg of beryllium is adjusted to pH 9.5 with ammonium hydroxide, and 10 to 15 ml of butyric acid is added. The solution is then extracted with 50 ml of chloroform for 3 to 5 min. With four extractions, 99 per cent of the beryllium is extracted. In the presence of iron and aluminum, beryllium is selectively extracted if the sodium salt of EDTA is added before the butyric acid.

4–2.4 Ion Exchange

The beryllium complex of ethylenediaminetetraacetic acid (EDTA) at pH 4 is much weaker than the corresponding complexes of iron and aluminum. This difference in stability is utilized for the separation of beryllium from iron, aluminum, and titanium with the cation-exchange resin Amberlite IR-120. Hydrogen peroxide is used to complex titanium. The procedure described below,[26] when tested at the New Brunswick Laboratory, gave good recovery of beryllium but was rather time consuming. If a group were run simultaneously, the time per sample could be shortened.

In another ion-exchange separation method [27] beryllium is separated from copper and nickel. A 10 per cent ammonium carbonate solution of the sample, pH 8.5 to 9, is passed through an SBS resin (presumably a cation-exchange sulfonated polystyrene). The copper and nickel are retained on the column; the beryllium passes through. The column is then washed with an ammonium carbonate solution

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to remove all the beryllium. The copper and nickel are eluted with $2N$ hydrochloric acid. In the same publication, a separation of beryllium from MoO_4^{-2} and PO_4^{-3} with the same resin is described. When the solution at pH 3 to 4 is passed through the column, the beryllium is retained on the resin. The column is washed with ammonium hydroxide (1+19) and then with water. The beryllium is eluted with $2N$ hydrochloric acid.

Separation of Iron, Aluminum, and Titanium from Beryllium—Ion Exchange.

Procedure. A sulfate solution, free from silica, containing approximately 20 mg of beryllium in 200 ml of solution, is treated with 20 ml of a 10 per cent EDTA solution (10 g of the disodium salt in 100 ml of solution. The volume is made up to 400 ml. The pH is adjusted to 3.5 by means of a 10 per cent sodium hydroxide solution, and 1 ml of hydrogen peroxide is added. The resin, Amberlite IR-120, is loaded into a 1.8-cm-diameter column to a height of 12 cm. The resin is converted to the sodium form by passing through it 100 ml of 10 per cent sodium chloride solution and then washing the column with 150 ml of water. The beryllium solution is passed through the column at a rate of about 5 to 6 ml per minute. The column is washed with 150 ml of a 0.5 per cent EDTA solution at pH 3.5, then it is washed with 200 ml of water. The retained beryllium is eluted with 150 ml of $3N$ hydrochloric acid followed by 100 ml of water.

4–3 METHODS OF DETERMINATION

The determination of beryllium in metal or oxide is often done by gravimetric methods in which beryllium is precipitated as hydroxide and then ignited to the oxide. The precipitation as phosphate followed by ignition to the pyrophosphate is rarely used.

There is also extensive use of a volumetric empirical method in which beryllium hydroxide is treated with sodium fluoride to liberate sodium hydroxide for titration with a standard acid.

4–3.1 Gravimetric Methods

The precipitation of beryllium as hydroxide in the usual procedure requires the prior removal of interfering elements. Precipitation of beryllium hydroxide with ammonium hydroxide is complete at a pH of 8.5. A slight excess of ammonium hydroxide in the presence of ammonium salts above this pH causes no appreciable redissolution of the hydroxide.

The procedure of Brewer [28] in which beryllium hydroxide is precipitated in the presence of ethylenediaminetetraacetic acid (EDTA) has been applied to the determination of beryllium in beryllium metal. The beryllium complex with EDTA is more readily decomposed with

ammonium hydroxide than the stable complexes formed by other elements.[29] A series of analyses at the New Brunswick Laboratory which compared this method with the one employing separation of interfering elements indicated that the two methods were in fair agreement. The average value was 0.1 per cent low at the 99.7 per cent beryllium level.

The ignition of beryllium hydroxide to beryllium oxide has to be done carefully because appreciable loss of beryllium oxide by volatilization occurs at temperatures above 700°C in the presence of moisture.[30] The moisture must be driven off gradually at a low temperature before final ignition at 1100°C.

(a) *Determination of Beryllium in Beryllium Metal: Removal of Impurities with 8-Hydroxyquinoline.* The following procedure has been used for many years and consists in the preparation of a sulfuric acid solution of the metal, removal of silica, and an 8-hydroxyquinoline (oxine) separation of the aluminum, iron, etc. The hydroxide of beryllium is precipitated and ignited to the oxide at 1100°C. A correction is made for any silica present in the precipitate.

Procedure. A 5-g sample is transferred to a 500-ml Erlenmeyer flask, and 120 ml of sulfuric acid (1+1) is added slowly until the metal is dissolved. Two hundred milliliters of water is added, and the flask is heated until the salts are dissolved. The solution is filtered through a Whatman No. 42 filter paper into a 500-ml volumetric flask, and the filter paper is washed four times with hot sulfuric acid (1+19) and three times with hot water.

The insoluble material is ashed in a platinum crucible at 600°C, and the silica in the residue is volatilized with 5 drops of concentrated sulfuric acid, 2 to 3 drops of concentrated nitric acid, and a few milliliters of 48 per cent hydrofluoric acid. The residue is fused with potassium pyrosulfate, and the cooled melt is dissolved in water. This solution is added to the original filtrate in the 500-ml volumetric flask. The solution is diluted to volume, is mixed thoroughly, and is used for the determination of total beryllium, chromium, manganese, iron, copper, and nickel.

A 50-ml aliquot of the above solution is pipetted into a 250-ml volumetric flask and made to volume. A 50-ml aliquot of the diluted solution (equivalent to 0.1 g of metal) is transferred to a 400-ml beaker. Fifty milliliters of 2*N* ammonium acetate solution is added, and the solution is adjusted to a pH of 4.5 by the addition of sulfuric acid or ammonium hydroxide. Then 5 ml of a 5 per cent oxine solution (5 g dissolved in 10 ml of acetic acid; the resulting solution diluted to 100 ml) is added. The solution is allowed to stand 18 hr and is then filtered through a Whatman No. 40 filter paper. The precipitate is washed with cold water.

To the filtrate containing the beryllium, 10 ml of nitric acid (1+1) and 20 ml of sulfuric acid (1+1) are added, and the solution is evaporated to fumes. (To prevent spattering, infrared lamps may be used in place of a hot plate for heating the solution.) The solution is cooled, 150 ml of water is added carefully, and heat is applied until the salts are dis-

solved. After the addition of a slight excess of ammonium hydroxide, made from tank ammonia, the solution is filtered through a Whatman No. 40 filter paper, and the residue is washed four times with a warm 2 per cent ammonium nitrate solution (2 g dissolved in 100 ml; the solution made slightly ammoniacal). The paper is placed in a 25-ml platinum crucible and dried, charred, and ashed at 600°C. The crucible is transferred to a muffle furnace at 1100°C for 1 hr or until constant weight is attained. The covered crucible is kept over concentrated sulfuric acid while it cools and is then weighed quickly.

The beryllium oxide precipitate must be corrected for the silica present. Fourteen milliliters of sulfuric acid (1+1) is added to the crucible containing the beryllium oxide. The crucible is heated until all the beryllium oxide dissolves, and the solution is then transferred to a 250-ml beaker. The solution is heated to heavy fumes of sulfur trioxide, cooled, diluted with 100 ml of water, and heated until the salts have dissolved. The silica is filtered on a Whatman No. 42 filter paper, which is then washed with hot water and ignited at 1100°C in a platinum crucible. The silica is volatilized with sulfuric and hydrofluoric acids, and the residue is reignited. The weight of the silica found is deducted from the weight of the beryllium oxide precipitate, and the total beryllium present in the sample is computed.

(b) *Determination of Beryllium in Beryllium Metal: Hydroxide Precipitation in the Presence of Ethylenediaminetetraacetic Acid.* Interfering elements form stable complexes with EDTA in an ammoniacal solution; whereas the beryllium complex is unstable. This difference in stabilities is the basis of a simple separation procedure. The complete procedure for the determination of total beryllium consists in preparation of a sulfuric acid solution of the metal, removal of the silica, precipitation of the beryllium in the presence of EDTA, ignition of the precipitate at 1100°C, and correction for the silica present in the precipitate.

Procedure. A 5-g sample of beryllium metal is weighed into a 500-ml Erlenmeyer flask. The flask is placed in crushed ice, and 120 ml of sulfuric acid (1+1) is added cautiously in small amounts. The solution is cooled, 200 ml of water is added, and then the flask is heated until all the salts are dissolved. The solution is filtered through an 11-cm Whatman No. 42 filter paper directly into a 500-ml volumetric flask. The paper is washed with hot water five or six times.

The paper and residue are ashed at 600°C, and the residue is treated with 5 drops of concentrated sulfuric acid, 2 to 3 drops of concentrated nitric acid, and a few milliliters of 48 per cent hydrofluoric acid to volatilize any silica. Any residue is fused with potassium pyrosulfate and decomposed with water, and the solution is added to the filtrate in the volumetric flask. The solution is diluted to volume and mixed well. A 50-ml aliquot is transferred to a 250-ml volumetric flask and diluted to volume. After this dilution, a 50-ml aliquot is transferred to a 400-ml beaker. This aliquot should contain approximately 0.1 g of beryllium. The sample is diluted to 200 ml. Forty milliliters of a 10 per cent EDTA solution (10 g of disodium salt in 100 ml of solution) and a few drops of

thymol blue are added. The solution is heated to 80°C, and ammonium hydroxide is added until the indicator is deep blue.

The solution is allowed to stand overnight and is filtered through a Whatman No. 40 filter paper. (A watch glass cover is used to prevent the precipitate from drying and adhering to the beaker walls.) The precipitate is washed with a 2 per cent ammonium nitrate solution (2 g dissolved in 100 ml; the solution made alkaline to thymol blue with ammonium hydroxide). The filter paper is placed in a tared 30-ml crucible, dried, charred, ashed at 600°C, and then ignited at 1100°C for 1 hr. During the cooling and weighing periods, the crucible is covered with a well-fitting cover.

A correction is made for any silica present. After the addition of 14 ml of sulfuric acid (1+1), the crucible is heated until all the impure oxide is dissolved. The solution is transferred to a 250-ml beaker and evaporated to strong fumes of sulfur trioxide, then it is cooled and diluted with 100 ml of water. The beaker is heated to dissolve the salts, and the solution is filtered through a Whatman No. 42 filter paper. The paper is washed with hot water. The silica is determined by volatilization with hydrofluoric acid, and the weight of silica is subtracted from the weight of the ignited beryllium oxide.

(c) *Determination of Beryllium: Phosphate Precipitation in the Presence of Ethylenediaminetetraacetic Acid.* Precipitation of beryllium ammonium phosphate with subsequent ignition to beryllium pyrophosphate has the advantage of giving almost four times as much weight per equivalent beryllium content as does the beryllium oxide method. Prior removal of phosphate, if present, is not required. In addition, since the precipitate is somewhat granular, occlusion of impurities is less troublesome. Slight departures from constant theoretical $Be_2P_2O_7$ composition, however, may occur if the conditions of precipitation are not meticulously controlled.

EDTA is added to the solution to complex [18, 28, 31–34] many metal ions other than beryllium and to prevent their precipitation along with the $BeNH_4PO_4$. Provided that the amount of these metal ions (magnesium, calcium, iron, aluminum, copper, nickel, etc.) is roughly known, a slight excess of the chelating agent can be added.

Beryllium, being only slightly complexed at a pH of 5 to 5.5 by this excess, is then precipitated with very little loss. (For example, 500 g of the tetrasodium salt of EDTA will complex 1 mole of iron but only 0.002 mole of beryllium.)

Procedure. The test solution, containing preferably about 10 mg of beryllium, is treated to remove silica, organic material, and fluorides. Members of the ammonium hydroxide group are precipitated at a pH of 8.5 with ammonium hydroxide (tank ammonia added to carbon dioxide–free distilled water), filtered, washed, and redissolved in the original beaker with dilute sulfuric acid. The solution is diluted to 100 ml and adjusted to a pH of 2. Five milliliters of a 15 per cent ammonium phosphate solution (15 g of monobasic salt in 100 ml of solution; pH

adjusted to 5.5) and a slight excess of a 15 per cent EDTA solution (15 g of disodium salt in 100 ml of solution; pH adjusted to 5.5) are added, and the combined solution is thoroughly mixed. Ammonium acetate solution, 2*N*, is added slowly and with constant stirring to a pH of 5.5. The solution is simmered at just below boiling for 10 min and cooled in a water bath for 1 hr. The granular precipitate is filtered, redissolved, and reprecipitated. Only 1 ml of each of the two reagents is used for the second precipitation. Final weighing after ignition at 1000°C is made as $Be_2P_2O_7$.[33]

4–3.2 Volumetric Methods

The titration of beryllium has been tried by various methods: (1) direct titration with sodium hydroxide; [35] (2) iodometric titration of the acid resulting from the hydrolysis of a beryllium salt; [35, 36] (3) hydrolysis of a fluoberyllate in the presence of calcium chloride followed by an iodometric titration of the resulting acid; [37] (4) precipitation of beryllium hydroxide followed by dissolution in excess hydrochloric acid and the iodometric determination of the excess acid; [38] (5) hydrolysis of a beryllium sulfate solution by a mixture of potassium iodide and iodate followed by determination of the liberated iodine with sodium thiosulfate; [39] (6) precipitation of beryllium as $BeNH_4AsO_4$ in the presence of ethylenediaminetetraacetic acid (EDTA),[40] and in its absence,[41] followed by the titration of arsenic iodometrically; [40] and (7) the potentiometric titration of the beryllium solution with standard fluoride solution.[42]

Another procedure, one that is used to the greatest extent for rapid control work, involves the titration of the alkali released when sodium fluoride is added to a beryllium salt. This method, similar to that developed for the determination of aluminum by Craig,[43] has been used since 1945 by The Brush Beryllium Company. It consists of precipitating beryllium as the hydroxide at a pH of 8.5. An excess of sodium fluoride is then added, the beryllium hydroxide is converted to very weakly ionized beryllium fluoride, and the hydroxyl ions are released as sodium hydroxide. This released alkali is then titrated with standardized sulfuric acid. Since aluminum reacts in an identical manner, it must be absent or corrected for if present. Zirconium, hafnium, the rare-earth elements, uranium, and thorium interfere and must be absent. Magnesium causes a sluggish end point but otherwise does not interfere. A rather complete study of the above method was made by McClure and Banks.[44] In a modification of the above procedure, Zolotukhin [45] treats the solution with sodium tartrate before neutralizing the beryllium sulfate solution to the phenolphthalein end point with 0.2*N* sodium hydroxide. Potassium fluoride solution neutralized to phenolphthalein is added, and the liberated base is titrated with 0.1*N* hydrochloric acid.

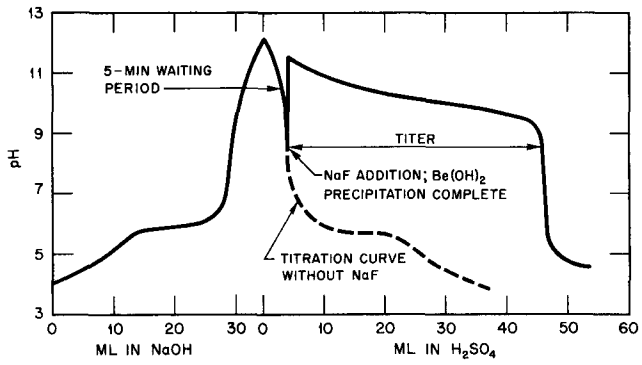


Fig. 4.1—Potentiometric titration curve for 0.2 g of beryllium as beryllium sulfate treated by the empirical titrimetric procedure.

In practice, the above reaction does not seem to take place stoichiometrically, owing, perhaps, to such complicating factors as the amphoteric character of beryllium. However, if the conditions of the titration are closely duplicated, the method, although empirical, becomes very useful because of its fair precision and relative speed. The titration must be performed precisely and slowly. It is important to provide enough time for the reactions to come to equilibrium. The 1*N* titrating acid is standardized in terms of beryllium equivalent by titrating the alkali released from an aliquot of a standard beryllium sulfate solution.

The aluminum in the sample behaves in exactly the same manner as the beryllium and is included in the final results as beryllium. Since duplicate beryllium determinations on the same sample may differ by as much as 0.4 per cent, corrections for aluminum would be of little significance unless this correction should amount to about 0.2 per cent of beryllium.

Figure 4.1 shows the potentiometric titration curve [46] obtained when 0.2 g of beryllium sulfate is treated by the empirical titrimetric procedure.

(a) *Determination of Beryllium: Empirical Titration in the Presence of Sodium Fluoride.*

Special Reagents. 1. *Sulfuric Acid, 1N.* In a pyrex bottle, 504 ml of reagent-grade sulfuric acid (specific gravity 1.845) is made up to 18 liters with water. The solution is cooled, agitated by air bubbling through it for several hours, and aged for several weeks. This solution is standardized by titrating, exactly as given in the procedure below, an aliquot of the standard beryllium sulfate solution of the same volume and same free sulfuric acid concentration as the sample solution aliquot. This standardization is done in duplicate with each group of samples to be analyzed.

2. *Standard Beryllium Sulfate Solution.* A standard solution containing 10 g of beryllium per liter is made from high-purity beryllium sulfate.

Procedure. A 25-ml aliquot of the beryllium solution made from the metal as described in Sec. 4–3.1(a) is diluted to 300 ml in a 600-ml beaker. To the solution is added dropwise 50 per cent carbonate-free sodium hydroxide (2000-g pellets in 2 liters of water; the solution filtered with suction through a medium-porosity fritted-glass filter, and stored in polyethylene) until a permanent precipitate forms. Five drops of phenolphthalein indicator (4 g in 400 ml of ethyl alcohol) is added; then 5*N* carbonate-free sodium hydroxide (65.7 ml of the 50 per cent solution diluted to 250 ml) is added, dropwise and with constant stirring, to a definite pink color.

Sulfuric acid (1+1) is slowly added, again dropwise and with constant stirring, until the pink color of the indicator is just discernible. The beaker is covered with a watch glass and placed in a water bath to cool. Then, while the solution is being stirred with a magnetic stirrer, 1*N* sodium hydroxide solution is added slowly to a pH of 9.5 as measured with a type E glass electrode. The sides of the beaker and the electrodes are washed down, and the solution is allowed to stand for a timed 5 min. The stirrer is again started, and 1*N* sulfuric acid from a water-jacketed buret is added slowly until the solution pH is adjusted to exactly 8.5 and remains constant for 30 sec. The buret is filled and the temperature of its surrounding water jacket is noted.

To the beaker is added 15 g of sodium fluoride powder and the mixture is thoroughly stirred. The 1*N* sulfuric acid is added from the buret at a rate of 15 ml per minute until the pH of the solution is again adjusted to 8.5 and remains constant for 30 sec. The volume of 1*N* sulfuric acid used is corrected for standard temperature and for buret calibration errors.

The titer of the sulfuric acid in terms of beryllium is obtained from the average value determined by titrating two equal aliquots of the standard beryllium solution. The amount of beryllium in the sample is then calculated in the usual fashion.

$$\% \text{ Be} = \frac{(\text{Titer, g/ml})\ (\text{vol. of titrant, ml})\ 100}{\text{Wt. of sample, g}}$$

The Brush Beryllium Company has used a modification of the preceding method, replacing the glass electrode with a mixed indicator consisting of phenolphthalein, thymolphthalein, and methyl orange. At the New Brunswick Laboratory, results by the volumetric method are generally about 0.5 per cent lower than by gravimetric methods.

4–3.3 Colorimetric Methods

The colorimetric determination of beryllium is employed chiefly in the analysis of air samples in health physics work. Occasionally, however, it is necessary to determine small amounts of beryllium in the

analysis of metallic beryllium. One example of this is the determination of beryllium oxide in beryllium metal.

The methods used for the determination of beryllium are legion and employ reagents, chiefly dyes, such as Solochrome Brilliant Blue B (British Color Index No. 723),[47] Chrome Blue K,[48] and Eriochrome Cyanine R,[49, 50] as well as acetylacetone,[18, 51] quinizarin,[52] acid alizarin BB,[53] quinizarin-2-sulfonic acid,[54] quinalizarin,[55, 56] resorcinol,[57] naphthazarin,[52, 58-60] 8-hydroxyquinaldine,[61] Beryllon I (diazotized H acid and H acid),[62] Beryllon II (diazotized H acid with Chromotropic acid),[62-66] Thorin,[67] salicylic acid,[68] sulphosalicylic acid,[69-71] *p*-nitrobenzeneazoorcinol,[72-74] and many other reagents. In many of these methods, ethylenediaminetetraacetic acid (EDTA) is used to complex elements that would interfere with the beryllium determination.

Among the numerous reagents listed above, *p*-nitrobenzeneazoorcinol appears to have been used to the greatest extent, particularly in the determination of the oxide content of beryllium metal. When *p*-nitrobenzeneazoorcinol is added to a moderately alkaline solution containing beryllium, a red-brown lake results. The dye is nearly specific for beryllium but reacts also with magnesium and, to a much smaller extent, with zinc. Metals like copper, iron, nickel, and calcium, which form colored ions that are precipitated in the alkaline solution, as well as magnesium and zinc, can be readily removed or can be inactivated by the addition of EDTA to form their soluble complexes. These elements are usually not present in the beryllium oxide found after the dissolution of beryllium metal in a methanol-bromine mixture. The zone of optimum alkalinity is rather critical and narrow.[75] There are certain disadvantages: Beer's law does not hold, the reagent is not too stable, and it is necessary to prepare new calibration curves with each set of samples. In spite of these drawbacks, the method has proven quite satisfactory in routine work. The procedure used is given in Secs. 4–4.15(a) and 4–4.15(b), which cover the determination of beryllium oxide in beryllium metal.

4–4 ANALYSIS OF IMPURITIES IN BERYLLIUM METAL

The analysis of impurities in beryllium metal is important for two reasons. It is necessary to analyze for neutron absorbers, which adversely affect the neutron economy, and for certain elements like oxygen, which can affect the metallurgical properties of the metal.

The undesirable effect of neutron-absorbing elements in beryllium metal can be conveniently expressed as the total danger summation (TDS), defined as the sum of the products of concentration and danger coefficient for each impurity. The danger coefficient is a measure of the ability of an impurity to absorb thermal neutrons compared

with the ability of some reference substance to absorb thermal neutrons. The danger coefficients of each element referred to various materials are listed in Chap. 11, Trace Elements, Sec. 11–1.1. Accordingly, all impurities contribute to the TDS, and a large concentration of a low-cross-section element is as undesirable as a low concentration of a large-cross-section element.

For the determination of trace impurities in beryllium metal and compounds, spectrochemical analysis is an excellent complement to the standard chemical procedures. A large number of elements which are difficult to determine in trace amounts by chemical procedures can be determined quickly and easily by spectrochemical methods. The spectral pattern of beryllium is simple, and the determination of many impurities can be made by direct examination of the sample spectra. For elements requiring increased sensitivity of detection, separation or concentration procedures are required. One such procedure is a physical method, known as carrier distillation, in which the volatile impurity elements are separated from a refractory matrix by fractional distillation and their arc spectra are simultaneously recorded to permit spectrographic determination. Other procedures require a chemical separation of the impurities, followed by spectrographic examination of the concentrates. The spectrographic procedures for beryllium analysis are discussed in Chap. 12, Spectrochemical Methods.

Discussed below are chemical methods of analysis for impurities in beryllium metal. These methods are readily modified for use with other compounds of beryllium.

4–4.1 Iron in Beryllium

The quantities of iron usually found in beryllium metal are such that either colorimetric or volumetric methods are satisfactory. The most commonly used method is the *o*-phenanthroline colorimetric procedure.

(a) *Colorimetric Determination of Iron in Beryllium Metal: o-Phenanthroline.* In this method hydroxylamine hydrochloride is used as a reducing agent to obtain iron(II). Beryllium does not interfere because the color is developed at a pH of 4.0 to 4.5. Nickel, if present in large amounts, may interfere. However, in work done at the New Brunswick Laboratory, it was found that an amount of nickel equivalent to four times the amount of iron present does not affect the iron determination in the presence of beryllium. When the nickel concentration is equivalent to eight times the amount of iron present, the color fades after 15 min.

Procedure. An aliquot of the solution of the sample containing 100 to 150 μg of iron is pipetted into a 150-ml beaker, and the volume is

diluted to about 50 ml. Then 20 ml of 3*N* ammonium acetate, 3 ml of 10 per cent hydroxylamine (10 g of hydroxylamine hydrochloride in 100 ml of solution), and 10 ml of 0.1 per cent *o*-phenanthroline (0.1 g in 100 ml of solution) are added to the sample solution. The pH is checked with pHydrion paper. If the pH is not found to be 4.0 to 4.5, more 3*N* ammonium acetate is added to reach this range.

The solution is diluted to 100 ml in a volumetric flask and mixed. The absorbancy is measured in 2-cm cells at 515 mμ. A reagent blank carried through the procedure is used as a reference. The iron concentration is determined from a standard calibration curve prepared from solutions containing 0, 50, 100, 150, 200, and 250 μg of iron. These solutions are processed as outlined in the procedure.

(b) *Volumetric Determination of Iron in Beryllium Metal: Dichromate.* The volumetric method used is the time-tested one in which ferric iron is reduced with stannous chloride and then titrated with potassium dichromate.

Procedure. Two grams of beryllium metal is weighed into a 250-ml wide-mouth Erlenmeyer flask. A mixture of 25 ml of water, 5 ml of concentrated nitric acid, and 15 ml of 70 per cent perchloric acid is added in small portions. If the reaction becomes too vigorous, the flask is placed in a cold-water bath.

After solution of the sample, the flask is placed on a hot plate, and the solution is evaporated to strong fumes of perchloric acid. Fuming is continued for 10 min. The solution is cooled, and 100 ml of water is added carefully.

Fifteen milliliters of concentrated hydrochloric acid is added, and the solution is brought just to the boiling point. The ferric iron is reduced by the dropwise addition of stannous chloride solution (6 g dissolved in 60 ml of concentrated hydrochloric acid; the solution diluted to 100 ml; and a few pellets of tin added) until the solution becomes colorless, then an excess of 3 drops is added. The solution is immediately placed in an ice bath and cooled to room temperature.

The solution is removed from the ice bath, and 15 ml of a saturated solution of mercuric chloride is added. The solution is allowed to stand for a period of 5 to 10 min. Then 15 ml of mixed acid solution [300 ml of sulfuric acid (1+1) and 150 ml of concentrated phosphoric acid diluted to 1 liter] and 4 to 5 drops of sodium diphenylamine sulfonate indicator (0.317 g of barium diphenylamine sulfonate and 0.5 g sodium sulfate dissolved in 100 ml of water; the solution filtered or decanted before use) are added. The solution is titrated with standard potassium dichromate (1.5356 g of reagent-grade potassium dichromate in 1 liter of solution; 50 ml of this stock solution is diluted to 500 ml to obtain 1 ml equivalent to 0.000175 g of iron), and the iron content is calculated.

4–4.2 Aluminum in Beryllium

Aluminum has been determined in beryllium metal and oxide by gravimetric,[77] colorimetric,[23, 78] and fluorometric [79, 80] methods. The gravimetric method, in which the aluminum is weighed as oxinate

after removal of interfering elements by mercury electrolysis, and the fluorometric method, in which Pontachrome Blue Black R gives an orange-red fluorescence with aluminum, appear to be equally satisfactory. The colorimetric method,[23] involving the extraction of aluminum oxinate, has the disadvantage that a certain amount of beryllium is partially extracted with the aluminum. This coextraction causes uncertainty in the determination.

(a) *Gravimetric Determination of Aluminum in Beryllium: 8-Hydroxyquinoline.* The procedure for the gravimetric determination of aluminum as employed at The Brush Beryllium Company, in which both iron and aluminum are determined and a correction is made for iron, is as follows.

Procedure. A 50-ml sample aliquot (representing a 0.5-g sample) is pipetted into a 400-ml beaker. Five milliliters of concentrated nitric acid is added, and the solution is brought to a boil to oxidize the iron. After the solution has cooled, concentrated ammonium hydroxide is added with constant stirring until a slight but definite permanent precipitate is formed. Glacial acetic acid is added slowly and is stirred in vigorously until all the precipitate is in solution. It is important to use only as much acid as is necessary to dissolve all the precipitate that may stick to the sides of the beaker. If necessary, the solution is heated with vigorous stirring in order to get all the precipitate into solution. After the solution has been cooled to room temperature, the pH is adjusted to 5.1 to 5.4 with ammonium acetate or glacial acetic acid.

The solution is heated to approximately 60°C, and 4 to 10 ml of oxine solution [100 g of 8-hydroxyquinoline (oxine) dissolved in 200 ml of glacial acetic acid; the resulting solution diluted to 2 liters, and filtered if necessary] is added until the yellow coloring is observed. After vigorous stirring, 20 ml of 4*N* ammonium acetate is added, and the solution is allowed to cool to room temperature. The pH is adjusted to 5.5 with ammonium acetate or acetic acid.

After the solution has been allowed to stand for 2 to 3 hr, it is filtered with suction through a weighed medium-porosity Selas crucible with an asbestos mat. The beaker is washed with the aid of a policeman with warm (60°C) ammonium acetate wash water (20 ml of 4*N* ammonium acetate diluted to 1 liter; the resulting solution made acid to litmus, pH 5.7, with glacial acetic acid and filtered if necessary). The precipitate in the crucible is washed five times with warm ammonium acetate wash solution and four to five times with cold water. The precipitate is dried in an oven at 120°C for a minimum of 3 hr. The aluminum and iron oxinates are weighed. A correction is made for the iron content of the mixed oxinates, and the concentration of aluminum in the sample is then calculated.

(b) *Fluorometric Determination of Aluminum in Beryllium: Pontachrome Blue Black R.*[79, 80] The fluorometric method for the determination of aluminum in beryllium consists in the elimination of the iron, which interferes, by a methyl ethyl ketone extraction from a

hydrochloric acid solution of the metal; the adjustment of the aqueous phase to a pH of 8; and the development of the orange-red fluorescence with Pontachrome Blue Black R.

Procedure. A 0.5-g sample of beryllium metal is weighed into a 250-ml Erlenmeyer flask. Twenty-five milliliters of distilled water is added. The beryllium is dissolved by the slow addition of 25 ml of concentrated hydrochloric acid. After the solution has been cooled to room temperature, 1 ml of 30 per cent hydrogen peroxide is added and mixed in by swirling the flask. The solution is transferred to a 250-ml separatory funnel. After the addition of 75 ml of methyl ethyl ketone, the separatory funnel is stoppered tightly, shaken vigorously for 1 min. and allowed to stand until the phases have separated. The aqueous phase is drawn off and collected in a 250-ml volumetric flask. (Care must be taken not to run any ketone, which contains the iron, into the flask.) The stem of the funnel is washed out with water, and the washings are added to the volumetric flask. The volume is made to 250 ml. and the contents of the flask are thoroughly mixed. A 2-ml aliquot is pipetted out and transferred to a 100-ml beaker. (Experimental work has shown that a 2-ml aliquot is correct for samples containing from 0.03 to 0.10 per cent aluminum. If results indicate an aluminum content greater than 0.10 per cent, the determination should be repeated on a 1-ml aliquot.)

Two standards are prepared by adding 5 ml and 10 ml of an aluminum standard solution containing 1 μg of aluminum per milliliter to two 100-ml beakers. To each of the three 100-ml beakers, 10 ml of 20 per cent ammonium acetate (20 g in 100 ml of solution) is added. Ten milliliters of the acetate solution is added to a fourth 100-ml beaker to serve as a blank to set the fluorometer to zero. The pH of each solution is adjusted with a pH meter to 4.8 with hydrochloric acid and ammonium hydroxide. The solutions are heated to boiling and then cooled to about 80°C. To each beaker is added 1.5 ml of 0.1 per cent Pontachrome Blue Black R (0.1 g dye in 100 ml of solution; this reagent is made by National Aniline Division, Allied Chemical and Dye Corporation, New York 6, N.Y.). The solutions are cooled to room temperature, and the volume of each is made to 50 ml. The fluorescent intensities are determined in a fluorometer (the filter of the ultraviolet source passes 300 to 400 mμ whereas the one used for the fluorescent light emitted passes 650 to 700 mμ), and the amount of aluminum in the sample is calculated by reference to the standards.

4–4.3 Nickel in Beryllium

Dimethylglyoxime has proven satisfactory for the colorimetric determination of nickel [81] in beryllium. When dimethylglyoxime is added to a basic solution of nickel, the color of the compound formed is changed to wine-red or brown by the addition of iodine. The direct colorimetric determination of nickel in beryllium gives high results because many elements interfere.[82] The direct method often can be used in the analysis of beryllium oxide.[83] Satisfactory results are best obtained by separating the nickel dimethylglyoxime with chloroform

before developing the color. Copper in amounts greater than the nickel may interfere and can be removed by a dithizone extraction in carbon tetrachloride.[84] It is, however, more readily removed by washing the chloroform extract with dilute ammonium hydroxide.

Colorimetric Determination of Nickel in Beryllium: Dimethylglyoxime Extraction.

Procedure. An aliquot of the original metal solution, containing about 25 μg and not over 200 μg of nickel and prepared as described in Sec. 4–3.1(a), is treated with 5 ml of chloroform plus 20 ml of 20 per cent ammonium citrate (20 g in 100 ml of solution) per 0.25 g of beryllium. After thorough mixing, 6 to 7 ml of concentrated ammonium hydroxide is added, and the solution is again mixed. The solution should be alkaline; otherwise more ammonium hydroxide must be added. Three milliliters of 1 per cent dimethylglyoxime (1 g dissolved in 100 ml of ethyl alcohol) is added. The solution is shaken vigorously for 1 min, and the chloroform phase is drawn off into a 60-ml separatory funnel. The beryllium solution is again extracted with 5 ml of chloroform, and this extract is added to the first chloroform extract. The combined extract is shaken with dilute ammonium hydroxide (1+19) for 1 min. The chloroform phase is drawn off and evaporated to dryness on a steam bath. Two milliliters of nitric acid is added to the residue, and the solution is rinsed into a 50-ml graduated cylinder. The volume is adjusted to about 25 ml with water. Two milliliters of iodine solution (12.67 g of iodine and 25 g of potassium iodide in 1 liter of solution) is added, and the solution is mixed. Ten milliliters of concentrated ammonium hydroxide is added, and the solution is again mixed. The volume is adjusted to 48 ml with water. Two minutes before the sample is read, 2 ml of the ethanol solution of dimethylglyoxime is added, and the solution is mixed.

The samples are read within 15 min, because of fading of the color, at 538 mμ in 2-cm cells against a blank carried through the procedure. The nickel content is determined by taking solutions of 0, 25, 50, 100, and 150 μg of nickel, each with 5 ml of sulfuric acid (1+1), carrying them through the above procedure, and then making a standard curve from the readings obtained.

4–4.4 Manganese in Beryllium

The colorimetric determination of manganese by oxidation to permanganate in acid solution appears to be entirely satisfactory.[85] There has been excellent agreement among cooperating laboratories on analyses of exchange samples.[86] The purple-violet color produced shows conformity to Beer's law up to concentrations of 15 mg of manganese per 100 ml of solution. A bleached blank can be prepared by discharging the permanganate color with sodium nitrite. In this way the color due to other metal ions that may be present is cancelled out, and the absorbancy of the manganese color only is measured. Periodate is the usual oxidant employed.

Colorimetric Determination of Manganese in Beryllium: Periodate Oxidation.

Procedure. The analysis is performed on an aliquot of the solution prepared as described in Sec. 4–3.1(a). A 25-ml aliquot of the sample solution, representing a 0.25-g sample and containing 3 ml of sulfuric acid, is transferred to a 150-ml beaker. A reagent blank and a 50-μg standard are prepared by adding 6 ml of sulfuric acid (1+1) and water to 0 and 50 μg of manganese. Five milliliters of phosphoric acid and 20 ml of nitric acid are added to each solution. The beakers are covered with ribbed watch glasses, and the solutions are brought to a boil on a hot plate. The solutions are removed from the hot plate, 0.5 g of potassium periodate is added to each beaker, and the solutions are again placed on the hot plate and boiled until the periodate dissolves. The solutions are then transferred to a steam bath for 15 min to allow the color to develop fully. The solutions are diluted to 50 ml.

The absorbancies of the solutions are measured in 5-cm cells at a wave length of 525 mμ. The blank is used as a reference. The sample is then decolorized by the addition of a few grains of sodium nitrite and reread against the blank. The value of this latter reading is subtracted from that of the first reading before the quantity of manganese is calculated by reference to a calibration curve. The calibration curve is prepared from solutions containing 0, 20, 40, 60, 80, and 100 μg of manganese processed as outlined above.

4–4.5 Chromium in Beryllium

The well-known *s*-diphenylcarbazide colorimetric method [87] for chromium(VI) has been used almost exclusively for the determination of this element in beryllium. Quite a number of laboratories have used this method with good agreement.[88] The chromium is oxidized to the (VI) state with persulfate in the presence of silver. It is not necessary to add sodium azide to destroy any permanganate formed, as some procedures state, because the *s*-diphenylcarbazide solution destroys the permanganate color. The resulting chromate reacts with *s*-diphenylcarbazide to form a red-purple colored complex, which is stable and obeys Beer's law.

Colorimetric Determination of Chromium in Beryllium: s-*Diphenylcarbazide.*

Procedure. The analysis is carried out on an aliquot of the solution prepared as described in Sec. 4–3.1(a). An aliquot containing from 30 to 80 μg of chromium is transferred to a 400-ml beaker. One milliliter of dilute phosphoric acid (1+4) and enough water to make a total volume of 250 ml are added. The pH is adjusted to 0.9 to 1.0 with a 50 per cent sodium hydroxide solution (50 g in 100 ml of solution). Ten milliliters of silver nitrate solution (0.25 g in 100 ml of solution), 10 ml of 10 per cent ammonium persulfate solution (10 g in 100 ml of solution), and a few glass beads are added. The beaker is covered with a ribbed watch

glass, and the solution is boiled for at least 25 min. During this time the volume of the solution is kept above 150 ml. The solution is cooled to room temperature and is transferred to a 250-ml volumetric flask containing 2 ml of a freshly prepared 0.5 per cent solution of *s*-diphenylcarbazide (0.5 g dissolved in 100 ml of acetone).

The solution is made to volume and mixed. The absorbancy is read immediately in 2-cm cells at a wave length of 540 mμ. A reagent blank is used in the reference cell. The chromium concentration is determined by reference to a calibration curve prepared from solutions containing 0, 20, 40, 60, 80, and 100 μg of chromium treated in the same way as the samples.

4–4.6 Silicon in Beryllium

Silicon can be determined by the conventional gravimetric procedure. The beryllium metal is dissolved with sulfuric acid (perchloric acid can also be used), and the silica is dehydrated by heating the solution to fumes of sulfur trioxide. Since some silicon may be lost as silanes during dissolution,[89] it is necessary to collect the evolved silanes in a solution of ammonium hydroxide. The conventional method is not very satisfactory for silicon below 1000 ppm. Colorimetric methods are more suitable for concentrations below this level.

(a) *Gravimetric Determination of Silicon in Beryllium.* For the gravimetric procedure, a 5-g sample is taken, and, after the removal of the silica, the solution may be reserved for the determination of aluminum, total beryllium, calcium, magnesium, iron, copper, and nickel.

Procedure. A 5-g sample is transferred to a 500-ml Erlenmeyer flask fitted with a two-hole stopper. A buret containing 120 ml of sulfuric acid (1+1) is placed in one hole. A tube in the other hole leads into a series of two U-tubes, the first being empty, the second containing dilute ammonium hydroxide with a drop of phenolphthalein indicator. The sulfuric acid is added slowly to the sample, and the resultant gases are passed through the ammonium hydroxide to recover the silanes. After the addition of the acid, 50 ml of water is added slowly through the buret. When gas evolution has stopped, the contents of the U-tubes are washed into the Erlenmeyer flask, and the sides of the flask are washed down. The solution is heated for 15 to 20 min until fumes of sulfur trioxide appear. After the solution has cooled, 100 ml of water is added, and the flask is heated until the salts have dissolved. The solution is boiled and filtered through a No. 42 Whatman filter paper. The paper is washed well. The residue and paper are ignited at 1000° C and weighed. Following treatment with hydrofluoric acid and a few drops of sulfuric acid, the crucible is heated and weighed again, and the silicon content of the sample is calculated.

(b) *Colorimetric Determination of Silicon in Beryllium Metal: Molybdenum Blue.* This method has been studied intensively by Carlson and Banks.[89] They pointed out that silicon may be lost, presumably as silane, when sulfuric acid alone is used for the solution of

the metal. Solution of the beryllium in sodium hydroxide, followed by the addition of hydrofluoric acid, gave good recovery. The method has also been used satisfactorily without the addition of hydrofluoric acid. Beer's law is obeyed with concentrations up to 180 μg of silicon per 100 ml when the procedure as outlined below is followed. Interfering elements are phosphorus, germanium, and arsenic; high concentrations of sodium and potassium halides, nitrates, and sulfates prevent maximum color development. Since sodium hydroxide is used for the solution of beryllium metal, a similar salt concentration should be present in the corresponding standards to eliminate this source of error.

Special Reagents. 1. *Ammonium Hydroxide, 20 Per Cent.* An approximately 20 per cent solution is prepared by bubbling ammonia through distilled water contained in a pyrex bottle immersed in an ice bath. The density of the final solution should be less than 0.92. The solution is stored in plastic bottles. Commercial ammonium hydroxide contains considerable soluble silicon, thus necessitating a laboratory preparation. A glass container can be used for the above preparation since tests have shown that only negligibly small quantities are introduced into the solution from the container.

2. *Molybdic Acid, 10 Per Cent.* A 10 per cent solution is prepared by dissolving 25 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in about 200 ml of distilled water. The solution is acidified by the addition of 20 ml of concentrated sulfuric acid. The solution is cooled and diluted to 250 ml. It has been found that Baker and Adamson ammonium molybdate gives a much lower blank than other reagent-grade products. It is not necessary to store this solution in a plastic bottle.

3. *Reducing Solution.* This reagent is prepared by dissolving 27 g of sodium bisulfite, 2 g of sodium hydroxide, and 0.5 g of 1-amino-2-naphthol-4-sulfonic acid (technical) in distilled water and diluting to 250 ml. This solution is best stored in a translucent plastic bottle and may be rejuvenated by the addition of a second portion of the amino acid. Although the authors state[82] that the solution is stable for at least a month, the experience of the New Brunswick Laboratory shows that in hot weather it deteriorates in a week.

Procedure. A 0.2-g sample of the metal is weighed into a fluorothene beaker and dissolved in an alkaline solution containing 3 g of sodium hydroxide. The solution is acidified with dilute sulfuric acid. After the addition of 0.5 ml of hydrofluoric acid (1+1), the solution is warmed for 30 min on a hot plate at low temperature. The solution is cooled to room temperature, and 40 ml of a saturated boric acid solution is added. Four milliliters of 10 per cent molybdic acid reagent is added, and the pH is adjusted to 1.2 to 1.3 with the 20 per cent ammonium hydroxide solution. After 8 to 12 min, 4 ml of 20 per cent tartaric acid (200 g of reagent-grade tartaric acid plus a few crystals of thymol dissolved in 1 liter of water) is added, and the solution is mixed. Immediately thereafter, 1 ml of the reducing solution is added, and the solution is again mixed. The solution is transferred to a 100-ml volumetric flask, made to volume, and mixed. After 20 min, the absorbancy

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is determined against distilled water at 815 mμ in 5-cm cells. A calibration curve is prepared in the usual manner with standard silicon solutions (prepared from sodium metasilicate, standardized gravimetrically by perchloric acid dehydration, and stored in plastic bottles). The appropriate quantities of hydrofluoric acid and sodium salts should be added to the standards.

(c) *Colorimetric Determination of Silicon in Beryllium Oxide: Molybdenum Blue.*

Procedure (Low-fired Beryllium Oxide).[89] A 1-g sample of the oxide is weighed into a fluorothene beaker and dissolved in a minimum quantity of hydrochloric acid (see Sec. 4–1 on the solubility of beryllium oxide in hydrochloric acid). After dilution with water, 0.5 ml of hydrofluoric acid (1+1) is added, and the solution is warmed for 30 min at low temperature on a hot plate. The solution is cooled, and the silicon is determined as described in Sec. 4–4.6(b).

Procedure (High-fired Beryllium Oxide).[89a] To a 200-mg sample of oxide in a 125-ml platinum dish, 20 ml of diluted (1+19) redistilled hydrofluoric acid [150 ml of 48 per cent hydrofluoric acid plus 50 ml of water redistilled from a nickel still, collecting only the first 150-ml fraction; distillate diluted (1+19) for dilute acid; both concentrations stored in polyethylene or fluorothene] is added. The dish is warmed on the steam bath, water being added occasionally to restore the original volume, and the sample is dissolved by stirring. Two grams of boric acid is added. The solution is transferred to a Bakelite beaker, 4 ml of 10 per cent molybdate reagent is added, and the volume is brought up to about 50 ml. The pH is adjusted to 1.2 to 1.3 on a meter with ammonium hydroxide or hydrochloric acid. After 15 min, 30 ml of hydrochloric acid (1+1) is added, followed by 2.0 ml of the reducing solution.

The solution is transferred to a 100-ml graduate, diluted to volume, and returned to the beaker. After 15 min the optical measurements are made in 2-cm cells at 815 mμ against water. The silica content is calculated by reference to a standard curve prepared from standard silica solutions carried through the procedure described above.

4–4.7 Copper in Beryllium

Of the many organic reagents that give sensitive color reactions with copper, dithizone appears to be the best suited to the determination of this element in beryllium. Copper in 0.1*N* acid reacts with dithizone in a carbon tetrachloride solution to form a red-violet complex that is soluble in the organic phase. Although bismuth, silver, gold, mercury, and palladium interfere, they have not been found in beryllium in amounts requiring separation.

Colorimetric Determination of Copper in Beryllium: Dithizone.

Procedure: An aliquot of the sample solution, chosen to contain about 25 μg of copper and prepared from the metal sample as described in

Sec. 4–3.1(a), is adjusted to a pH of 1 with ammonium hydroxide and transferred to a separatory funnel. Exactly 15 ml of 0.005 per cent dithizone solution (5 mg dissolved in 100 ml of carbon tetrachloride) is added, generally from a buret, and the solution is shaken vigorously for 2 min. The layers are allowed to separate, and the lower (organic) phase is collected in a 50-ml volumetric flask. A second extraction with 15 ml of the dithizone solution is made as above, and the organic phase is added to the 50-ml flask. The aqueous phase is washed several times with small portions of carbon tetrachloride, and these washings are added to the flask. The combined dithizone extract is diluted to volume with carbon tetrachloride and mixed well. About one-half of the extraction is filtered through a dry No. 40 Whatman filter paper into a small, dry, glass-stoppered Erlenmeyer flask.

A 2-cm cell is rinsed with a portion of this solution and then filled, and the absorbancy is read at 515 mμ against a blank carried through the procedure. If a filter photometer is used, a green filter (No. 54) is employed. The copper concentration is determined by reference to a standard curve made from readings obtained by taking 0, 20, 40, and 60 μg of copper through the above procedure.

4–4.8 Molybdenum in Beryllium

When occasionally the determination of molybdenum is necessary, the colorimetric thiocyanate method has proven satisfactory. It should be pointed out that in the analysis of beryllium metal it is necessary to oxidize [123] the molybdenum; otherwise low results may be obtained. The following procedure has been used for beryllium metal or oxide.

Colorimetric Determination of Molybdenum in Beryllium: Thiocyanate.

Procedure. A 0.50-g sample of beryllium metal is transferred to a 250-ml beaker [alternatively an aliquot of the solution as prepared in Sec. 4–3.1(a) can be used]. Fourteen milliliters of sulfuric acid (1+1) is added in small portions. The reaction is allowed to subside after each addition. After the sample has decomposed, 15 ml of water is added slowly, and the beaker is heated on a steam bath until the salts have dissolved. The hot solution is filtered through an 11-cm No. 42 Whatman filter paper, which is then washed with hot water.

The precipitate is ignited in a platinum crucible at 600°C. The residue is treated with hydrofluoric acid, a few drops of nitric acid, and a few drops of sulfuric acid. The solution is evaporated to complete dryness, and the residue is ignited for a few minutes at 1000°C. It is then fused with potassium bisulfate. The melt is added to a beaker and dissolved in hot water; then this portion is added to the main beryllium solution. One milliliter of ferric sulfate solution (3.6 g in 1 liter of solution) and 2 ml of saturated bromine water are added. The solution is boiled to expel excess bromine and evaporated to approximately 40 ml. The solution and the following reagents are now cooled to 5 to 10°C in an ice-water bath: 20 per cent ammonium thiocyanate solution (100 g in 500 ml of solution); 35 per cent stannous chloride solution (350 g of stannous chloride dissolved in 100 ml of warm concentrated hydrochloric acid, the solution cooled and diluted to 1 liter

with freshly boiled and cooled water; a few pieces of metallic tin are added); butyl acetate solution (butyl acetate saturated with a few crystals of ammonium thiocyanate and stored in a brown-glass bottle); and wash solution [4 ml of 20 per cent ammonium thiocyanate, 4 ml of 35 per cent stannous chloride, and 100 ml of sulfuric acid (1+9) mixed together].

The sample solution is transferred to a 250-ml separatory funnel and made up to approximately 70 ml with cold-water rinsings of the beaker. Four milliliters of 20 per cent thiocyanate is added, and the solution is gently mixed. After the addition of 10 ml of 35 per cent stannous chloride solution, the solution is again gently mixed and allowed to stand for 5 to 10 min to permit complete reduction of the iron. Twenty-five milliliters of butyl acetate solution is pipetted into the separatory funnel, and the funnel is shaken for 1½ min. The phases are allowed to separate, and the aqueous phase is drawn off. The butyl acetate is washed with approximately 40 ml of the wash solution. The wash solution is drawn off. The butyl acetate phase is collected in a 50-ml graduated cylinder and diluted to 50 ml with methanol.

The absorbancy of the solution is measured in a 5-cm cell at 470 mμ A reagent blank similarly prepared is used as a reference. The quantity of molybdenum present is then read from a calibration curve. Data for the calibration curve are obtained by processing as outlined above standard solutions, prepared from ammonium molybdate, containing 5, 10, 20, 30, 40, and 50 μg of molybdenum.

4–4.9 Rare Earths in Beryllium

It is necessary to determine the rare earths in beryllium because several of them are strong neutron absorbers. Gadolinium is the worst offender in this respect.

The only method in general use is a spectrographic determination after concentration of the rare earths from a relatively large sample of beryllium. In one procedure,[6] the rare earths are separated from beryllium by precipitation as the oxalates with added thorium as a carrier. The thorium is removed by an extraction of the 8-hydroxyquinoline (oxine) compound with chloroform, and the rare earths are isolated as oxinates with added lanthanum as a carrier and an internal standard for the subsequent spectrographic determination. The oxinates are ignited to oxides, which are then analyzed spectrographically. At least 96 per cent of tracer quantities of rare earths are recovered. Carriers such as thorium and yttrium in a fluoride precipitation also function in the same manner. Magnesium and calcium have also been used as carriers.

In another satisfactory procedure [6a] a fluoride precipitation with added yttrium carrier is used to separate the rare earths from the bulk of the beryllium. The yttrium also serves as an internal standard in the final spectrographic determination. The fluorides are then dis-

solved, and the remaining beryllium, calcium, and magnesium are removed with an ion-exchange column (Dowex 50 or Amberlite IR-120). The rare earth-yttrium mixture is then analyzed spectrographically.

Both procedures reported extend the lower limit of determination when a 50-g sample is used to 0.1 ppm of the five rare earths with the highest thermal-neutron cross sections: samarium, europium, gadolinium, dysprosium, and erbium. Larger quantities of rare earths require less sample. The spectrographic determinations are discussed in Chap. 12, Spectrochemical Methods.

(a) *Separation of Rare Earths in Beryllium: Oxalate Precipitation With Thorium as a Carrier.*

Special Reagent—Thorium Nitrate Tetrahydrate. High-purity thorium nitrate tetrahydrate is treated to remove rare earths. About 10 g is dissolved in 25 ml of 8*M* nitric acid and equilibrated for 5 min with 50 ml of dibutoxytetraethylene gylcol (pentaether). The aqueous phase is discarded. The organic phase is washed for 2 min with 10 ml of 8*M* nitric acid. The aqueous phase is again discarded. The thorium is removed from the organic phase by washing for 2 min each with five 50-ml portions of water. The water extracts are combined, and the thorium is precipitated with ammonium hydroxide. The thorium hydroxide is filtered and dissolved in 8*M* nitric acid. The solution is evaporated to dryness on a steam bath.

Procedure. A 10- to 50-g sample of beryllium metal suspended in water is dissolved with sufficient concentrated hydrochloric acid to give a solution 0.25*M* in excess hydrochloric acid when made up to 300 to 800 ml. The solution is digested on a hot plate for a few minutes and filtered through Whatman No. 42 paper to remove traces of undissolved oxide. The paper is ignited in a platinum crucible, and the residue is fumed with a few drops of concentrated sulfuric acid. The dissolved residue is then added to the main solution.

One hundred milligrams of purified thorium nitrate tetrahydrate is added and dissolved by stirring. Stirring is continued with the addition of 3 g of oxalic acid dissolved in 100 ml of hot water. The solution is heated on a hot plate to near boiling and cooled for about one hour.

The oxalates are filtered with vacuum on a medium-porosity fritted-glass filter crucible. The crucible sides and the precipitate are washed with dilute oxalic acid solution (1 g in 100 ml of solution). The crucible is then placed in a 150-ml beaker. Fifteen milliliters of concentrated nitric acid and 1 ml of 70 per cent perchloric acid are added, and the beaker is heated on a hot plate until the precipitate dissolves. The crucible is washed with water and removed. The solution is evaporated to near dryness. The residue is taken up in 2 ml of concentrated nitric acid and about 5 ml of water. If the solution is not clear, the evaporation to near dryness is repeated after the addition of a few more drops of 70 per cent perchloric acid. When the residue yields a clear solution with the diluted nitric acid, the solution is diluted to about 100 ml. The oxalates are reprecipitated by adding 1 g of oxalic acid in 30 ml of hot

water. After filtration and destruction of the oxalates as before, the residue is taken up in 2 ml of concentrated nitric acid and diluted to about 50 ml.

Ten milliliters of glacial acetic acid is added, and the pH is adjusted with concentrated ammonium hydroxide to a reading of about 2.0 on a pH meter. After the solution has been cooled to room temperature, 3 g of 8-hydroxyquinoline (oxine) is added to it, and the pH is adjusted to 4.20. The mixture is transferred to a 250-ml separatory funnel and is extracted with five 10-ml portions of oxine in chloroform (10 g dissolved in 50 ml) and washed with two 25-ml portions of chloroform. The phases are allowed to separate, and the chloroform phase is discarded.

The aqueous phase is transferred to a 250-ml beaker, and 1 mg of lanthanum as a solution of the nitrate is added. About 10 per cent by volume of concentrated ammonium hydroxide is added, and the solution is heated until the precipitate flocculates. The hot solution is filtered through Whatman No. 42 filter paper. The precipitate is ignited in a platinum crucible to the oxides for the spectrographic determination.

(b) *Separation of Rare Earths in Beryllium: Fluoride Precipitation With Yttrium as a Carrier.*

Procedure. Fifty grams of beryllium metal or oxide is weighed into a 400-ml polyethylene beaker containing 150 ml of water. In the case of beryllium metal, 430 ml of 48 per cent hydrofluoric acid is added in small portions. For beryllium oxide, 160 ml of 48 per cent hydrofluoric acid is added, and the sample is warmed on a steam bath until dissolved. Sufficient 48 per cent hydrofluoric acid is added to the solution to raise the acidity to 2.5*N*. A yttrium chloride solution (15.0 mg of yttrium oxide dissolved in 5 ml of concentrated hydrochloric acid; the solution evaporated to near dryness, and the residue dissolved in water) is added quantitatively. To the solution is then added a mixture of 0.25 g of magnesium oxide and 0.25 g of calcium oxide, dissolved in just enough hydrochloric acid to yield a clear solution. The solution is heated on the water bath for 1 hr, stirred vigorously with a plastic stirring rod, then allowed to stand for at least 4 hr and preferably overnight.

The solution is filtered, after some filter pulp has been added, through a Whatman No. 54 filter paper supported on a plastic funnel, and washed with 2.5*N* hydrofluoric acid. The filtration requires several hours. The precipitate, consisting of coprecipitated yttrium, calcium, and magnesium fluorides, contains about 98 per cent of the added yttrium oxide and the rare earths. (For work of high accuracy or for substantial quantities of rare earths, it is suggested that a second precipitation be carried out by adding additional amounts of yttrium, calcium, and magnesium to the filtrate. Since 98 per cent of the 2 per cent rare earths that escaped precipitation in the first separation is collected in the second precipitation, the recovery of the rare earths can be considered complete, and it is unnecessary to determine the actual yield. If only one precipitation is carried out, the yttrium yield should be determined as a precaution.)

The mixed fluorides are transferred to a platinum crucible and ignited at a temperature not exceeding 550°C. To the residue, 5 ml of hydrofluoric acid and 5 ml of sulfuric acid are added. The crucible is

heated on a sand bath until fumes of sulfur trioxide cease to escape. Two additional milliliters of sulfuric acid is added, and the solution is again evaporated just to dryness (the residue is not ignited). The crucible is placed in a 250-ml beaker containing 100 ml of 1*N* hydrochloric acid and heated until a clear solution results. If this is impossible, any insoluble material is filtered off, ignited, treated with hydrofluoric acid and sulfuric acid, and then is dissolved with a separate portion of 1*N* hydrochloric acid.

The resulting acid solution is poured through a glass column (1 in. ID) that contains a settled resin bed of about 8 in. of Dowex 50 or Amberlite IR–120 (100 to 150 mesh), previously washed with hydrochloric acid (1+1). The full flow rate of the column, 3 to 5 ml per minute, is used. The beryllium, calcium, and magnesium are eluted by passing about 600 to 800 ml of 1*N* hydrochloric acid through the column. Beryllium and magnesium are eluted first. The completeness of the removal of the calcium is determined by testing a fresh portion of the eluate with ammonium oxalate and ammonia.

After the removal of beryllium, magnesium, and calcium, the yttrium and rare earths are eluted with 12*N* hydrochloric acid. For a quantitative recovery of these elements, 250 ml of eluate is sufficient. The hydrochloric acid solution is evaporated just to dryness. The residue is dissolved in 10 ml of water. One hundred milliliters of hot 4 per cent oxalic acid solution is added.

After the precipitate has been allowed to settle overnight, the solution is filtered, and the precipitate is washed with a 1 per cent oxalic acid solution. The precipitate is ignited in a tared platinum crucible, cooled, and weighed. The residue is analyzed spectrographically.

4–4.10 Uranium in Beryllium

The determination of uranium in beryllium is occasionally made. Since the amounts found are generally in the parts-per-million range, fluorometric methods are employed. The uranium is extracted from a nitric acid solution of beryllium with tributyl phosphate (TBP) and then stripped from the TBP with hot water and ammonium carbonate. The amount of uranium in the final aqueous solution is determined fluorometrically.

Fluorometric Determination of Uranium in Beryllium: Tributyl Phosphate Extraction.

Procedure. A sample of beryllium metal large enough to contain from 10 to 100 μg of uranium is transferred to a 400-ml beaker. Twenty-five milliliters of nitric acid (1+4) is added, and the beaker is surrounded with cracked ice. (It is necessary to work under a hood.) Then 90 ml of hydrochloric acid (2+1) is added in small portions. After each addition the vigorous reaction must be allowed to quiet down before more acid is added. After all the acid has been added and the reaction is complete, the solution is placed on a hot plate and brought to a boil. The beaker is transferred to a steam bath, and the solution is evaporated to dryness.

The beryllium salts are redissolved with 100 ml of nitric acid (1+1). The solution is transferred to a 500-ml separatory funnel. One hundred milliliters of TBP is added, and the funnel is shaken for 2 min. The solution is allowed to separate into two phases, and the aqueous phase is drawn off and discarded. The TBP phase is washed twice with 100-ml portions of nitric acid (1+1). After each of these washings, the aqueous phase is drawn off and discarded.

The uranium is stripped from the organic phase by repeated washings with 100-ml portions of hot water. These washings are collected in a liter beaker. After the addition of the third portion of hot water, a small spoonful (Coors No. 1) of ammonium carbonate is added to the succeeding portions. The washing process is continued until the final aqueous phase tests alkaline to Alkacid paper. The organic phase is discarded.

The combined aqueous phase is transferred to a liter separatory funnel and washed once with 100 ml of diethyl ether. The aqueous phase is then drawn off in the same beaker as before and placed on a steam bath for evaporation to dryness. The residue is treated with 25 ml of nitric acid (1+1), and the solution is transferred to a 100-ml volumetric flask. The beaker is washed well with water, and the washings are added to the flask. After the solution has been adjusted to volume, the amount of uranium present is determined fluorometrically as described in Chap. 1, Uranium.

4–4.11 Copper, Lead, Cadmium, Nickel, Zinc, Cobalt, and Indium in Beryllium

Occasionally polarographic methods are very useful in determining certain metallic impurities such as zinc, lead, cadmium, cobalt, and indium. Nickel and copper can also be determined polarographically; however, earlier in this chapter, their determination by colorimetric procedures is described (see Secs. 4–4.3 and 4–4.7). For the polarographic determination of all these metals except indium, a hydrofluoric acid solution of beryllium containing tartaric acid is exhaustively extracted at pH 7.5 and 9.0 with dithizone in chloroform. The dithizone is destroyed, and the residue is taken up in 0.1 potassium chloride solution. A polarogram is made of the lead and the cadmium. Pyridine is added to the polarographic cell, and a polarogram is made of the copper, nickel, and combined zinc-cobalt. The zinc-cobalt mixture is separated by washing the organic extract with dilute hydrochloric acid. Zinc passes into the acid wash; cobalt remains in the organic phase.

For the determination of indium in beryllium,[90] the indium is extracted with 8-hydroxyquinoline in chloroform. Iron and molybdenum are extracted with diethyl ether from the ignited residue after dissolution in a hydrochloric acid solution. The concentration of indium is determined polarographically in a base electrolyte consisting of hydrochloric acid, sodium formate, and hydrazine hydrochloride.

Polarographic Determination of Copper, Lead, Cadmium, Nickel, Zinc, and Cobalt in Beryllium: Dithizone Extraction.

Procedure. A 1-g sample of beryllium metal suspended in 20 ml of water is dissolved in a polyethylene beaker with 10 ml of 48 per cent hydrofluoric acid added in small portions. After the addition of 3.5 g of tartaric acid dissolved in 10 ml of water, concentrated ammonium hydroxide is added until the pH of the solution is near 7 when tested with an indicator paper. More ammonium hydroxide is then added until the pH is 7.5 as read on a meter.

The solution is transferred to a 100-ml separatory funnel, and it is extracted with 10-ml portions of 0.02 per cent dithizone in chloroform until the final dithizone extract remains green after 3 min of shaking. The organic extracts are collected in a 150-ml beaker. The pH of the aqueous solution is readjusted to 9.0 with concentrated ammonium hydroxide, and exhaustive dithizone extractions are again performed. The extracts are combined. The aqueous phase is discarded.

The organic phase is evaporated to dryness on a hot plate at low temperature. When the residue is cool, 5 drops of concentrated sulfuric acid, 0.5 ml of nitric acid, and 0.5 ml of 70 percent perchloric acid are added. The beaker is covered with a watch glass and heated on a hot plate at medium temperature until the solution is colorless. The cover is removed, and the solution is evaporated to dryness. Forty milligrams of potassium chloride dissolved in 2.0 ml of water plus 2 drops of concentrated hydrochloric acid are added. The beaker is kept on a hot plate at low temperature until the solution is evaporated to near dryness, that is, until the salt appears dry but the odor of the hydrochloric acid is still noticeable. Five milliliters of water is added to the cooled beaker, the beaker is swirled until the salts dissolve, and the solution is transferred to the polarographic cell.

Three drops of a 0.2 per cent methyl cellulose solution (0.2 g of methyl cellulose suspended in 100 ml of water; the suspension heated to near boiling and cooled) are added, the solution is deaerated, and the polarograms of the lead and cadmium are recorded. After the addition of 5 drops of pyridine to the cell, the copper, nickel, and combined zinc-cobalt waves are recorded.

If both zinc and cobalt are present, they can be separated after the extraction step by washing the combined organic extract with three 20-ml portions of 0.05*M* hydrochloric acid. The zinc, lead, and cadmium are re-extracted into the acid; the cobalt, copper, and nickel remain in the organic phase. Both phases are evaporated to dryness and processed as described above.

The half-wave potentials in volts versus the mercury-pool anode are approximately: copper, —0.35; lead, —0.48; cadmium, —0.72; nickel, —0.98; zinc, —1.12; and cobalt, —1.15.

The concentrations of the elements in the sample are determined by referring to concentration versus wave-height plots prepared by recording the wave heights of known amounts of the element in 0.1*N* potassium chloride.

4–4.12 Boron in Beryllium

The amount of boron occurring in beryllium metal and beryllium oxide is generally so low that sensitive colorimetric procedures must

be employed for its determination. The method [91] that has been used to the greatest extent depends on the distillation of methyl borate from an acid solution, followed by color development in an acid solution with turmeric (curcumin). This method has been reviewed by Possidoni de Albinati and Rodriguez Pasques.[92] In general the color is developed in an oxalic acid medium,[91] but the use of trichloracetic acid for color development is recommended by Philipson [93] and has been applied to the determination of boron in beryllium oxide.[94] In the latter method, distillation is avoided by forming tetraphenylarsonium fluoborate, which is extracted with chloroform. Another method recently developed at the New Brunswick Laboratory [95] is based upon the rapid dissolution of beryllium metal in a methanol-bromine mixture. After the sample is in solution, the boron is distilled from the reaction flask. The distillate it neutralized with lime and evaporated to dryness. Color development is carried out with diaminochrysazin.[96, 97]

(a) *Colorimetric Determination of Boron in Beryllium Metal: Acid Dissolution. Distillation. Turmeric.*

Special Reagents. 1. *Oxalic-Hydrochloric Acid Solution.* Forty grams of reagent-grade oxalic acid is transferred to a 500-ml quartz flask and 270 ml of water and 160 ml of 95 per cent ethanol are added. After the

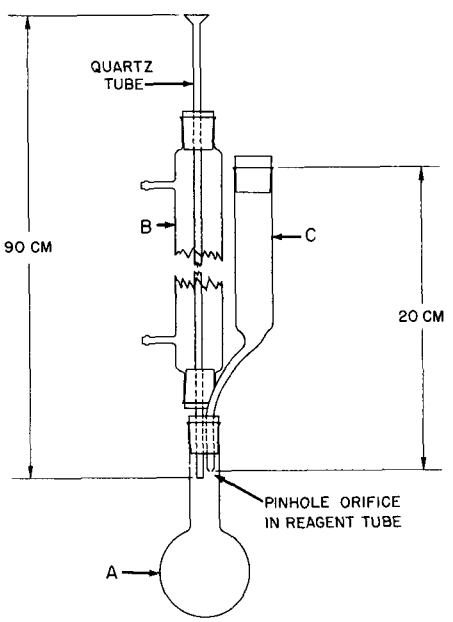


Fig. 4.2—Dissolution apparatus. A, quartz distilling flask. B, reflux condenser. C, quartz reagent tube.

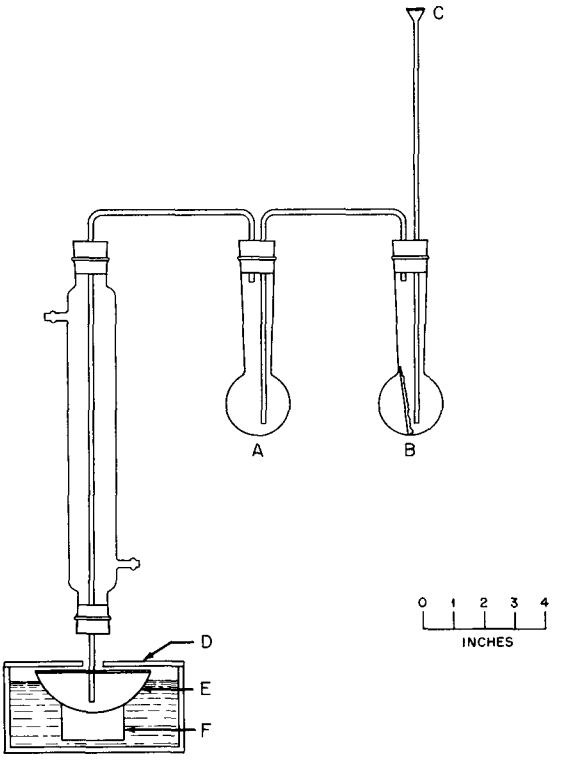


Fig. 4.3—Distillation apparatus. A, sample flask. B, flask containing methanol and sodium hydroxide. C, tube. D, plastic cover. E, receiving dish. F, wooden block.

oxalic acid dissolves, 50 ml of hydrochloric acid is added, and the solution is mixed thoroughly. This solution can be used for several months.

2. *Turmeric, 1 Per Cent Extract.* Two grams of turmeric powder is added to a 250-ml quartz Erlenmeyer flask containing 200 ml of boron-free 95 per cent ethanol, and the solution is stirred mechanically for 4 hr. The solution is filtered through boron-free Whatman No. 42 filter paper into another quartz flask. The extract is stored in the dark.

3. *Boron-free Filter Paper.* A quantity of Whatman No. 42 paper is placed in a Buchner funnel and washed well with dilute hydrochloric acid. It is rinsed with water until acid-free, and then with ethanol, after which it is sucked dry and stored.

Special Apparatus. The dissolution and distillation apparatus are shown in Figs. 4.2 and 4.3. All tubing and flasks are made of quartz.

Procedure. In a 60-ml quartz distillation flask, A, Fig. 4.2, 0.25 g of sample and 2.5 ml of nitric acid (1+4) are placed. The flask is connected to a reflux condenser, B, by means of a rubber stopper that also holds a quartz reagent tube, C. The bottom orifice of this tube is of capillary size, and the top is closed by means of a rubber stopper. The

assembled distilling flask is placed in an ice bath, and 3 ml of water and 6 ml of concentrated hydrochloric acid are added dropwise to the flask through the reagent tube, C. The addition is regulated by loosening and closing the rubber stopper. After the hydrochloric acid has been added and the reaction has ceased, the ice bath is removed, and the solution is gently refluxed for 10 min. The flask is then cooled and is removed from the condenser.

The pH is adjusted to between 2 and 4 (as indicated by Alkacid test paper) by means of saturated ammonia water (water, in a quartz container, saturated with tank ammonia). A gelatinous precipitate forms; the precipitate redissolves in 10 to 15 min if the flask is shaken occasionally. If the precipitate should dissolve in less than 10 min, more ammonia water must be added dropwise. On the other hand, if more time is required for redissolving than the maximum time allotted, more hydrochloric acid is added dropwise. In the case of reagent blank solutions, this step is accomplished with methyl red indicator. Ammonia water is added until the neutral point is reached, and hydrochloric acid is added to the return of the red color, then 2 drops in excess. During this adjustment, the solution must be kept cool by means of an ice bath and mixed gently.

Any fumes collected in the sample flask, A, are blown out by means of a gentle stream of nitrogen. Then 25 ml of redistilled methanol (anhydrous methanol redistilled over potassium or sodium hydroxide) containing 10 g of calcium chloride per 100 ml of solution is added, and the flask is connected to the still, as shown in Fig. 4.3. The apparatus in Fig. 4.3 includes a 200-ml receiving dish (4.5-in.-diameter No. 7 Amersil or No. 4A Coors porcelain dish) and a flask, B, containing 25 ml of redistilled methanol and a pellet of sodium hydroxide. The receiving dish is supported in an enclosed cold-water bath, which consists of a 6-in. crystallizing dish fitted with a plastic cover and is protected from the heat of the burners by a Transite board. A wooden block turned as indicated in Fig. 4.3 is used to support the receiving dish. The condenser tube from flask A passes through the center hole of the cover almost to the bottom of the receiving dish.

Immediately after the distilling flask has been connected to the still, 5 ml of 0.1*N* calcium hydroxide suspension (0.80 g of boron-free distilled calcium dissolved in 400 ml of water; the suspension stored in quartz) is added to the receiving dish. Flasks A and B are immersed in beakers of hot water, and the beakers are heated gently. The water temperature surrounding flask B is kept between 80 and 82°C; the temperature of the water surrounding flask A is kept between 76 and 80°C. As the alcohol in flask B distills, successive 25-ml portions of redistilled methanol are added through tube C, Fig. 4.3, until a total of about 125 ml of distillate has been collected. The volume of the solution in flask A is maintained at approximately 35 ml by controlling the difference in the temperature of the two water baths and the depths to which the flasks are immersed.

When the receiving dish contains approximately 125 ml of distillate, heating is discontinued. The stoppers are loosened, and the tip of the condenser tube of flask A is rinsed with 10 ml of water. An additional 5 ml of 0.1*N* calcium hydroxide suspension is immediately added to the distillate, and the dish is placed on a steam bath and evaporated to dryness.

The dried residue is removed from the steam bath and allowed to cool to room temperature. Two milliliters of oxalic-hydrochloric acid solution is added, and the dish is manipulated so as to bring the reagent into contact with all the residue. Two milliliters of 1 per cent turmeric extract is added, and the dish is swirled until the reagents are thoroughly mixed. The dish is placed in a water bath held at 55±1°C containing enough water to just float the dish. It is allowed to remain in the bath for 30 to 45 min after reaching dryness; then it is removed and cooled to room temperature. With the aid of a rubber-tipped stirring rod, the residue is extracted with 90 per cent ethanol, added in 3- to 5-ml portions. The extracts are decanted into a graduate, and the extractions are continued until a volume of 25 ml is obtained. The extract is filtered through a dry Whatman No. 42 filter paper.

The absorbancy of the solution is determined in 5-cm cells at a wave length of 540 mμ. For use as a reference, 5 ml of the 0.1*N* lime suspension is taken to dryness, and the color development is carried through as given in the procedure. Known amounts of boric acid solution (0.5 to 1.5 μg of boron) containing 5 ml of 0.1*N* lime suspension are also evaporated to dryness and carried through the same color development. The boron concentrations of the solutions are obtained from an absorbancy-concentration curve and are corrected for a reagent-still blank that is carried through the entire procedure. A correction is also made for the average loss of boron in the over-all procedure. This correction is determined occasionally by analyzing samples with and without added boron. The recovery is generally about 90 per cent.

If a residue is noted on dissolving the metal sample, it is treated separately after the distillation. The solution remaining in flask A is filtered through a Whatman No. 42 boron-free filter paper, and the residue is washed with hot water until it is free of acid and soluble salts. The paper is placed in a platinum crucible. Five milliliters of 0.1*N* lime is added, and the solution is evaporated to dryness. The paper is ashed, and the residue is fused with 1 g of reagent-grade boron-free sodium carbonate. The fused cake is transferred to a 60-ml quartz distilling flask with the aid of 5 ml of distilled water. The flask is connected to a reflux condenser. Through the quartz reagent tube, 2.5 ml of nitric acid (1+4) and 4 ml of concentrated hydrochloric acid are added. The boron is then determined as given in the procedure above starting with the addition of ammonia as described in Sec. 4–4.12(a)(2). A reagent blank must be run including the sodium carbonate and the paper.

(b) *Colorimetric Determination of Boron in Beryllium Metal: Bromine in Methanol Dissolution, Distillation, Diaminochrysazin.*

Special Reagent—Diaminochrysazin Reagent. One hundred and twenty-five milligrams of diaminochrysazin is dissolved in 100 ml of concentrated sulfuric acid and stored in a tightly stoppered quartz flask. This reagent, also called Boran, can be obtained from the La Motte Chemical Products Company, Chestertown, Md. The sulfuric acid should have a low boron content and should be water-white. Merck reagent-grade sulfuric acid is satisfactory.

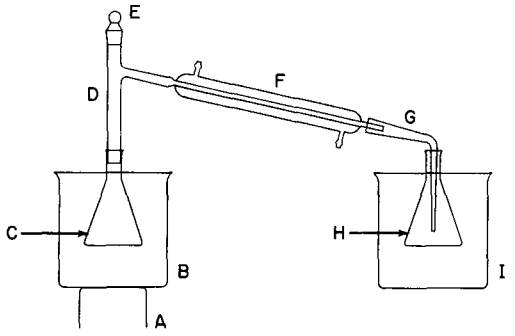


Fig. 4.4—Dissolution and distillation apparatus. A magnetic stirrer. B and I, 800-ml beakers for water baths. C, 250-ml distillation flask (standard taper 24/40). D, connecting tube (standard taper 24/40) with side arm about 3 in. above the joint. E, stopper. F, water-cooled 18-in. condenser attached to D by rubber stoppers. G, adapter, quartz or borosilicate. H, 250-ml receiving flask.

Special Apparatus. The distillation apparatus shown in Fig. 4.4 is made entirely of quartz, except for the adapter, G, which can be made of pyrex.

Procedure.[95] Fifty milliliters of boron-free water (1 g of redistilled calcium metal dissolved in 1 liter of distilled water: the solution redistilled from quartz) is added to the 250-ml quartz receiving flask calibrated for 100 ml. The receiving flask is connected so that the condenser adapter, G, extends slightly into the water. Fig. 4.4. The receiving flask is cooled in an ice bath.

A 1-g sample of beryllium is weighed into a dry distillation flask, C, and 100 ml of boron-free anhydrous methanol (4 g of redistilled calcium metal dissolved in 500 ml of methanol; solution distilled from quartz and stored in quartz) is added. The flask is connected to the condenser, F, and immersed in an ice bath. Then 2 ml of bromine is added to the distillation flask, and the flask is stoppered quickly. The reaction rate is controlled by the rapid intermittent immersion of the distillation flask into the ice-water so that no vapors enter the condenser. Care must be taken that water from the receiving flask is not drawn back into the distillation flask. Generally, the hydrogen evolving from the reaction prevents this drawback. When dissolution is complete, not more than 1 drop of distillate should have formed in the condenser. The distillation flask is then partially immersed in water maintained at 90 to 100°C, and 50 to 60 ml of distillate, as measured by the calibration mark on the receiving flask, is collected. Once this volume has been collected, the receiving flask is removed, and 15 ml of thoroughly shaken calcium hydroxide suspension (1 g of redistilled calcium added to 500 ml boron-free water; suspension stored in quartz) is added to the flask.

To each of three 250-ml quartz Erlenmeyer flasks, 15 ml of the calcium hydroxide suspension and 50 ml of boron-free water are added. Then 0, 1, and 2 ml of the standard boron solution containing 1 μg of boron as boric acid per milliliter are added to each of the three flasks, respectively. The sample distillate and the standards are evaporated

to dryness on a hot plate at medium temperature and then dried for 5 min longer. Next they are transferred to a drying oven and dried for an additional 30 min at 160 to 170°C. The flasks are removed from the drying oven and cooled to room temperature. Ten milliliters of the diaminochrysazin reagent is pipetted into each flask. Over a period of 15 min, the reagent is frequently swirled around the walls of the flask to dissolve all the residue and to eliminate hydrobromic acid gas bubbles in the flask.

The absorbancy of each standard and sample is determined by using the standard containing no boron as reference. In the absorbancy measurements, a wave length of 525 mμ, a slit width of 0.1 mm, and 2-cm cells are used. When the sample solution is measured, it may be necessary to wait a minute or two until all gas bubbles have disappeared from the cell. The quantity of boron in the beryllium is calculated from the absorbancy readings of the standards, preferably from a graphic plot, since occasionally the origin is not quite zero.

4–4.13 Carbon in Beryllium

The present practice is to determine the total carbon in beryllium by combustion in a current of oxygen. The experience of the New Brunswick Laboratory indicates that a temperature of 1300°C and the use of an ignited Sinderite bed are necessary for complete combustion of the carbon. Commercial equipment employing an induction furnace and conductrometric apparatus has been used by certain installations. Beryllium carbide has been determined [98] by treating the metal with a solution of potassium hydroxide and then burning the liberated methane to carbon dioxide. The carbon dioxide is absorbed in Ascarite and weighed in the usual manner. Graphitic carbon has been determined [99] by decomposing the carbide by prolonged heating with dilute acid, filtering the graphitic carbon on asbestos, and then burning in oxygen and absorbing the carbon dioxide as above.

The following procedure has been used for several years in the routine analysis of beryllium metal for total carbon. The sample is burned in an atmosphere of oxygen. The carbon dioxide produced is absorbed in a barium hydroxide solution, which is titrated with dilute hydrochloric acid.

Determination of Carbon in Beryllium Metal: Combustion, Volumetric.

Special apparatus. The apparatus, which is a conventional combustion train, consists of a pressure regulator, a preheater to oxidize any carbonaceous material in the oxygen, a U-tube for absorbing any carbon dioxide present in the oxygen, a sample combustion tube held in a combustion furnace, and an absorption and titration system.

1. *Pressure Regulator.* This regulator should be capable of maintaining a pressure of 3 to 4 in. of mercury.

2. *Preheater.* A Vycor combustion tube 750-mm long and 19-mm in ID is filled with copper oxide wire and heated to 650°C.

3. *Absorption Tube.* This U-shaped Schwartz tube, 100 mm in height, is filled with Ascarite and Drierite.

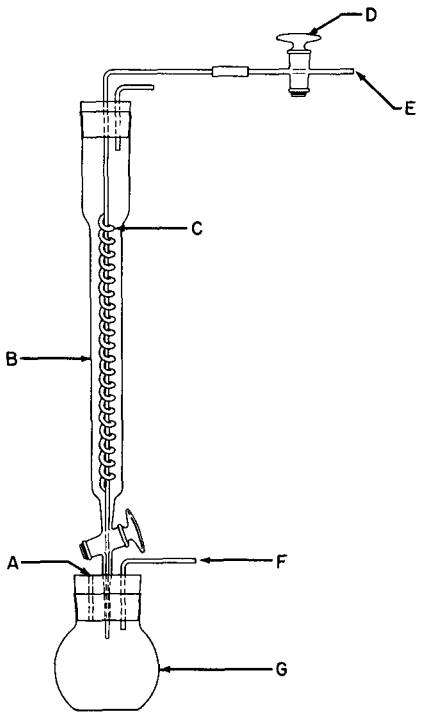


Fig. 4.5—Apparatus for absorption of carbon dioxide in carbon determination. A, hole for 10-ml buret. B, Zackerl–Krainick absorption buret containing 10 ml of barium hydroxide solution. C, glass spiral rod. D, stopcock. E, outlet to combustion tube. F, outlet tube. G, 100-ml receiving flask.

4. *McDanel Combination Tube.* This tube is 30 in. long and 1½ in. in OD. At the entrance end, a breech connector is attached with dental plaster.

5. *Burrell High-temperature Tube Furnace, Model A2–9.* This furnace is used to heat the combustion tube to 1300°C.

6. *Absorption and Titration System.* A stopcock connects the combustion tube and a Zackerl–Krainick absorption buret, the tip of which leads into a receiving flask. Also leading into the flask is a 10-ml buret. (See Fig. 4.5.)

7. *Combustion Boats (5 in. by 1 in. by ⅝ in.).* These boats should be made of material such as zircon ceramic ware having good resistance to thermal shock.

Procedure. Blank Run: The furnace is heated to 1300°C, and the oxygen flow is started. The stopcock to the absorption buret is closed. Ten milliliters of 0.05*N* barium hydroxide [6.3 g of $Ba(OH)_2 \cdot 8H_2O$ and 244 g of $BaCl_2 \cdot 2H_2O$ in 1 liter of solution] and 4 drops of thymolphthalein indicator solution (0.5 g in 100 ml of ethyl alcohol) are added to the absorption buret. The 10-ml buret is filled with 0.05*N* hydrochloric

acid (4.2 ml of concentrated hydrochloric acid diluted to 1 liter; standardized against sodium hydroxide solution). The ignited boat is filled two-thirds full with 10 to 15 g of Sinderite (ignited for 30 min in a stream of oxygen at 1300°C, reground, and reignited at 1000°C). Sinderite is required to ensure complete combustion of beryllium.

The boat is placed in the combustion tube for 2 min with no oxygen flowing. The oxygen is then turned on. The stopcock to the absorption buret is opened, and the oxygen is allowed to bubble through the train for 30 min at a rate of 30 ml per minute. The barium hydroxide is then drained into the receiving flask. The absorption buret is washed three times with boiled distilled water. The barium hydroxide is titrated slowly, and with swirling, with 0.05*N* hydrochloric acid to the disappearance of the blue color. The blank run is repeated until constant results are obtained.

Sample Run: A 0.5-g sample is mixed thoroughly with 10 to 15 g of Sinderite, and the mixture is placed in the boat. The stopcock to the absorption buret is closed. Ten milliliters of 0.05*N* barium hydroxide and 4 drops of indicator are added to the absorption buret. The 10-ml buret is filled with 0.05*N* hydrochloric acid.

The boat containing the sample is placed in the combustion tube and preheated for 2 min. The oxygen is turned on. The stopcock to the absorption buret is opened, and the oxygen is allowed to pass through the train for 30 min as in the blank run. The barium hydroxide is drained into the receiving flask. The absorption buret is washed three times with boiled distilled water. The barium hydroxide is titrated with hydrochloric acid as before.

The difference in the volume of hydrochloric acid used for the blank run and for the sample run is equivalent to the amount of carbon dioxide absorbed by the barium hydroxide. Thus the percentage of carbon present can be calculated by the following equation:

$$\%C = \frac{(V_1 - V_2)(N_{HCl})(0.0060)100}{\text{Sample wt., g}}$$

where V_1 equals milliliters of hydrochloric acid required to titrate blank; V_2 equals milliliters of hydrochloric acid required to titrate sample; and N_{HCl} equals the normality of the hydrochloric acid.

4–4.14 Nitrogen in Beryllium

Although statements have been made to the effect that nitrogen can be determined by a vacuum-fusion technique, the results obtained by this method are generally considerably lower and more erratic than those obtained by the chemical method. Therefore, the micro-Kjeldahl method, with minor modifications, is used by most laboratories for the determination of nitrogen in beryllium metal. The sample is dissolved in hydrochloric acid, and the ammonia is steam distilled, after the addition of sodium hydroxide solution, in a modified Parnas and Wagner micro-Kjeldahl distillation apparatus. The ammonia is titrated with 0.01*N* hydrochloric acid. A mixed bromocresol green–methyl red indicator is used in the titration.

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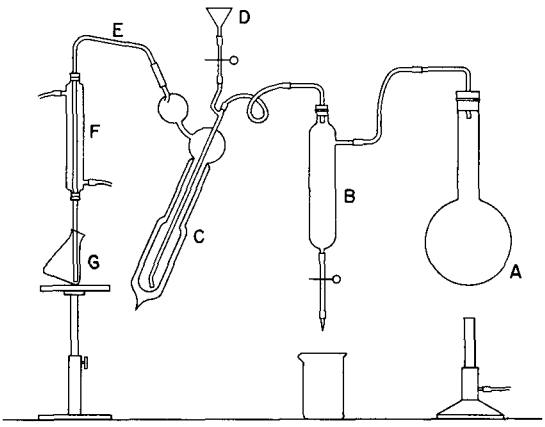


Fig. 4.6—Distillation apparatus for micro-Kjeldahl determination of nitrogen. A, steam generator. B, steam trap. C, distillation flask. D, introduction funnel. E, tube to condenser. F, condenser jacket. G, Erlenmeyer receiving flask.

Determination of Nitrogen in Beryllium Metal: Micro-Kjeldahl.

Special Apparatus. The distillation apparatus, Fig. 4.6, is similar to that described by Niederl and Niederl,[100] except that the distillation bulb in which the digested sample is placed has a volume of 200 ml instead of the 75-ml volume usually found in commercial equipment. A few drops of sulfuric acid are added to the water in the steam generator, A.

Procedure. A 0.5-g sample of beryllium metal is weighed into a 100-ml beaker. After the addition of 5 to 10 ml of redistilled water (redistilled from sulfuric acid), the beaker is covered with a watch glass. The sample is dissolved slowly, to avoid spattering, with 20 ml of hydrochloric acid (1+1). The solution is heated gently for 15 min to ensure complete solution.

The Parnas and Wagner micro-Kjeldahl distillation apparatus is steamed out, then cooled. Thirty-five milliliters of 50 per cent sodium hydroxide (50 g in 100 ml of solution) is poured into the distillation flask, C, through the funnel, D. Five milliliters of 2 per cent boric acid (2 g in 100 ml of solution) and 4 drops of mixed indicator (0.0166 g of methyl red and 0.0834 g of bromocresol green in 100 ml of ethanol) are added to the Erlenmeyer receiving flask, G. The tip of the condenser outlet is immersed under the surface of the liquid. The sample solution is transferred to the distillation flask, C, through the funnel with small portions of redistilled water. All connections are closed. A flame is applied to the steam generator, A, and the distillation is allowed to proceed for 5 min from the first observation of condensation in the steam trap. The receiving flask is lowered so that the condenser tip is above the liquid level, and the distillation is continued for an additional 2 min. The contents of the receiving flask are titrated with 0.01*N* hydrochloric acid (standardized by titrating the distillate obtained with 5 ml of a standard nitrogen solution, prepared from ammonium chloride and containing 100 μg per milliliter, carried through the procedure) to a faint pink. A reagent blank is carried through the entire procedure.

4–4.15 Beryllium Oxide in Beryllium

At the present time beryllium metal generally contains about 0.1 to 0.5 per cent beryllium oxide. Since oxygen may cause lack of ductility in beryllium, the determination of oxygen is essential and has been made by several different methods.

The method that has been used to the greatest extent is the hydrogen chloride volatilization method [101] in which the beryllium metal is distilled as the chloride; the oxide is left behind and is determined colorimetrically. Although it is used to a considerable extent, this method has certain drawbacks. It is time consuming and requires considerable attention to detail. Several workers have found that it does not always give reproducible results; the beryllium oxide in certain instances may be carried over in the chloride gas stream. Modifications of this method consist in using chlorine [102] or bromine [103] in place of the gaseous hydrogen chloride.

Several selective solution methods have been used which employ hydrochloric acid,[102] copper sulfate,[104] and methanol-bromine [105] to dissolve the beryllium metal and leave the beryllium oxide unreacted. At the New Brunswick Laboratory the results obtained with the hydrochloric acid solution method [102] are high compared to the hydrogen chloride volatilization method [101] and low compared to the copper sulfate method.[104] The methanol-bromine method has given satisfactory agreement with the hydrogen chloride volatilization method when used on beryllium metal melted under vacuum. The same method can be applied to other beryllium metal samples if they are first heated to 600°C in an atmosphere of dry helium. If appreciable amounts of carbide or nitride are present, high results may be obtained. This method is fairly rapid, and many samples can be run at one time. It is used at present by several laboratories engaged in the routine determination of oxygen.

The conventional vacuum-fusion method has not proved satisfactory for beryllium metal. However, the microvacuum-fusion method of Booth, Bryant, and Parker,[106] employing a platinum bath, does give good results. This method is an extension of the work of Gregory and coworkers.[107, 108] Apparently, with the conventional vacuum-fusion technique, the beryllium is volatilized and reacts, in the cooler part of the furnace, with the carbon monoxide formed, thus giving low results. The microvacuum-fusion method for beryllium oxide is described in Chap. 11, Trace Elements.

The Smiley method,[109] in which the carbon monoxide formed is swept out of the fusion furnace in a current of argon, oxidized to carbon dioxide, removed, and measured by a capillary trap or conduc-

tivity apparatus, has been applied to the determination of oxygen in beryllium metal.[110] The beryllium metal is wrapped in copper foil and is dissolved in a bath of molten nickel.

The oxide content of beryllium metal can be determined by measuring the beryllium metal and beryllium carbide content [98] by hydrogen- and methane-evolution procedures and then calculating the oxide content from the total beryllium present, but this method is long and painstaking. Also, since the results are obtained from the differences between large numbers, they may be significantly affected by only minor variations in the total beryllium, beryllium metal, and beryllium carbide values.

Radioactivation methods have been employed for determining oxygen in beryllium powder.[111, 112] The method [112] in which F^{18} is produced by the reactions

$$_3Li^6 + {}_0n^1 \rightarrow {}_2He^4 + {}_1H^3$$

$$_8O^{16} + {}_1H^3 \rightarrow F^{18} + {}_0n^1$$

appears to give results comparable to those obtained by the hydrogen chloride volatilization method. Lithium fluoride is added to the sample prior to irradiation. The oxygen content of the added lithium seems to be the limiting factor for the sensitivity of this method. The lower limit for oxygen in beryllium by the procedure, therefore, is about 0.1 to 0.2 per cent.

A recent article [113] describes a procedure for finding the oxygen content of massive or powdered beryllium metal by irradiating the sample with 14.5-Mev neutrons and measuring the 7.4-sec N^{16} activity produced in the reaction, $_8O^{16}(n, p)_7N^{16}$. Oxygen contents in the range 0.01 to 2.0 per cent are measured. As little as 0.001 per cent of oxygen can be detected, provided the intensity of short-lived reaction products from other impurities is sufficiently low.

Most of the above methods are generally applicable only when more than about 0.2 per cent beryllium oxide is present in the metal. The determination of less than 0.1 per cent beryllium oxide in beryllium metal still remains a difficult problem. The methods of Smiley,[109] of Booth, Bryant, and Parker,[106] and of Coleman and Perkin [113] seem to be the only methods currently available which might be used below this level.

(a) *Determination of Beryllium Oxide in Beryllium Metal: Selective Dissolution with Bromine in Methanol.*[105]

Special Reagent—p-Nitrobenzeneazoorcinol. Twenty-four grams of sodium hydroxide and 18 g of boric acid are dissolved in water and diluted to 1 liter. The solution is transferred to a 2-liter beaker, and 75 mg of *p*-nitrobenzeneazoorcinol is added. After 2 hr of mechanical

stirring, the solution is filtered and stored in the dark. The solution should be examined before use and filtered if a turbidity has developed.

Procedure (*High-temperature Metal—Vacuum-cast or High-temperature Reduction*). A 0.5-g sample of powder or fine chips is placed in a dry 250-ml extraction flask, and 10 ml of methanol (water content less than 0.1 per cent) is added. Then 50 ml of methanol containing 3 ml of bromine is added slowly in 2- or 3-ml portions. (The reaction is very vigorous and should be carried out under a well-ventilated hood.) When all particles of metal appear to be dissolved, 50 ml of methanol–hydrochloric acid solution (40 ml of concentrated hydrochloric acid diluted to 500 ml with methanol) is added. The contents are mixed by swirling every few minutes over a period of 30 min. The solution is transferred to a 150-ml beaker, and any residue is washed from the flask into the beaker with methanol. The solution is filtered with vacuum through a 15-ml fritted-glass crucible. (Some fine-porosity crucibles filter more rapidly than others. The more rapidly filtering type is used.) The residue and crucible are washed with methanol until the wash is free of bromine color. The crucible is removed from the filtering flask, and the bottom and outside of the crucible are washed with water.

The crucible is transferred to a 150-ml beaker, and 15 ml of concentrated sulfuric acid and 10 ml of concentrated nitric acid are added. The beaker is covered with a watch glass, and the residue is dissolved by heating on a hot plate until fumes of sulfuric acid evolve. The solution is cooled and diluted with about 100 ml of water. The solution is transferred to a 500-ml volumetric flask. The crucible and beaker are washed twice with 100-ml portions of hot water, and these washings are added to the volumetric flask. The solution is diluted to 500 ml.

In four of five 50-ml centrifuge tubes are placed, respectively, 0, 1, 3, and 5 ml of a standard beryllium solution containing 20 μg of beryllium per milliliter. Twenty milliliters of sulfuric acid (3+97) is added to each tube. Twenty milliliters of the sample solution is placed in the fifth tube. To all tubes 1 ml of an aluminum nitrate solution (34.8 g of aluminum nitrate nonahydrate in 500 ml of solution), containing 5 mg of aluminum, and about 2 g of solid ammonium chloride are added. Each tube is diluted to about 35 ml with water. The aluminum and beryllium are precipitated by the addition of 5 ml of concentrated ammonium hydroxide. The suspensions are stirred thoroughly with glass rods. The suspensions are centrifuged, and the supernatant liquids are carefully decanted. The tubes are drained by standing them inverted on a dry towel for about 5 min. Twenty milliliters of the *p*-nitrobenzeneazoorcinol reagent is added to each tube, and the hydroxides are dispersed in the solution by stirring with the glass rods. The solutions are warmed in a water bath at 80 to 90°C for 5 min and then cooled to room temperature. The solutions are transferred to 50-ml volumetric flasks and diluted to volume.

The absorbancy of each solution is measured at 520 mμ in 2-cm cells. The solution containing no beryllium is used as a reference. Since Beer's law is not obeyed, a smooth curve through the plot of absorbancy versus concentration of the standards must be drawn. The standard curve should be determined with each set of samples analyzed.

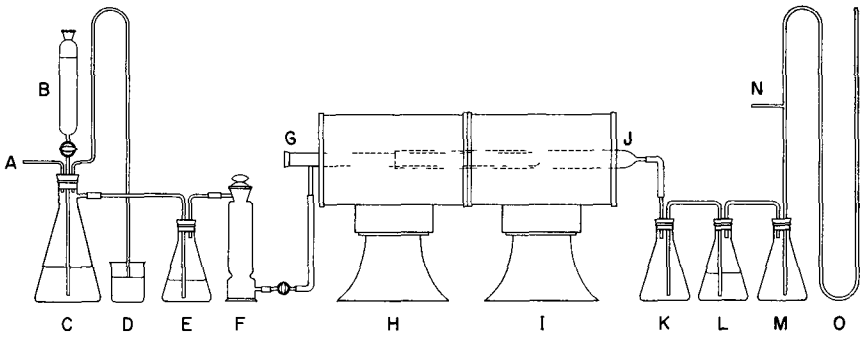


Fig. 4.7—Apparatus for determination of berryllium oxide content of beryllium metal by hydrogen chloride gas evolution method. A, helium gas inlet. B, 250-ml separatory funnel filled with hydrochloric acid. C, 2-liter flask half filled with concentrated sulfuric acid. D, 30-in. mercury manometer and reservoir. E, 500-ml flask partially filled with concentrated sulfuric acid. F, drying tower filled with anhydrous magnesium perchlorate. G, clear quartz tube, ⅞ in. in OD and 22 in. long, with 3/16-in.-diameter side arm near open end and 3/16-in. orifice at opposite end. H, tube furnace, temperature variable from 600 to 800°C. I, tube furnace, maintained at 900 to 1000°C. J, fused-quartz tube, 1,25 in. in OD, 1 in. in ID, 30 in. long, with reduced end. K, L, and M, 500-ml flasks (L containing sulfuric acid). N, lead to water aspirator. O, water manometer.

Procedure (*Low-temperature Beryllium—Electrolytic*). A 1-g sample held in a platinum boat is placed in a small combustion tube (pyrex can be used). Helium, from which oxygen has been removed by a hot copper train, is passed through the combustion tube. The tube is heated for 1 hr at 200°C to remove moisture. Over a period of 30 min, the temperature is raised to 600°C and is then kept at 600°C for the remaining 30 min. The tube is cooled to room temperature. A 0.5-g sample is weighed out, and the procedure as described above for high-temperature metal is followed.

(b) *Determination of Beryllium Oxide in Beryllium Metal: Hydrogen Chloride Volatilization.* This procedure is used to a certain extent at present and is given below because for many years it has been the standard procedure for the determination of beryllium oxide in beryllium metal.

Special Apparatus. The violatilization train is shown in Fig. 4.7. This apparatus is assembled in a well-ventilated hood. All operations, including sample preparation, should be carried out in the hood.

Procedure. The sample may be powdered metal, small slivers, or a solid piece. Powdered metal, however, should be first cold-compacted into a ¼- to ½-in.-diameter pellet in a die by means of a 3-ton hydraulic press.

The combustion boat of slipcast high-fired beryllium oxide is ignited for half an hour in a muffle furnace at about 1000°C and cooled in a desiccator. The sample is weighed and placed in the cooled boat. For samples

containing greater than 1 per cent beryllium oxide, approximately 0.2 g of sample is sufficient. For lower beryllium oxide contents, 0.25 to 0.50 g of sample is used. The boat (or boats) is placed in the cold middle zone of the side-arm quartz tube G, which is then closed with a neoprene rubber stopper. With only the orifice end of this tube in the furnace and with the sample boat cold, the entire train is flushed with oxygen-free helium gas for 1 hr. The dry hydrogen chloride gas, which is formed by dropping concentrated hydrochloric acid into sulfuric acid, is started flowing through the train, the helium flow is cut off, and the hydrogen chloride gas rate is adjusted to about 5 bubbles per second. This flow is continued for about half an hour with a suction of 2 to 3 in. of water, maintained by means of the water aspirator, at the exit end of the outer quartz tube. The side-arm quartz tube is pushed into the tube furnace so that the sample is brought into the middle of the hot zone of the first furnace (previously adjusted to 600°C) and so that the orifice end of this quartz tube is at the middle of the hot zone of the second furnace (maintained at above 900°C).

After 30 min, the temperature of the first furnace is gradually increased to 800°C. The hydrogen chloride gas flow is continued for 15 to 20 min after beryllium chloride stops coming off. (A total of about 90 min in the hot zone suffices for a 0.2-g sample.) The flow of hydrochloric acid solution into the concentrated sulfuric acid flask is discontinued, the stopcock leading into the side arm of the quartz tube is closed, and the water aspirator is shut off. The boat is removed from the quartz tube very carefully because the residue is very light and pulverulent and is easily lost with the slightest draft. When the boat is cool, the residue is transferred to a 150-ml beaker. Water, a few drops of nitric acid, and 3 ml of sulfuric acid (1+1) are added. The solution is heated to strong fumes of sulfuric acid and then cooled. After the addition of 25 ml of water, the solution is boiled vigorously for a minimum of 15 min to dissolve all soluble salts. The solution is then filtered, and the beryllium content is determined by the colorimetric *p*-nitrobenzeneazoorcinol method as given in Sec. 4–4.15(a).

4–4.16 Fluorine in Beryllium

Although the usual method of separating fluorine by distillation as hydrofluosilicic acid,[114] followed by titration with thorium nitrate or by a colorimetric determination [115] with the aluminum–Solochrome Cyanin complex, has been used to determine fluorine in beryllium, the pyrohydrolytic method of Warf, Cline, and Tevebaugh [116] has been used to a greater extent. This method consists of hydrolyzing the fluoride at 700 to 800°C in a current of steam [116] or in a current of oxygen containing steam.[117] The fluoride, which is volatilized, is absorbed in a small volume of dilute standard sodium hydroxide solution or water and then determined by an acidimetric titration or, if the fluorine is low, as is usually the case, by a spectrophotometric determination.[118] Although the apparatus of Warf, Cline, and Tevebaugh or of Susano, White, and Lee [119] can be used, the recent work of Powell and Menis [117] indicates that their procedure may be more satisfactory.

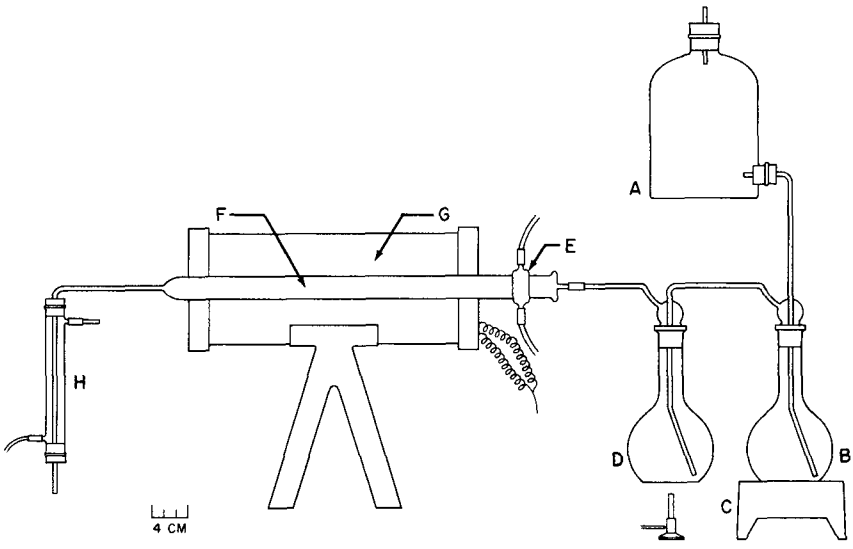


Fig. 4.8—Pyrohydrolysis apparatus. A, 2-liter bottle filled with distilled water. B, 500-ml Florence type wash bottle. C, Fisher electric heater, 500 watt. D, 500-ml Florence type wash bottle. E, copper condenser, attached to platinum tube. F, platinum reaction tube. G, electrical furnace, 800 to 900°C. H, glass condenser.

The following procedure is that developed by the Iowa State University group, using an apparatus similar to that of Warf, Cline, and Tevebaugh.

(a) *Determination of Fluoride in Beryllium Metal: Pyrohydrolysis, Volumetric.*

Special Apparatus. The pyrohydrolysis apparatus is shown in Fig. 4.8.

Procedure.[118] The furnace is heated to 700 to 800°C, and steam is passed through the apparatus at a rate of 0.5 g per minute. The tip of the condenser should just dip beneath the surface of water held in a silver or platinum dish receiver. A sample of beryllium (usually about 2 g), containing from 0.5 to 40 μg of fluorine, is weighed into a platinum foil boat and inserted in the platinum reaction tube of the pyrohydrolysis apparatus. A steam rate of 0.5 g per minute is maintained until the vigorous evolution of hydrogen has subsided, and it is then increased to 5 g per minute and maintained at this rate until a total of 35 ml of distillate has been collected. The distillate is transferred to a 50-ml Nessler tube. Two milliliters of 0.05*N* hydrochloric acid and 1 ml of 0.1 per cent indicator solution (0.10 g of sodium alizarin sulfonate dissolved in 1 liter) are added, and the solution is diluted to the mark with redistilled water.

The solution is titrated to a pink end point with 0.0004*N* thorium nitrate (5.52 g of thorium nitrate tetrahydrate in 1 liter of solution; 10 ml of this stock solution diluted to 1 liter). A reference solution is

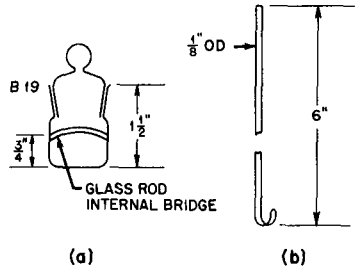


Fig. 4.9A—Special weighing bottle. (a) Sample container. (b) Manipulator.

prepared by adding 40 ml of redistilled water, 1.0 ml of the indicator solution, and 2.0 ml of 0.05*N* hydrochloric acid to a 50-ml Nessler tube and diluting to the mark with redistilled water. A volume of 0.0004*N* thorium nitrate equal to that required by the sample is added to the reference solution. The reference solution is now titrated with a standard sodium fluoride solution (2.11 g in 1 liter of stock solution stored in rubber or plastic bottle; 10 ml of this stock solution diluted to 1 liter to give 10 μg per milliliter) until the color matches that of the end point of the sample. The amount of sodium fluoride added is a measure of the quantity of fluoride in the sample.

(b) *Determination of Fluorine in Beryllium Metal: Distillation, Colorimetric.*[115]

Special Reagents. 1. *Standard Aluminum Solution.* This solution is made by dissolving 1.867 g of aluminum ammonium sulfate, $NH_4AL(SO_4)_2 \cdot 12H_2O$, in water and diluting the solution to 100 ml. Ten milliliters of the solution is diluted to 100 ml to obtain a standard solution containing 111 μg of aluminum per milliliter.

2. *Buffer Solution, pH 4.5.* Thirty-two grams of reagent-grade ammonium chloride is dissolved in 220 ml of water. Twenty-five milliliters of reagent-grade glacial acetic acid and 7.5 ml of ammonia solution (specific gravity, 0.880) are added. When the solution is cool, the pH is adjusted to 4.5 with a pH meter. The solution is made up to a volume of 300 ml.

3. *Aluminum–Solochrome Cyanine Reagent.* The following reagents are added in the order given to 450 ml of water in a 600-ml beaker, with thorough mixing after each addition: 13.4 g of reagent-grade ammonium chloride; 1 ml reagent-grade glacial acetic acid; 20 ml Solochrome Cyanine solution [prepared by dissolving 0.25 g of dye in 10 ml of hydrochloric acid (1+99) and diluting the solution to 100 ml]; and 10 ml of the standard aluminum solution. Then ammonium hydroxide solution (1+9) is added to bring the pH to 4.5. The solution is diluted to 500 ml and filtered through a Whatman No. 1 filter paper. One crystal of thymol is added to prevent mold growth.

Special Apparatus. Figure 4.9A shows the special sample container designed to fit into the reaction flask of the distillation apparatus shown in Fig. 4.9B.

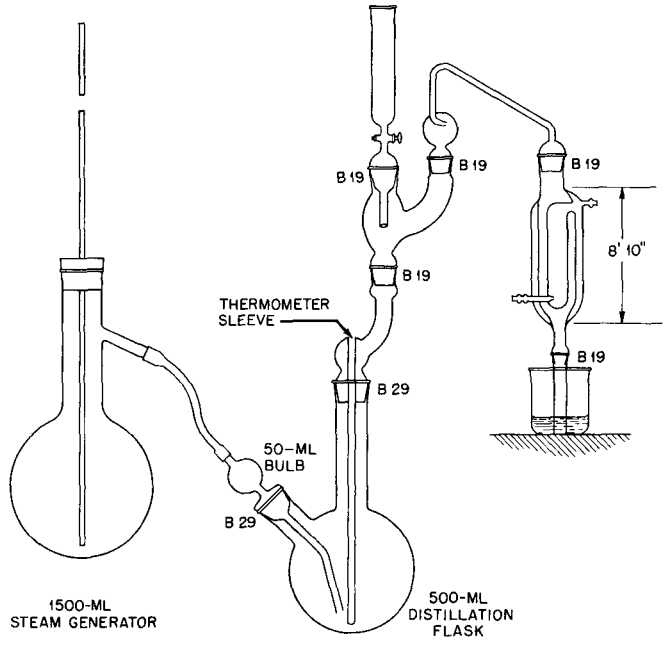


Fig. 4.9B—Distillation apparatus.

Procedure. A 1-g sample is weighed into the special sample container, Fig. 4.9A, and the container is transferred to the distillation flask, Fig. 4.9B, through the B29 socket arm with the container manipulator. The container is left in the flask for all the ensuing operations. Five milliliters of 40 per cent sodium hydroxide solution (40 g dissolved in 1 liter), 20 ml of water, and 2 drops of 1 per cent phenolphthalein solution (1 g dissolved in 50 ml of ethanol; the solution diluted to 100 ml and filtered if necessary) are added to the distillation receiver. Ten milliliters of water is added to the beryllium sample in the distillation flask via the tap funnel. Then 60 ml of sulfuric acid (1+1) is added cautiously to the flask via the tap funnel. When the reaction has become quiescent, the water in the steam boiler is brought to a boil, and the temperature of the contents of the distillation flask is brought to 160°C. This temperature is maintained during the distillation. Steam is passed through the distillation flask until the volume of solution in the receiving beaker is 240 ml. The distillation is then discontinued.

The distillate is transferred quantitatively to a 250-ml volumetric flask, and the volume is adjusted to 250 ml. A suitable aliquot (containing more than 2 and less than 15 μg of fluorine and having a volume not exceeding 25 ml) is pipetted (not by mouth) to a 150-ml beaker. Hydrochloric acid (1+9) is added until the solution is just colorless. Then 0.5 ml of acetylacetone solution (1 ml of acetyl acetone dissolved in water; the solution diluted to 500 ml) is added. The pH of the solution is adjusted with a meter to 6.0 to 8.0, and the solution is quantitatively transferred to a 250-ml separatory funnel. As little water as possible is used in the transfer.

The acetylacetone complex of beryllium is extracted by shaking for 2-min periods with four successive 20-ml volumes of purified chloroform (1 liter washed with two 300-ml portions of 4 per cent sodium hydroxide solution, then washed with two 300-ml portions of water and filtered through chloroform-wetted Whatman No. 541 filter paper). The solvent layers are discarded. The aqueous phase is filtered quantitatively through 9-cm Whatman No. 541 paper into a 50-ml volumetric flask. The total volume of the solution plus washes must be kept below 30 ml. Two milliliters of the buffer solution is added, and the solution is mixed. After the addition of 15 ml of aluminum–Solochrome Cyanin reagent, the solution is again mixed and is diluted to 50 ml. The flask is placed in a water bath maintained at 60°C for 15 min. The flask is removed and cooled by cold-water immersion for 20 min.

The absorbancy of the solution is measured on a spectrophotometer in a 1-cm cell at a wave length of 535 mμ against a reference solution made by adding the dye and the buffer to water instead of to the sample raffinate. A blank determination is carried out on the reagents and is measured against the above reference solution. The fluorine present in the sample is calculated. Over the range 0 to 20 μg of fluorine, the relationship between the amount of fluorine present and the absorbancy observed should be linear.

4–4.17 Chlorine in Beryllium

Chlorine in beryllium metal has been determined by distilling the chlorine as chloride followed by nephelometric determination;[120] by direct determination after solution, either by a nephelometric[121] or a potentiometric method; or by removing the chloride in a current of steam at high temperatures and then determining the chloride colorimetrically.[122]

The following procedures employ solution of the sample in sulfuric acid, followed by determination of the chloride present in the solution either nephelometrically[121] or potentiometrically.

(a) *Direct Nephelometric Determination of Chlorine in Beryllium Metal.*[121]

Special Apparatus. A 200-ml reaction flask, a reflux condenser with a ground-glass joint, and a dropping funnel are cleaned with cleaning solution and then rinsed out thoroughly with distilled water.

Procedure. A 1-g sample containing 10 to 100 μg of chlorine is transferred to the 200-ml reaction flask, and 10 ml of water is added to the flask. The condenser is fitted into position with the dropping funnel containing 15 ml of sulfuric acid placed on top of the condenser. The acid is then added to the reaction flask. A violent reaction is avoided by adding the acid slowly in small portions and by cooling the flask by immersing it in a beaker of cold water.

When the metal is practically all decomposed, the contents of the flask are boiled for a few minutes. If more water is needed to dissolve the salts completely, it is added sparingly. When the temperature has gone down to about 30°C, 2 ml of nitric acid (1+1) is added and mixed in thoroughly to oxidize the reduction products of sulfuric acid.

If the solution is not clear, it is filtered through a Whatman No. 42 filter paper into a 100-ml beaker. The paper is washed sparingly with water.

The pH of the cooled solution is adjusted to 2.0, as measured with pHydrion paper, by the addition of concentrated ammonium hydroxide. (A pH meter with a calomel electrode should not be used for this pH measurement.) After each addition of ammonium hydroxide, the solution is stirred to dissolve the beryllium hydroxide completely.

The solution is transferred to a 100-ml volumetric flask. One milliliter of 0.1*N* silver nitrate is added, and the volume is adjusted to 100 ml with water. The flask is heated on a water bath at a temperature of 46°C for 15 min. and the turbidity of the solution is read on a nephelometer. Water is used as a blank. The quantity of chlorine present is then read from a calibration curve.

Solutions containing beryllium and chloride are used for the preparation of the calibration curve. Ten grams of beryllium metal is cautiously dissolved in 100 ml of sulfuric acid (1+1). The solution is made up to about 250 ml. Ten milliliters of nitric acid (1+1) is added. The flask is heated on a steam bath until the salts dissolve. The solution is filtered through a Whatman No. 42 filter paper into a 600-ml beaker, and 5 ml of 0.1*N* silver nitrate is added to the filtrate. The solution is heated on a steam bath for an hour, stored in a dark place overnight, and then filtered through a Whatman No. 42 paper that has been previously washed twice with hot distilled water. The filtrate is adjusted with concentrated ammonium hydroxide to a pH of 2.0 as measured with pHydrion paper. The solution is transferred to a 500-ml volumetric flask and diluted to the mark. Fifty-milliliter aliquots, equivalent to a 1-g sample, are transferred to 100-ml volumetric flasks. A standard sodium chloride solution containing 100 μg of chloride per milliliter (0.1649 g in 1 liter of solution) is added to each aliquot to make standard solutions containing 0, 10, 20, 50, and 100 μg of chlorine, respectively. One milliliter of 0.1*N* silver nitrate is added to each standard, and the volumes are adjusted with water. The flasks are heated on a water bath at 46°C for 15 min, and the turbidities are read on a nephelometer. Water is used as a blank.

(b) *Direct Potentiometric Determination of Chlorine in Beryllium Metal.* This method is based on the measurement of the potential difference between two silver–silver chloride electrodes dipping into two solutions, joined by a liquid bridge, containing different amounts of chloride but the same beryllium and sulfuric acid concentrations. For very low chloride concentrations (less than $10^{-4}M$) the most accurate procedure involves measurements made against a known reference solution and comparison with a standard curve prepared from solutions containing less chloride than the reference. This procedure compensates for the effect of the solubility of silver chloride on the chloride concentration. In the absence of a standard beryllium solution containing either no chloride or a small known amount of chloride, an approximation of the chloride content can be obtained by adding different known amounts of chloride to two aliquots of the sample solution, one quantity being appreciably larger than the other.

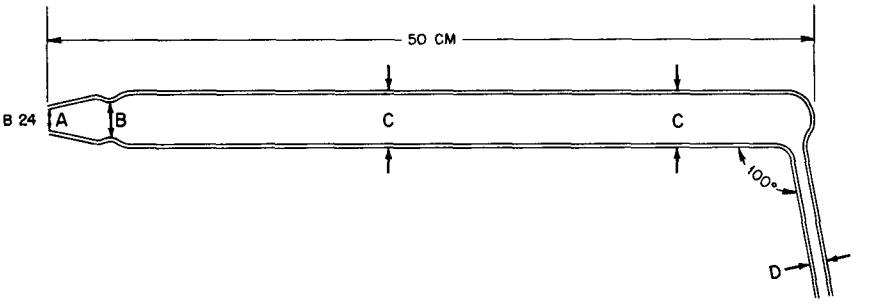


Fig. 4.10—Pyrohydrolysis tube. A and B are not less than 1.7 cm in ID; C is not greater than 2.9 cm in OD and 2.5 cm in ID; and D is approximately 0.8 cm in OD.

The difference in potential between these two solutions is measured, and the data are substituted in the following equation:

$$E=0.0591 \log \frac{C_1+x}{C_2+x}$$

where E is the potential difference in volts; x is the original molar concentration of the chloride; and C_1 and C_2 are the molar concentrations of the added chloride.

Procedure. Two grams of beryllium metal is dissolved under a reflux condenser with sulfuric acid (see Sec. 4–4.17(a)).

The solution is transferred to a 100-ml volumetric flask and made to volume with water. Two aliquots of 40 ml each are transferred to 50-ml volumetric flasks. To the aliquots are added 20 and 40 μg of chloride to give molar concentrations of $(1.13\times10^{-5}+x)$ and $(5.63\times10^{-5}+x)$, respectively. The potential difference, E, between these two solutions is measured, and the original chloride concentration, x, is calculated according to the above equation.

(c) *Colorimetric Determination of Chlorine in Beryllium: Pyrohydrolysis.*[122] For amounts of chloride down to 2 ppm, the colorimetric determination [122] has proven satisfactory. This procedure involves heating the sample to 1100 to 1200°C in a current of steam. The hydrogen chloride formed is collected in the condensate, and the chloride is determined colorimetrically after the addition of mercuric thiocyanate and ferric alum.

Special Reagents. 1. *Redistilled Water.* Freshly redistilled water is used throughout the reagent preparation and procedure.

2. *Ferric Alum Solution.* About 600 ml of concentrated nitric acid is boiled to remove nitrous fumes; then 560 ml of the hot acid is added to 120 g of ferric alum dissolved in 430 ml of boiling water in a 2-liter beaker. Complete solution is achieved by gentle heating under a cover glass. The solution is cooled in an atmosphere free from chlorine, made up to 1 liter, and stored in a well-stoppered bottle.

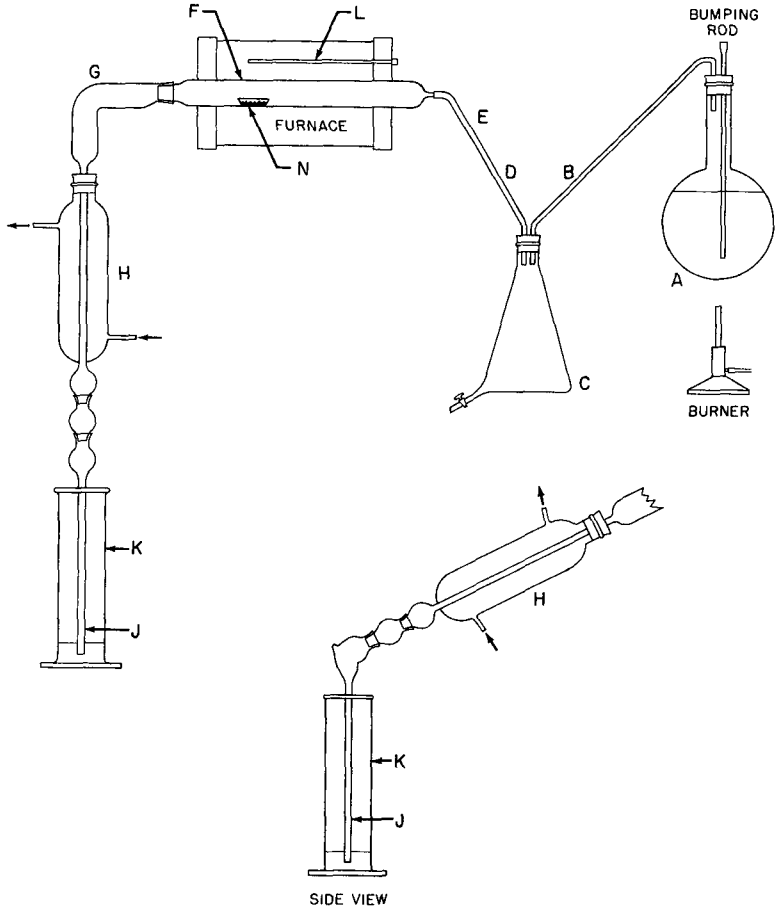


Fig. 4.11—Pyrohydrolysis apparatus. A, steam generator containing redistilled water with a pellet of sodium hydroxide. B, D, and E, side arms. C, splash trap. F, silica reaction tube. G, silica adapter. H, silica condenser. J, pyrex delivery tube. K, Nessler cylinder. L, thermocouple. N, silica boat with sample.

3. *Mercuric Thiocynate Solution.* Ten grams of mercuric thiocyanate is dissolved in 600 ml of ethyl alcohol at 60°C. The solution is filtered and allowed to crystallize. The crystals are filtered off, and a saturated solution is prepared from them in ethyl alcohol at room temperature. This solution contains about 4 g of solid reagent per liter of solution.

Special Apparatus—Pyrohydrolysis Apparatus. The sample is pyrohydrolyzed in a clear silica reaction tube, 2.5 cm in ID and 50 cm long, fitted with a standard-taper joint at one end and sealed at the other end. A side arm, 0.5 cm in ID and 10 cm long, is sealed near the closed end at an angle of 100° with the main tube, Fig. 4.10. The complete apparatus is shown in Fig. 4.11. The furnace is heated with four

Globar type elements connected so that a pair in parallel is in series with the other pair in parallel. This arrangement enables high temperatures to be achieved rapidly. The temperature is regulated by a Variac. The adapter, G, and condenser, H, are silica, and the delivery tube, J, is pyrex. Polyethylene tubing at B and D connect the splash trap, C, with the reaction tube, F, and the steam generator, A. A 100-ml cylinder, K, receives the condensate.

Procedure. The temperature of the reaction tube is raised to 1000°C, and the apparatus is steamed out until, when water is passed through the condenser jacket, 100 ml of condensate gives no turbidity with 1 ml of nitric acid and 1 ml of 2 per cent silver nitrate solution. The reaction tube is then cooled to about 400°C.

Oxide samples are ground to a fine powder in an agate mortar and then weighed into a silica boat. For metal samples, fine turnings, flake, or dust is weighed out. If the sample contains 250 ppm or less, a 1-g sample is taken. If the chloride content is above this value, the weight of the sample used should contain about 250 μg.

The adapter, G, is disconnected from the reaction tube, F. A 100-ml cylinder, K, containing 5 ml of water, is placed under the delivery tube, J, so that the tip is just under the liquid surface. (Cylinders should be reserved for this purpose only and should be kept stoppered and full of water when not in use.) The boat containing the sample is inserted into the reaction tube so that it is in the hottest position, as near to the outlet as possible. The adapter, G, is quickly reconnected, and the flow of steam is started. The temperature of the furnace is raised to between 1100 and 1200°C. The flow of steam should be slow until the temperature reaches 1100°C, and then it should be increased until 1.5 to 2 ml of condensate is collected per minute. When the volume of liquid in the cylinder is about 80 ml, the flow rate of steam is again increased while a further 10 ml is collected. The delivery tube is then disconnected and washed down into the cylinder. The volume is adjusted to 100 ml.

An aliquot of 20 ml or less containing 20 to 50 μg of chlorine is placed in a 25-ml volumetric flask, and 2 ml of ferric alum solution and 2 ml of mercuric thiocyanate solution are added. (The volumetric flask used also should be reserved for this purpose and should be kept stoppered and full of water when not in use.) If the total condensate contains less than 100 μg of chlorine, it is transferred to a silica beaker and evaporated, after the addition of 1 drop of 0.1*N* sodium hydroxide, to about 15 ml. If the solution contains between 50 and 100 μg of chlorine, this 15 ml of solution is diluted to 25 ml, and a 10-ml aliquot is used for color development. If the 15 ml of solution contains less than 50 μg, the entire solution is used.

The solution is allowed to stand for at least 10 min after the addition of reagents. The absorbancy is then measured, within the next 20 min, at 480 mμ in 2-cm cells. A reagent blank similarly prepared is used as a reference. The quantity of chlorine present is then read from a calibration curve. Data for the calibration curve is obtained by preparing standard aliquots containing 0, 10, 25, 50, 75, and 100 μg of chlorine (0.165 g sodium chloride dissolved in 1 liter; 50 ml of this solution diluted to 1 liter to give 5 μg of chlorine per milliliter), diluted to about 20 ml in 25-ml volumetric flasks, and processed as outlined in the procedure.

The above method is suitable for chlorine contents down to 2 ppm. The upper limit depends upon the aliquot taken.

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CHAPTER 5

ALLOYS AND CERAMICS

By R. W. Bane*

5–1 ALLOYS

5–1.1 Aluminum Alloys

Uranium–aluminum alloys are used extensively for nuclear reactor fuel in the form of plates, rods, slugs, or tubes. Accurate knowledge of the uranium content of these fuel assemblies is a prerequisite for control of fissionable material inventories and for ascertaining the ultimate uranium loading in the reactor. The degree of homogeneity and distribution of the fissionable material in a fuel element is of extreme importance. A nonuniform distribution will lead to asymmetrical temperature gradients within the fuel, with possible buckling, distortion, and even rupture of the cladding. The end result will be reactor shutdown. Numerous methods have been proposed for determining the fissionable material (uranium or plutonium) in aluminum alloys. Various nondestructive procedures have been developed for determining the homogeneity and total uranium in fuel elements. The nondestructive methods include gamma counting,[1] X-ray densitometry,[2] gamma-ray transmission,[3] and mass density.[4]

The composition of uranium–aluminum alloys can be measured by X-ray emission spectrography using a solid sample [5] or by a solution technique.[6] A gravimetric procedure provides for the separation and determination of uranium and aluminum.[7] The "alkaline peroxide" spectrophotometric method,[8] when corrected for iron and chromium, can be performed with an accuracy of ± 1 per cent in the direct determination of uranium in uranium–aluminum alloys.[6] The volumetric analysis of uranium by the lead reductor–ceric sulfate titration is probably the most popular method for uranium–aluminum alloys. Aluminum may be determined spectrophotometrically.[9, 10] A volumetric analysis for aluminum by ethylenediaminetetraacetic acid (EDTA) titration is applicable over a wide range of uranium–aluminum alloys.[11, 12] The determination of iron and nickel, minor components of some uranium–aluminum alloys, is made spectrophotometrically. The potentiometric ferric solution titration of U(IV) has been adapted to the routine analysis of uranium–aluminum alloys.[13–15] Tho-

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rium and aluminum in binary alloys can be determined over a wide range by EDTA titration after solvent extraction separation.[16]

(a) *Nondestructive Methods.* (1) *Gamma-ray Counting.* Gamma-ray counting [1] provides a nondestructive means for the measurement of the uranium concentration in U^{235}–aluminum alloys. It has been used as a fast, accurate method of monitoring the production of cast reactor slugs for inventory and control purposes. The gamma radiation from U^{235} and U^{234} is measured with a scintillation counter consisting of a NaI(Tl) crystal mounted on a photomultiplier tube. The counts are accumulated at the rate of 10^5 to 10^6 counts/min on a scaler. The counting rate varies linearly over the range of 4.0 per cent to 7.6 per cent U^{235}, with a measurement precision at the 95 per cent confidence level of ± 0.5 per cent. When the alloy contains appreciable amounts of U^{238}, the beta radiation from U^{238} decay products is filtered out with aluminum foils.

(2) *X-ray Absorption.* X-ray densitometry [2] has been applied to the quantitative determination of uranium in uranium dioxide–aluminum and uranium–aluminum fuel elements. This nondestructive method is based upon the densitometric measurement of the attenuation of X rays by the fuel plate as recorded on a radiographic film. The density of the film is scanned and recorded, and the composition of the plate is read from a plot of density vs. weight of uranium per square inch. It is necessary to expose a standard sample on each film. The method has been used for aluminum-clad plates of uranium dioxide–aluminum in the range of 10 per cent to 55 per cent uranium dioxide and for uranium–aluminum alloys in the range of 5 to 30 per cent uranium. Since fuel elements are very often radiographed for other purposes, this method for quantitatively determining the uniformity and homogeneity of flat-plate elements can be economically adapted to production inspection.

(3) *Gamma-ray Absorption.* A nondestructive gamma-ray transmission method has been described for measuring the uranium content of uranium–aluminum alloy plates.[3] The attenuation of gamma radiation is nearly a linear function of the uranium content over the range of 0.085 to 0.115 g of uranium per square centimeter. The average uranium content is measured over an area of 0.72 cm^2 to an accuracy of ± 0.0006 g per square centimeter in less than 1 sec. Variations in thickness and homogeneity of the fuel throughout the plate can be determined.

The instrument developed to measure the uranium content of plates 0.080 in. thick clad on both sides with 0.030 in. of aluminum can be adapted to other thicknesses. The gamma radiation from a 0.15-curie Am^{241} source contained in an aluminum capsule with a thin window (0.010 in. thick) is collimated by a lead plate with a 0.360-in. aperture.

The gamma radiation transmitted through the uranium–aluminum alloy enters a thallium-activated sodium iodide crystal 2 mm thick. The produced light pulses are detected and integrated by a converted 6292 photomultiplier whose d-c output current is measured with a micromicroammeter. The uranium content is read from a plot of d-c current reading vs. uranium concentration in grams per square centimeter.

(4) *Mass Density.* A rapid nondestructive mass-density method has been applied to the determination of the composition of uranium–aluminum alloys.[4] The wide difference in atomic mass between aluminum and uranium makes possible a precise and sensitive means of analysis. A simple hydrostatic method of density measurement is used in which the volume of the sample is determined by the loss in weight in distilled water. The relation of the weight fraction of uranium to the measured density in the two-phase system of aluminum and UAl_4 compound in the range of 0 to 68.8 wt. % uranium is represented by the equation

$$\text{Wt. fraction of U} = 1.2408 - \frac{3.3502}{\text{density of alloy}}$$

The equation was derived for natural uranium using 2.7000 g/cm^3 as the density of aluminum and 6.062 g/cm^3 as the density of UAl_4. Factors that can influence a density–composition correlation, such as porosity or internal voids, U^{235} enrichment, the presence of UAl_3 as a nonequilibrium phase, the presence of uranium carbide, and variations in composition and density of aluminum and UAl_4 compound, were found to have negligible effect with the alloys studied. Over the range of particular interest, 7 to 21 wt. % uranium, the reproducibility of the density values corresponds to an uncertainty of ± 0.03 wt. % uranium. For any particular alloy system, good correlation between the calculated composition and chemical analysis is ample evidence that the correct parameters have been selected. It may be necessary to experimentally determine the densities of the alloy components (e.g., the density of aluminum is quite variable from a value of 2.7000 g/cm^3 for high-purity wrought aluminum to as high as 2.7100 g/cm^3 for 2S aluminum), and it is necessary for accurate analysis that the density of the aluminum melting stock be known fairly closely. An alternative method is to calibrate the plot of weight per cent uranium vs. density by wet chemical analysis of the entire density specimen for several uranium compositions in the range of interest.

This simple mass-density technique can be used to determine the total uranium loading in finished aluminum-clad uranium–aluminum alloy fuel plates, tubes, and rods. It has been applied to the evalua-

tion of uniformity of uranium composition in aluminum-clad coextruded uranium–aluminum alloy tubes.[17]

(b) *X-ray Emission Spectrographic Method.* (1) *Solid Sample.* X-ray spectrography with a solid sample is a rapid and accurate means for determining the composition of uranium–aluminum alloys.[5] The interference of impurities is negligible, and the matrix attenuation is small. A flat polished section of the alloy is irradiated with polychromatic X rays, and the intensity of the re-emitted fluorescent X-ray characteristic of uranium is measured. Since only atoms near the surface of the sample are excited, this method does not determine the average composition throughout a specimen unless the alloy is homogeneous.. The procedure can be used to advantage in ascertaining the degree of homogeneity achieved in cast ingots by comparing the X-ray fluorescence of sliced wafers taken from a number of planes throughout the ingot. Drillings, turnings, and milling chips can also be analyzed by pressing them into briquettes under very high pressures.

The accuracy of the X-ray spectrographic method is a function of the quality of the standards used for calibration and the reproducibility of the sample preparation. In general, the precision is comparable to that with wet chemical methods and is dependent upon the counting statistics. The counting precision at the 95 per cent confidence limit is ± 0.62 per cent for 100,000 counts and 0.28 per cent for 500,000 counts. In the range of a few per cent of uranium and higher, 100,000 counts can be accumulated in a few minutes with a tungsten 50-kvp 40-ma excitation source. The minimum amount of uranium measured is 0.05 wt. % with the range calibrated to 20 wt. %. The following equation provides a convenient calculation of the counting time required for any desired precision

$$T_A = \frac{640R}{S^2U^2A^2}$$

where T_A = time in minutes for A per cent relative precision at the 95 per cent confidence level

R = count rate in counts per second

S = sensitivity, $\frac{dR}{dU}$ at value of uranium

U = uranium content in weight per cent

Procedure: Uranium. The uranium–aluminum alloy in the form of an ingot or rod is sliced with a silicon carbide wheel. The surface of interest is ground flat and smooth with 180-grit silicon carbide paper and is then polished with 500-grit paper. This operation requires only a few minutes and produces a surface that will give reproducible fluorescence intensities independent of sample orientation in the plane of its surface. The specimen is mounted and excited with polychromatic X

rays through a 9/16-in. aperture. The fluorescence uranium $L\alpha_1$ intensity is measured with a scintillation counter. The per cent of uranium is read from a standard curve plotting count rate per second vs. weight per cent uranium. The curve is calibrated with chemically analyzed homogeneous uranium–aluminum alloys.

(2) *Solution Sample.* The principal disadvantage of X-ray fluorescence analysis with a solid sample is the need to prepare metal alloy standards of known composition. This is usually justified only when a large number of analyses are required on alloys varying over a small range. Another inherent disadvantage is that only the composition in a small area near the surface is determined. These difficulties can be alleviated by use of the solution technique.

Bauman, Zopatti, and Read [6] have described a rapid X-ray fluorescence solution method for the analysis of uranium–aluminum alloys. Careful control of the acid concentration eliminates the need for an internal standard or background correction. Therefore the time of analysis is considerably shortened since readings at only one goniometer setting are taken for each solution. The method is very flexible and can be applied to the analysis of a few samples of completely unknown uranium content or to control work on a routine basis where 60 analyses per 8 hr may be performed with an accuracy of ±1 per cent.

Procedure: Uranium. A 1.0000-g sample of uranium–aluminum alloy is dissolved by warming it with 50 ml of (1+4) fluoboric acid. When solution is near completion, 10 ml of (1+1) nitric acid is added, and the warming is continued until a complete, clear solution is obtained. The solution is transferred to a 100-ml volumetric flask and diluted to volume with water. This solution contains 1 g of alloy, 10 ml of fluoboric acid, and 5 ml of nitric acid in a volume of 100 ml. It is important to maintain this ratio of concentration of sample size and final volume of solution. A portion of the sample solution is transferred to a Teflon cup fitted with a bottom window of 0.00025-in. Mylar film. The solution is irradiated with X rays from a tungsten 50-kvp 40-ma excitation source with the goniometer set at the $UL\alpha_1$ peak, which has a Bragg angle of approximately 26.13° for a lithium fluoride crystal. The re-emitted X rays are detected with a scintillation counter, and the scaler measures the elapsed time for recording a predetermined number of counts. The per cent of uranium is read from a standard curve plotting counts per second vs. weight of uranium.

The standard curve plotting counts per second vs. weight of uranium is obtained by analysis of standard solutions. The standard solutions are prepared to contain 1.0000 g of metal by diluting carefully measured volumes of uranium and aluminum stock solutions to 100 ml with water. When the total weight of metal is exactly 1.0000 g, each 100-ml standard will contain 10 ml of fluoboric acid and 5 ml of nitric acid. This ratio and concentration must be carefully controlled. The aluminum stock solution is prepared by warming 20.0000 g of 99.99 per cent pure aluminum with 800 ml of (1+3) fluoboric acid. When the reaction

ceases, 100 ml of nitric acid is added, and the mixture is warmed to give complete solution. This solution is diluted to volume with water in a 1-liter flask. The uranium stock solution is prepared by dissolving 5.895 g of U_3O_8 (5.000 g of uranium) with 200 ml of (1+3) fluoboric acid and 50 ml of (1+1) nitric acid. The mixture is warmed gently until solution is complete. The solution is diluted with water to 1 liter in a volumetric flask. Both stock solutions will contain 10 ml of fluoboric acid and 5 ml nitric acid per gram of metal.

Standard solutions of normal uranium can be used for the analysis of enriched uranium by the use of a small negative correction:

$$\text{Per cent correction} = 0.01268 \times \text{per cent enrichment}$$

In practice a ±4 per cent change in sample weight causes no change in the signal from a given weight of uranium. In this case the weight of uranium is read from the standard curve, and the per cent composition is calculated.

It is necessary to run a set of standard solutions interspersed with each set of samples.

(c) *Gravimetric Methods.* Mechelynck[7] has described a gravimetric method for the determination of uranium and aluminum in alloys containing about 20 per cent uranium. Aluminum is precipitated from a hydrochloric acid solution of the alloy by the slow addition of a saturated ammonium carbonate solution to the color change of bromothymol blue. The uranium remains in solution as the carbonate complex. The aluminum hydroxide is separated, dissolved in hydrochloric acid, and reprecipitated with ammonium carbonate. The precipitate is washed, dried, and ignited to aluminum oxide at 1100°C. The combined filtrates are made acid and boiled to eliminate carbon dioxide. The uranium can either be precipitated with ammonia and ignited to U_3O_8 at 900°C or determined volumetrically by a redox titration.

(d) *Volumetric Methods.* (1) *Direct Ceric Titration, Indicator.* Bacon and Milner[18] have investigated the determination of uranium in uranium–aluminum alloy by the lead reductor–direct ceric titration procedure in the presence of phosphate using ferroin to indicate the end point. Stability studies of standard 0.02*N* ceric sulfate solutions indicated an average decrease in strength of 0.03 per cent per day. Temperature corrections may be as high as 0.03 per cent for a 1°C difference in the temperature of stock solutions. Primary standard potassium dichromate is preferred to arsenious oxide for determining the normality of the ceric solution. Experiments in which the reduced uranium from the lead column was collected directly under potassium dichromate or ceric ion solution gave values for uranium that were 1 per cent higher than theoretically expected. This indicates a small amount of U(III) is formed. However, values agreed with theory when the solution was titrated immediately in an air-filled receiving flask or after being transferred to another flask. By

careful standardization of the volumetric apparatus and of the ceric solution, they achieved a precision and accuracy of ±0.02 per cent uranium at the 20 per cent uranium level.

(2) *Ceric–Ferrous Titration, Indicator, and Back-titration.* The Argonne Low Power Reactor (ALPR) fuel is an aluminum alloy nominally containing 17.5 per cent uranium, 2.0 per cent nickel, and 0.5 per cent iron clad with aluminum. The ALPR alloy is completely dissolved in hydrochloric acid to give a green solution. The alloy can be dissolved to give a yellow solution of hexavalent uranium by the addition of nitric acid. However, it is necessary to remove nitric acid by fuming with sulfuric or perchloric acid. Uranium can be oxidized by the addition of hydrogen peroxide or bromine[19] to the hydrochloric acid solution of the uranium–aluminum alloy. However, bromine should be used with caution since ceric ion will react to some extent with bromide ion to give bromine. It may be necessary to add ceric ion and boil the solution before reduction to remove any bromine formed.

Uranium is determined volumetrically by reducing the uranium with metallic lead, adding an excess of ceric sulfate, and back-titrating with ferrous sulfate. Mechelynck and DeConde[20] likewise obtained a green tetravalent uranium solution upon dissolving a uranium–aluminum alloy with dilute sulfuric acid. By heating this solution in contact with an aluminum plate, they achieved quantitative reduction to tetravalent uranium. Although U(IV) can be titrated directly with ceric sulfate at room temperature in the presence of ferric sulfate or phosphoric acid,[21] the back-titration end point is sharper and easier to see. The possibility of overrunning the end point with subsequent loss of the sample is also eliminated.

Procedure: Uranium. The uranium–aluminum alloy is dissolved with hydrochloric acid using 10 ml per gram of sample. Water is added to control the rate of reaction. After the reaction has subsided, the beaker is heated for 30 min to ensure complete solution. The solution, which should be a clear green color with no residue, is diluted to a known volume with 3*N* hydrochloric acid. An aliquot containing about 125 mg of uranium is passed through a lead reductor. The column is washed with 0.8*N* hydrochloric acid. Twenty-five milliliters of 12*N* sulfuric acid and 3 drops of 0.025*M* ferroin are added to the combined eluates. An excess of standard 0.05*N* ceric sulfate is added from a weight buret, and the excess is back-titrated with standard 0.025*N* ferrous sulfate added from a weight buret. The uranium value is corrected for the iron by multiplying the per cent of iron by 2.13 and subtracting the product from the per cent of uranium as calculated from the titration.

If the alloy does not dissolve completely, e.g., if the alloy contains uranium oxide insoluble in hydrochloric acid, then nitric acid may be added and the mixture heated to completely dissolve the uranium. Nitric acid must be removed from the aliquot taken for uranium analysis by fuming with perchloric or sulfuric acid.

(3) *Potentiometric Titration, Platinum–Calomel Electrodes* [*See Chap. 15, Sec. 15–3.2(a)*]. The usual volumetric methods for the determination of uranium by titration with ceric sulfate or potassium dichromate require either a prior removal of impurity iron by mercury-cathode electrolysis followed by evaporation or the application of a correction for the iron present as determined by spectrophotometric analysis. Since iron is not an interference in the ferric solution titration of U(IV), considerable savings in time are possible particularly for the analysis of large numbers of samples by potentiometric titration with ferric iron.

The potentiometric–ferric sulfate titration is the standard method at Oak Ridge National Laboratory (ORNL) for determining the uranium content of uranium–aluminum alloys. A 7.5 per cent sulfuric acid solution of the alloy containing 25 to 35 mg of uranium is treated with Cr(II) to reduce the uranium to U(III, IV). The excess Cr(II) and U(III, IV) are titrated by manually operated potentiometric titration [13] with 0.1*N* ferric sulfate or by an automatic potentiometric titrator.[14] A platinum or gold indicator electrode and a saturated calomel reference electrode are used. The first end point, as indicated by a large shift in potential, is reached when all U(III) and Cr(II) has been oxidized to U(IV) and Cr(III). The second end point is indicated by a second large shift in the potential when all the U(IV) is oxidized to U(VI). The uranium content is calculated from the amount of ferric sulfate solution added between the potential shifts.

There is no interference from iron, chromium, nickel, cadmium, manganese, or aluminum. Cations of molybdenum, vanadium, tungsten, copper, and tin and the anions nitrate, fluoride, and phosphate interfere. The interference of vanadium is stoichiometric and may be corrected for by a separate determination of this element. Titanium introduces a third end point, but no error results if it is also detected. Small amounts of copper can be removed from the solution by placing a strip of cadmium metal in the solution and stirring the solution for 1 hr. The relative standard deviation using the automatic potentiometric titrator has been reported as 0.1 per cent.[22]

(4) *Potentiometric Titration, Polarized Platinum Electrodes* [*See Chap. 15, Sec. 15–3.2(a)*]. Sewalk and Goward [15] obtained a threefold increase in end-point sensitivity and more adequate prior warning of approaching end point by the use of platinum polarized electrodes in the ferric chloride potentiometric titration of uranium. The electrode assembly consists of a bubbler tube, a thermometer, and two platinum electrodes made by sealing 30-gauge platinum wire into 6-mm-ID soft-glass tubing with about 6 mm of platinum wire extending beyond the glass seal. The electrodes are polarized with 0.75 μa of current by

means of a 45-volt battery and a series 60-megohm carbon resistor. The electrode potential is measured with a vacuum-tube millivoltmeter. When applied to the analysis of uranium–aluminum alloys in the range of 5 to 40 per cent uranium, the coefficient of variation is 0.2 per cent. As with other titrations with ferric ion, impurity iron in the sample does not interfere.

Procedure: Uranium. A sample of uranium–aluminum alloy containing 0.1 to 0.3 g of uranium is dissolved by heating with a mixture of 15 ml of hydrochloric acid and 150 ml of water. When reaction has ceased, 1 ml of 30 per cent hydrogen peroxide is added, and heating is continued until the solution clears. The solution is cooled and passed through a Jones reductor to reduce the uranium. The reduced solution is aerated for 8 min. The flask is transferred to a combination hot plate and magnetic stirrer. Nitrogen is passed through the solution, and the temperature is raised to 90°C±1.0°C. The electrodes are polarized and connected to the voltmeter. With nitrogen still flowing, standard 0.05*N* ferric chloride solution is added from a buret. After an initial emf drop of approximately 100 mv, the voltage will remain relatively constant up to the end point, where an emf change of 180 mv will occur. During the titration the potentiometer will deflect with the addition of ferric chloride, the amount of deflection depending upon the nearness to the end point and the largest deflection occurring immediately before the end point.

(5) *Complexometric Titration.* An EDTA titration has been applied to the analysis of thorium and aluminum in binary alloys containing up to 80 per cent aluminum.[16] Thorium is separated by extraction into mesityl oxide and determined by titration with EDTA. Aluminum is precipitated with benzoate, dissolved, and titrated with EDTA.

Procedure: Thorium. The alloy is dissolved in hydrochloric acid with a trace of fluoride ion, and the solution is fumed with perchloric acid. The thorium is extracted into mesityl oxide from 10 per cent nitric acid solution salted with calcium nitrate. The thorium is back-extracted into water, and ammonium hydroxide is added until the solution is pink to Alizarin red S. Standard 0.02*M* EDTA solution is added until the pink color begins to fade. The pH is adjusted to 3.0, and the titration is continued to the color change of methylene blue from purple to green. Thorium is calculated from the expression

$$1 \text{ ml } 0.02M \text{ EDTA} \equiv 4.643 \text{ mg of thorium}$$

Procedure: Aluminum. Aluminum is precipitated from the aqueous layer as aluminum benzoate. The aqueous layer is diluted to about 200 ml with water and heated to 80°C. One milliliter of thioglycollic acid and 15 ml of a solution containing 3 g of ammonium benzoate, 2 g of ammonium acetate, and 1 g of ammonium chloride are added. Any precipitate of aluminum benzoate is redissolved by adding (1+1) hydrochloric acid. Ammonium hydroxide (1+4) is added to the hot solution until a permanent precipitate is just formed. The solution is boiled for

about 2 min, and the pH adjusted to about 4. Boiling is continued for 2 min, and the precipitate is allowed to digest warm for 30 min. The precipitate is filtered, transferred to a clean beaker, and dissolved with 20 ml of hot (1+1) hydrochloric acid. A 10 per cent excess of a standard 0.1*M* EDTA solution is added, and the solution is made just alkaline to methyl red. The solution is boiled for 2 min and cooled, and then 3 g of ammonium acetate is added. The pH should be 6.5. The excess EDTA is titrated with standard 0.1*M* ferric chloride to the brown-color end point of salicylic acid. The aluminum is calculated from the expression

1 ml of 0.1*M* EDTA≡2.697 m. of aluminum

(6) *EDTA Titration.* Aluminum in uranium–aluminum alloys can be accurately determined by an EDTA titration following the separation of uranium by adsorption on an ion-exchange resin.[11] A solution of the alloy in (2+1) hydrochloric acid with iron and uranium in their highest valence states is passed through a column of strongly basic anion-exchange resin (De-Acidite FF or Dowex-1). An excess of 0.1*M* EDTA solution is added, and the pH is adjusted to between 3.0 and 3.2. The solution is boiled for 5 min, cooled, and buffered with acetate. The excess EDTA is titrated with 0.05*M* zinc chloride until the dithizone indicator changes from green to red. An alternative EDTA titration method applicable after separation of the uranium is described by Milner and Woodhead.[23] Aluminum is reacted with an excess of EDTA, and the excess is titrated with ferric chloride using salicylic acid to indicate the end point.

(e) *Spectrophotometric Methods.* (1) *Aluminum with Aluminon.* Horton and Thomason [9] have described an ion-exchange spectrophotometric determination of aluminum that is applicable to uranium–aluminum alloys. The uranium is adsorbed from 9*M* hydrochloric acid along with nearly all interfering ions. Aluminum is determined with aluminon in the presence of pyridine used as a masking agent for nickel. The absorbance is measured at 525 mμ with a relative standard deviation of 1.5 per cent in the range of 5 to 50 μg of aluminum.

(2) *Nickel with Dimethylglyoxime.* Nickel in the ALPR is determined either spectrophotometrically or gravimetrically using dimethylglyoxime. The colorimetric method is recommended when the nickel is less than 1 per cent.

Procedure: Nickel. An aliquot of the sample solution from Sec. 5–1.1(d)(2) containing 50 to 120 μg of nickel is transferred to a 25-ml volumetric flask. One-half milliliter of a potassium citrate solution containing 0.5 g of potassium citrate per milliliter (citric acid or sodium citrate can be used) and 0.5 ml of saturated bromine water are added. The solution is cooled and made ammonical by the addition of approximately 3 ml of ammonium hydroxide. The heat of the neutralization reaction should not raise the temperature of the solution above room temperature. One-half milliliter of 1 per cent dimethylglyoxime in ethyl

alcohol is added, and the solution is diluted to volume with water. The absorbance is measured at 520 mμ within 5 min against a reference of water.

The gravimetric determination of nickel with dimethylglyoxime as described in standard texts can be used if the analyst so desires or if equipment is not available for the spectrophotometric determination.

(3) *Iron with 1,10-Phenanthroline.* Iron in the ALPR is determined spectrophotometrically as the ferrous 1,10-phenanthroline complex.

Procedure: Iron. An aliquot of the sample solution from Sec. 5–1.1(d)(2) containing 20 to 85 μg of iron is transferred to a 25-ml volumetric flask. Four milliliters of 10 percent hydroxylamine hydrochloride is added, and the solution is heated in a boiling-water bath for 5 min to ensure complete reduction of ferric ion to ferrous ion. The solution is cooled, and 5 ml of 0.25 per cent 1,10-phenanthroline is added. Ammonium hydroxide is added dropwise until the solution is slightly ammonical. Visual indication is noted by the appearance of aluminum hydroxide. Then 0.5 ml of acetic acid is added, the clear solution is diluted to volume with water, and the absorbance is measured at 510 mμ against a reference of water. Nickel does not interfere provided a rather large excess of 1,10-phenanthroline is used. The method has been tested with ratios of nickel to iron as high as 10 to 1.

5–1.2 Zirconium Alloys

Although aluminum is extensively used as a cladding material and in alloys with uranium for fuel-element production, it has definite limitations of corrosion resistance and thermal stability. With the advent of high-temperature and boiling-water reactors for ship propulsion and electrical power, production of zirconium has played an important role in reactor design as a fuel alloy, as cladding, and as a material of construction. Zirconium is easily fabricated and has the desirable properties of low thermal-neutron cross section, high corrosion resistance in water, and high thermal stability.

(a) *Uranium–Zirconium Alloys.* Numerous methods and techniques have been utilized for the analysis of uranium–zirconium alloys, X-ray emission spectrometry has been applied to the estimation of uranium in these alloys.[24, 25] Nondestructive methods for U^{235} in zirconium-base alloys have been developed to measure the homogeneity and total fuel loading of fuel ingots or plates.[26–28] Gravimetric methods for the determination of zirconium and uranium are accurate but rather time consuming.[29] Zirconium can be determined by ethylenediaminetetraacetic acid (EDTA) titration after a prior separation from uranium [30, 31] or by direct EDTA titration using a photometric end point detection.[32] Electrometric procedures have been proposed for the polarographic determination of uranium [33, 34] and the amperometric titration of zirconium.[34]

The analyst should be aware of the possible hazards in dissolving uranium–zirconium alloys with nitric acid. Explosions have occurred during the pickling or etching of such alloys.[35, 36] The explosions seem to be associated with the presence of a fairly heavy dark-colored oxide coating.[35] The addition of F^- to the HNO_3 eliminates the explosion hazard in pickling, etching, and dissolution of these alloys.[37] For the dissolution of low-zirconium alloys, a minimum mole ratio of F^- to zirconium of 4 is required to prevent the formation of a surface coating.

(1) *X-ray Emission Spectrometry: Uranium.* An X-ray emission procedure has been applied to the determination of uranium in zirconium-base fuel alloys as a rapid production-control method.[24] The analysis is performed on the flat surface of metal strip samples prepared by end-milling or shaper-machining to a 32-μin. finish, with deviation from flatness of less than 0.002 in. The uranium $L\alpha_1$ intensity to background ratio is recorded by a two-channel detector system. The concentration of the uranium is read from an analytical curve showing intensity ratio vs. per cent of uranium. Over the concentration range of 3.00 to 7.00 per cent uranium, the accuracy is ± 1 per cent of the amount present.

Powell and Taylor [25] have evaluated the use of a single-channel detector for X-ray fluorescence spectrometric determination of uranium in Zircaloy-2 fuel alloys. By careful control of instrumental and sample-preparation errors, the method can be as precise and accurate as wet chemical methods.

(2) *Gamma-ray Emission: U^{235}.* Accurate, rapid nondestructive autoradiometric methods that reduce cost and time of analysis have been developed to replace chemical and X-ray fluorescence procedures for determining uranium in zirconium-base alloys.[26] The methods are based upon the measurement of the total gamma radiation from U^{235}. By one method the homogeneity of a fuel ingot is measured, and the total uranium loading can be calculated. Another method determines directly the total uranium content of the fuel alloy. The accuracy is equivalent to that of the X-ray emission method at a cost savings of 50 per cent.

Judd and Leboeuf [27] developed a rapid monitoring system for production control of rod type uranium–zirconium fuel elements clad with Zircaloy. A gamma pulse spectrometer records only the gamma radiation of U^{235} above 130 kev. The scanning time is ~ 5 min per fuel element. The response is linear up to better than 12 per cent of uranium. The homogeneity of 1 in. segments can be determined with a relative standard deviation of about ± 1 per cent. The total uranium can be measured at the same time with a relative standard deviation of about ± 0.6 per cent.

Detection of the U^{235} 0.184-Mev gamma photon has been used in a nondestructive determination of the uranium distribution and total fuel load in UO_2–Zircaloy fuel plates.[28] The gamma photon is detected by a NaI(Tl) crystal, photomultiplier, amplifier, and a single-channel differential pulse-height analyzer. The horizontal homogeneity can be determined with a precision of ± 5 per cent and the total uranium with a precision of ± 1 per cent both at the 90 per cent confidence limit. The method is generally applicable to enriched fuel plates with cores less than about 0.2 in. thick.

(3) *Gravimetric Method for Zirconium.* Milner and Skewies[29] describe a long tedious gravimetric method for the determination of uranium and zirconium in binary alloys containing up to 25 per cent of zirconium with an error less than ± 1 per cent of the zirconium present. Zirconium is separated by cupferron–$CHCl_3$ extraction, ignited to ZrO_2, dissolved, precipitated as the mandelate, and finally ignited and weighed as ZrO_2. Uranium is precipitated with tannin from the cupferron solution, ignited to U_3O_8, dissolved, precipitated with NH_4OH, and ignited and weighed as U_3O_8.

Uranium–zirconium alloys can be analyzed for zirconium by precipitation of the zirconium with cupferron and ignition to ZrO_2. However, a double precipitation is necessary, and other elements precipitated by cupferron, such as iron, molybdenum, and uranium (IV), will interfere. Mandelic acid is a satisfactory reagent for the precipitation of zirconium in the presence of a large number of elements.[38] However, the halogen derivatives are superior reagents in many respects.[39] The method of Klingenberg and Pappucci[39] for the precipitation of zirconium with *p*-bromo (or *p*-chloro) mandelic acid has been applied to the determination of zirconium in uranium–zirconium alloys. Only a single precipitation is required for quantitative separation, and such elements as manganese, chromium, nickel, molybdenum, and iron do not interfere.

Procedure: Zirconium. A sample of the uranium–zirconium alloy containing about 100 mg of zirconium is distintegrated with 10 ml of HCl per gram of zirconium. Then 1 to 2 ml of HNO_3 is added to oxidize and dissolve the uranium. Five milliliters of H_2SO_4 is added, and the mixture is heated to complete solution. The solution is fumed until no more fumes of SO_3 are evolved. The beaker and walls are flamed with a Meker burner to ensure complete removal of excess H_2SO_4. The cooled residue is drenched with 10 ml of HCl and warmed to complete solution. The solution is diluted to about 75 ml, and 25 ml of 0.1*M* *p*-bromo- (or *p*-chloro) mandelic acid is added slowly with constant stirring. The precipitate is digested for 20 min at 80 to 85°C, and the solution is cooled and allowed to stand for several hours or overnight. The solution is filtered after the addition of filter pulp through Whatman No. 40 paper. The precipitate is washed with 1 per cent HCl containing 5 ml of 0.1*M* *p*-bromomandelic acid per 100 milliliters. (The filtrate

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should be checked for complete precipitation of the zirconium by the addition of 10 ml of 4 per cent *p*-hydroxyphenylarsonic acid solution.) The paper and precipitate are charred slowly and ignited to ZrO_2 at approximately 1000°C. When the amount of zirconium is small, the zirconium *p*-bromomandelate can be weighed directly. In this case the precipitate is finally washed ten times with H_2O and twice with 95 per cent ethanol, dried for 15 min at 100°C, cooled, and weighed as zirconium tetra-*p*-bromomandelate.

(4) *Volumetric Method for Zirconium.* Zirconium in uranium–zirconium alloys can be determined by an EDTA titration after a prior separation as zirconium mandelate.[30] The method has been described for alloys containing 4 to 10 per cent zirconium[31] and is stated to have an accuracy of ±1 per cent. It can be adapted to other alloy compositions by proper selection of the sample size.

Milner and Edwards[32] applied the EDTA titration to the direct determination of zirconium in uranium–zirconium alloys by detecting the end point photometrically. The method should be ideal for routine analysis and should save considerable time. Amounts of zirconium up to 100 mg can be measured with an accuracy of ±0.6 per cent as compared to ±1.0 per cent[30] for the visual end-point detection. The zirconium in dilute H_2SO_4 is complexed with an excess of 0.02*M* EDTA. The pH is adjusted, and the excess EDTA is titrated photometrically with standard ferric-ion solution. The pH is 2.3 using potassium benzohydroxamate as an indicator at a wave length of 520 mμ. The pH is 4 using sodium salicylate as an indicator and a wave length of 480 mμ. The addition of EDTA to a zirconium solution often causes the appearance of a precipitate difficult to redissolve. It is believed to be due to some form of hydrolysis or polymerization of zirconium in a solution that has stood for some time in a weakly acid medium. If the solution of zirconium is freshly fumed with H_2SO_4, cooled, and diluted and EDTA is added immediately, no precipitation occurs.

Procedure: Zirconium After Separation. A 2.5-g sample of uranium–zirconium alloy is dissolved by treatment with 1 ml of HF. When the reaction has ceased, 20 ml of HNO_3 is added slowly. The mixture is heated and stirred until solution is complete. Twenty-five milliliters of H_2SO_4 is added, and the solution is fumed. The solution is cooled, 10 ml of H_2O and 25 ml of HCl are added, and the solution is transferred to a 250-ml volumetric flask. The solution is diluted to the mark with H_2O. An aliquot containing 50 to 100 mg of zirconium is evaporated to fumes on a hot plate and heated until SO_3 ceases to be evolved. Twenty milliliters of HCl is added to the cooled residue, and the mixture is heated until the solution is clear. Twenty-five milliliters of H_2O is added, and the solution is heated to almost boiling. While stirring the solution, add 50 ml of a hot 16 per cent mandelic acid solution.[30] The temperature is maintained at 85°C for 90 min. The precipitate

of zirconium mandelate is filtered off and washed three times with 5 per cent mandelic acid–(1+50) HCl solution. The precipitate is washed back into the original beaker with H_2O. The paper is washed with 25 ml of hot (1+3) H_2SO_4 and finally with H_2O. The solution is boiled until the precipitate dissolves. The cooled solution is diluted to 250 ml with H_2O in a volumetric flask. An aliquot containing 13 to 36 mg of zirconium is taken, and 10 ml of 10 per cent ammonium tartrate solution and 10 ml of 0.05*M* EDTA solution are added.[40] The pH is adjusted to 2.0 with NH_4OH or $HClO_4$, and the solution is boiled for about 5 min. The solution is cooled and diluted to 100 ml, and the pH is adjusted to 2.0. The excess EDTA is titrated with 0.05*M* bismuth nitrate to the red end point of xylenol orange.

(5) *Volumetric Method for Uranium.* Zirconium does not interfere in the volumetric determination of uranium by reduction with a Jones or lead reductor and redox titration; however, if phosphoric acid is used in the titration, the precipitated zirconium phosphate masks the color of the indicator and overshooting of the end point takes place. Such elements as iron, titanium, molybdenum, ruthenium, and vanadium and the anions F^- and NO_3^- will interfere. Tungstate ion is also an interference; however, Dufour and Articolo [41] found that the presence of up to 5000 μg of tungsten in uranium-zirconium, or Zircaloy has no significant effect upon the Jones reductor–potassium dichromate method for uranium, provided the sample is fumed with H_2SO_4 prior to reduction to convert tungsten to nonionic tungstic acid.

In the case of Zircaloy–highly enriched U^{235} alloys, it has been found advantageous to remove the zirconium and other interfering elements prior to the uranium determinaton. A cupferron–chloroform extraction using solid cupferron is used. The coefficient of variation of a single determination is about 0.05 per cent.

Procedure: Uranium, No Separation. A sample containing 0.2 to 0.3 g of uranium is dissolved by treating it with 100 ml of aqua regia and 5 ml of H_2SO_4. When the initial reaction subsides, the mixture is heated and evaporated to fumes of SO_3 until the sample is completely dissolved. With alloys high in zirconium, it may be necessary to use a little HF to effect complete solution. The solution is fumed twice to completely eliminate NO_3^-, and the uranium is determined volumetrically using a lead reductor.

Procedure: Uranium, After Separation. A weighed sample of the alloy estimated to contain 1 to 1.5 g of uranium is treated in a platinum dish with 25 ml of water and 1 ml of HF for each 0.5 g of sample. After the reaction has subsided, 1 ml of 30 per cent hydrogen peroxide and 20 ml of (1+1) sulfuric acid are added. The solution is heated to fumes of SO_3 and cooled; after the sides of the dish have been washed down the dish is again heated to fumes. When the dish has cooled, the solids are dissolved in water, and the solution is made up to 500 ml in a volumetric flask. A 100-ml aliquot is treated with H_2S and allowed to stand

overnight in a closed flask. The solution is filtered, and the filter paper is washed with 2 per cent sulfuric acid (v/v) saturated with H_2S. The solution is evaporated to 90 ml, and 2 per cent potassium permanganate is added until the solution is pink. After it has been cooled to 5°C, the solution is transferred quantitatively to a 250-ml separatory funnel. Fifteen grams of solid cupferron is added, and the separatory funnel is shaken and then allowed to stand for 5 min. Twenty-five milliliters of chloroform, cooled to 5°C, is added, and the separatory funnel is vigorously shaken. The mixture is allowed to stand until the separation into layers is complete. The chloroform is drawn off into a second separatory funnel for further treatment.

Five milliliters of a 6 per cent cupferron solution and chloroform, cooled to 5°C, is added, and the funnel is shaken and separated as above. The extraction is repeated until the chloroform extract is clear. The combined chloroform layers are washed with 50 ml of (1+9) sulfuric acid cooled to 5°C; the washing is added to the aqueous extract.

After the solution has been evaporated to fumes and cooled, the sides of the beaker are washed with at least 15 ml of water, and 1 ml of $HClO_4$ is added. After being evaporated and fumed four times, the solution is run through a Jones reductor and aerated. Twenty milliliters of a 4 per cent ferric chloride solution is added, and 8 drops of a diphenylamine sulfonate indicator are added. The solution is then titrated with 0.027*N* potassium dichromate solution.

(6) *Electrometric Methods.* Elving and Olson [34] have reported the analysis of uranium–zirconium mixtures by a direct polarographic determination of the uranium and an amperometric titration of the zirconium.[42] The interferences in the titration of the zirconium are Fe(III), V(V), Sn(IV), Ti(IV), Hf(IV), and Nb(V). Any ion that is reduced in H_2SO_4 solution in the potential region of about -0.1 to -0.4 volt vs. S.C.E. would interfere in the polarographic determination of uranium. Within the range of 0.03 to 0.075 millimole of zirconium (2.7 to 6.9 mg of zirconium) and 0.04 to 0.08 millimole of uranium (9.5 to 19.0 mg of uranium), the errors are ± 0.6 per cent for zirconium and ± 1.1 per cent for uranium. The ranges can probably be safely extended by a factor of 10 from either end.

Procedure: Uranium. A sulfuric acid solution of the sample containing 10 ml of H_2SO_4 is diluted in a platinum dish with 10 ml of H_2O. Dilute, $\sim 0.001N$, $KMnO_4$ solution is added to the hot sample solution until the color of permanganate persists to ensure complete oxidation of the uranium. Two milliliters of HCl is added, and the solution is heated until copious fumes of SO_3 are evolved. The sample solution is cooled and diluted to 100 ml in a volumetric flask containing 1 ml of 0.1 per cent gelatin solution. A portion of the solution is transferred to the polarographic cell, the oxygen is removed with nitrogen, and a polarogram is recorded between 0.0 and -0.5 volt vs. S.C.E. The uranium concentration is determined by comparing the uranium wave height with a standard curve.

Procedure: Zirconium.[42] An aliquot of the gelatin-containing sample solution prepared for the determination of uranium, containing 0.02 to 0.1 millimole of zirconium (1.8 to 9.1 mg), is diluted to 50 ml with

1 ml of 1 per cent gelatin solution and 10 per cent H_2SO_4. Air is removed with nitrogen. The zirconium is titrated amperometrically by the addition of 0.05*M* to 0.10*M* cupferron solution in 1-ml increments until the end point is reached; smaller increments are then added. The current is read 1 to 1.5 min after each addition at a potential of −0.84 volt vs. S.C.E. The points obtained yield two straight lines intersecting at the equivalence point when the current in microamperes is plotted against the volume of cupferron in milliliters.

(b) *Uranium–Niobium–Zirconium Alloy.* The Experimental Boiling Water Reactor fuel element is representative of this type alloy. During experimental metallurgy and testing of fuel-plate production, chemical methods were used to analyze the alloy. After the composition had been fixed at 5 per cent zirconium and 1.5 per cent niobium, a rapid direct spectrographic technique was used for analyzing the large number of samples required during the reactor assembly.[43] The quantitative spectrographic method of direct-spark excitation on the alloy surface saves considerable analysis time and is economically feasible particularly for multiple alloy systems involving many samples. The accuracy attainable is normally adequate for the metallurgists' requirements. However, the spectrographic method is limited to a rather narrow concentration range and requires careful preparation of standard alloys. The chemical methods that will be described are applicable over wide concentration ranges and will be most useful for the analysis of research and experimental alloys. They are also useful as referee methods for control of the spectrographic analysis.

A gravimetric method for the determination of zirconium and niobium in ternary alloys of uranium is based upon separating zirconium and niobium from uranium with cupferron, isolating niobium by leaching the soluble carbonate, and weighing as the ignited oxides.[44] The separation of zirconium as insoluble barium fluozirconate and weighing [45] as ZrO_2 or titrating [46] with EDTA are accurate procedures but rather time consuming. A relatively rapid and simple ion-exchange technique has been used for separation of the three alloy constituents zirconium, niobium, and uranium.[47] Niobium is determined gravimetrically with cupferron. Zirconium is determined either gravimetrically with cupferron or volumetrically with EDTA. Uranium is determined gravimetrically with NH_4OH or volumetrically by redox titration. A solvent extraction and gravimetric determination of niobium or tantalum has been described for the analysis of binary alloys with uranium or ternary alloys with uranium and zirconium.[48]

A direct differential spectrometric method for the determination of niobium and uranium has been suggested for rapid and accurate routine control analysis.[49] An absorbance measurement of the peroxy-

niobic complex [50] formed in H_2SO_4 has been used for the determination of niobium in uranium alloys including the ternary uranium–niobium–zirconium.[51]

Electrometric methods have been described for the analysis of mixtures containing uranium, niobium, and zirconium. Zirconium is titrated amperometrically; niobium and uranium are determined by polarography.[34]

(1) *Gravimetric Methods.* A long and tedious gravimetric determination of zirconium and niobium was the first method used for the analysis of the ternary uranium alloy.[44] Zirconium and niobium are separated from uranium by precipitation with cupferron. The ignited mixed oxides are fused with carbonate, and zirconium is isolated by leaching the soluble niobium from the fusion melt with water. The residue is fused with pyrosulfate and dissolved, and the zirconium is precipitated with cupferron and ignited to ZrO_2. The leach is acidified, and niobium is precipitated with cupferron from an oxalate solution. The precipitate is ignited to Nb_2O_5. Telford [45] applied the separation of zirconium as insoluble barium fluozirconate to the analysis of uranium–niobium–zirconium alloys. The precipitate is dissolved in a mixture of H_3BO_3 and HCl, and the zirconium is precipitated with cupferron and ignited to ZrO_2. Milner and Barnett [46] utilized the separation of zirconium as barium fluozirconate and determined the zirconium volumetrically with EDTA. This permitted the determination of smaller amounts of zirconium. The procedure is rather lengthy, requiring a double precipitation of barium fluozirconate, a hydroxide precipitation of the zirconium, and two fumings with $HClO_4$ prior to the EDTA titration.

A solvent extraction–gravimetric method has been proposed for the determination of niobium (or tantalum) in uranium–zirconium-base alloys.[48] The niobium is separated by solvent extraction with methyl isobutyl ketone (hexone) from a 10*M* HF, 6*M* H_2SO_4, 2.2*M* NH_4F solution. The niobium is backwashed from the organic phase with a solution of 1 part 100 vol. H_2O_2 to 20 parts H_2O. The extracts are evaporated to fumes of H_2SO_4 to remove H_2O_2 and HF. Niobium is precipitated with tannic acid from an oxalate solution acetate buffered to pH 4.5. The precipitate is ignited to 800°C and weighed as Nb_2O_5. The procedure is applicable over a wide alloy range with an average error of ± 0.5 per cent of the amount present. The ion-exchange separation of the components of the ternary uranium–niobium–zirconium alloy is based upon the selective elution of each element from an anion-exchange resin column.[47] Zirconium is not absorbed from a solution of 9*M* HCl and 4*M* HF. Niobium is eluted with a solution of 7*M* HCl and 0.2*M* HF. Uranium is recovered from the resin with 0.5*M* HCl.

Procedure. A 2-g sample is dissolved by warming with 15 ml of HNO_3 in a platinum beaker or dish. When the reaction ceases, 5 ml of H_2O and 1 ml of 48 per cent HF are added, and heating is continued until a clear solution is obtained. Alloys containing higher concentrations of niobium and zirconium may be difficult to dissolve. Dissolution is more easily accomplished by separating the undissolved residue and igniting it in a platinum crucible. The resulting oxides will dissolve upon treatment with HNO_3 and HF. Two milliliters of $HClO_4$ is added, and the solution is evaporated to fumes. The cover and sides are washed down with 10 ml of H_2O, and the fuming is repeated until fumes cease to be evolved. Fifteen milliliters of a 9*M* HCl–4*M* HF solution is added, and the mixture is heated until the solution is clear. The cooled solution is passed through a 30-ml column of Dowex-AG1 X 8 (100 to 200 mesh) anion resin equilibrated by the passage of 50 ml of 9*M* HCl–4*M* HF solution. The resin is contained in a 50-cm-long 18-mm-OD polyethylene tube with a 1-mm wall which is drawn down at one end to about 3 mm in outside diameter. The constricted end is packed with small pieces of Teflon filter mat. The column is washed with 9*M* HCl–4*M* HF solution until a total of 100 ml of eluate is collected in a 140-ml polyethylene bottle. The eluate containing only zirconium is transferred to a platinum beaker. Ten milliliters of H_2SO_4 is added, and the solution is evaporated to fumes of SO_3. The cover and sides of the beaker are washed with H_2O, and fuming is repeated to completely eliminate HF. The solution is reserved for the zirconium determination.

Niobium is recovered from the resin column by elution with 7*M* HCl–0.2*M* HF until 200 ml of eluate is collected in a polyethylene bottle. Ten milliliters of H_2SO_4 is added to the eluate containing only niobium. The solution is evaporated in a platinum beaker to fumes of SO_3. The cover and sides are washed with H_2O, and the solution fumed again. The solution is reserved for the niobium determination.

Uranium is recovered from the column by elution with 200 ml of 0.5*M* HCl. The uranium in the dilute HCl eluate can be determined by precipitating with NH_4OH and igniting to U_3O_8 at 900°C. Alternatively the uranium can be determined by the lead reductor–ceric sulfate titration.

The H_2SO_4 solutions containing zirconium or niobium are diluted to 300 ml, and the acidity is adjusted to 10 per cent H_2SO_4. The solutions are cooled in an ice bath to 5°C. Twenty milliliters of cold 6 per cent cupferron solution is slowly added with stirring to the zirconium solution, and 10 ml of 6 per cent cupferron is added to the niobium solution. A few milliliters of paper pulp is added, and the slurry is filtered with the aid of suction through Whatman No. 42 filter paper. The precipitate is washed four or five times with cold 1*N* HCl containing a few milliliters of cupferron solution. The filter paper is folded over the precipitate and gently compressed to expell as much liquid as possible from the precipitate to prevent excessive frothing during ignition. The precipitate is heated in a platinum crucible with a low flame until completely charred. Care is taken to prevent flaming. Ignition is completed over the full flame of a Meker burner or in a muffle furnace at 900°C. Zirconium is weighed as ZrO_2; niobium, as Nb_2O_5.

Alternately the zirconium in the H_2SO_4 solution prepared from the first ion-exchange eluate may be determined volumetrically by adding

an excess of EDTA and back-titrating with bismuth nitrate[31] as described in Sec. 5–1.2(a)(4).

(2) *Spectrophotometric Methods.* Banks et al.[49] have reported a differential spectrophotometric method for the determination of uranium and niobium in binary alloys. The uranium is measured by the absorbance of U(VI) in 50 per cent H_2SO_4 at 420 mμ against a uranium reference solution. The niobium is determined from the absorbance of the H_2O_2 complex in H_2SO_4 read at 360 mμ against a niobium reference solution. A correction is made for the small uranium absorbance at this wave length. It is a rapid and accurate control method for the determination of niobium and uranium in alloys in which the approximate composition of the components is known. The procedure should be applicable to the ternary alloy uranium–niobium–zirconium.

A direct spectrophotometric method for the determination of niobium in uranium alloys has been used successfully for the analysis of uranium–niobium–zirconium and uranium–tin–niobium ternary alloys.[51] The method is based upon the measurement of the complex formed with H_2O_2 in H_2SO_4. At the wave length of maximum absorbance, 360 mμ, zirconium and tin do not interfere and uranium(VI) has an absorbance minimum. The small absorbance due to uranium is corrected for by measuring against a sample solution that contains no H_2O_2. Interferences include F^-, NO_3^-, Cl^-, titanium, tantalum, molybdenum, rhenium and iron.

Procedure: Niobium. A sample containing 5.5 to 9.0 mg of niobium is treated with 30 ml of aqua regia at room temperature. After the initial reaction subsides, the mixture is heated until reaction ceases. Fifteen milliliters of H_2SO_4 is added, and the mixture is heated to fumes of SO_3. Fuming is continued until the sample is completely dissolved. Sulfuric acid lost by prolonged fuming is replaced. The cover glass and sides of the beaker are washed with H_2O, and the solution is again evaporated to fumes. Strong fuming is continued for 15 min. The solution is cooled, 10 ml of HCl is added, and the solution is fumed again for 15 min to ensure complete removal of NO_3^-. The freshly fumed sample is transferred to a 50-ml volumetric flask by washing the beaker with hot freshly fumed H_2SO_4. After the solution has cooled to room temperature, 25 ml of a solution prepared by mixing freshly fumed H_2SO_4 with 4 ml of 30 per cent H_2O_2 in a 100-ml volumetric flask is added, and the mixture diluted to 50 ml with freshly fumed H_2SO_4. Care should be taken to guard against any sudden pressure increases during mixing due to H_2O_2 decomposition. Excessive bubble formation is indicative of the presence of NO_3^- or impurities, which catalyze the decomposition of H_2O_2. The absorbance is measured at 360 mμ in 1-cm silica cells against an unperoxidized sample of the same weight as the unknown. If the sample is measured against a reference solution of H_2O_2–H_2SO_4, then the absorbance is

corrected for the uranium in the sample by subtracting 0.000143 × milligrams of uranium.

The niobium concentration is read from a standard curve showing absorbance vs. milligrams of niobium.

(3) *Electrometric Methods.* Elving and Olson [34] describe polarographic and amperometric procedures for the analysis of uranium–niobium–zirconium mixtures. Zirconium is separated by precipitation as the phosphate from H_2O_2–H_2SO_4 solution, and the suspended $Zr(HPO_4)_2$ is titrated amperometrically with cupferron.[42] The uranium and niobium are determined simultaneously by polarography in HCl solution. The average errors are ±1.0 per cent for uranium, ±1.0 per cent for niobium, and ±0.5 per cent for zirconium.

(c) *Zircaloys.* The Zircaloys are zirconium-base alloys containing relatively small amounts of tin, iron, chromium, and nickel. The presence of these metals significantly increases the corrosion resistance of zirconium in hot water or steam. These complex alloys have been used extensively in high-temperature pressurized-water or boiling-water nuclear reactors as a cladding, heat exchanger, or structural material. The nominal compositions of the Zircaloys are as follows: Zircaloy-1 contains 2.5 per cent tin; Zircaloy-2 contains 1.5 per cent tin, 0.12 per cent iron, 0.1 per cent chromium, and 0.05 per cent nickel; Zircaloy-3 contains 0.25 per cent tin and 0.25 per cent iron; Zircaloy-4 contains 1.5 per cent tin, 0.12 per cent iron, and 0.1 per cent chromium. Spectrographic, X-ray fluorescence, polarographic, and chemical methods have been used to determine the minor alloy constituents of the Zircaloys.

(1) *Spectrographic Methods.* A direct spectrographic [52] analysis of Zircaloy by the point-to-plane spark method has been applied to massive metal, thin-walled tubes, and rolled sheets. The method is rapid and sufficiently accurate for quality control of alloy composition. The coefficients of variation are 4 per cent for tin, chromium, and niobium and 6 per cent for iron.

(2) *X-ray Emission Spectrometry.* X-ray fluorescence methods [53] have been described for the determination of tin, iron, chromium, and nickel in Zircaloy. In one method the alloy in the form of turnings or chips is converted to oxides by heating at 1000°C for 1 hr. The oxides are ground, mixed with an equal amount of cellulose, and briquetted to a 1-in.-diameter pellet at 60,000 lb pressure. The Kα line intensities for the four elements are measured in the X-ray emission spectrograph by the fixed-count technique. In a second method, although more time is required, the sensitivity is increased twofold. The zirconium is removed by extraction with thenoyltrifluoroacetone. The alloying elements are concentrated by precipitation with NaOH in the presence of cellulose powder, dried, and briquetted. Both methods are satisfactory

for routine specification checks. The X-ray emission spectrographic procedure can be carried out in one-fourth to one-half the time required for wet chemical methods with comparable precision and accuracy.

A direct solid-sample X-ray emission spectrometric method for the determination of uranium in Zircaloy–uranium alloy has been described for the range of 3.5 to 8.5 per cent uranium.[24, 25]

(3) *Volumetric Methods: Uranium.* The chemical determination of uranium in Zircaloy requires the separation of the uranium. A solvent-extraction–volumetric method [54] has been reported for the concentration range 2 to 6 per cent uranium with a precision of ±0.5 per cent at the 95 per cent confidence level. The alloy is dissolved in HF and HNO_3. The F^- is complexed with aluminum, and the uranium is extracted with 5 per cent TBP in kerosene. The uranium is back-extracted into aqueous $(NH_4)_2CO_3$, and NO_3^- is removed by fuming with H_2SO_4. Uranium is reduced in a lead reductor and titrated with standard 0.05*N* $K_2Cr_2O_7$.

Mercury-cathode electrolysis, as used for the separation of uranium in uranium–stainless steel alloys, has been applied to uranium–Zircaloy alloys.[55] The method is relatively rapid and requires a minimum of manipulation. After separation the uranium is determined by redox titration. The precision is about ±0.1 per cent at the 6 per cent uranium level.

> *Procedure: Uranium.* A sample of uranium–Zircaloy containing 50 to 200 mg of uranium is dissolved in a minimum amount of 10 per cent HF. A few milliliters of HNO_3 is added to oxidize the uranium; then 5 ml of H_2SO_4 is added. The solution is taken to fumes three times. After cooling, 25 ml of H_2O is added, and the solution is heated to dissolve any crystallized zirconium salts. A mercury-cathode electrolysis is carried out as described in Sec. 5–1.3. Uranium is determined in the electrolyzed solution by redox titration as described in Sec. 5–1.1(d).

(4) *Volumetric Methods: Tin.* Tin in Zircaloy can be determined [56] volumetrically by reduction to metallic tin with zinc and titration with KIO_3. More commonly tin is reduced to Sn^{+2} and titrated.[57-60] Walkden reduces the tin in Zircaloy-2 with aluminum and titrates the Sn^{+2} with I_2.[61] The precision is ±0.05 per cent, with a positive bias of 0.05 per cent due to the presence of chromium. Wood and Clark [58] describe a direct reduction of tin with aluminum and titration with KIO_3 in the presence of Ti^{+3}. They applied the method over the range of 0.01 to 20 per cent tin with a standard deviation of 0.015 at the 2 per cent level. Iron or nickel up to at least 20 percent, tungsten up to 10 per cent, and copper, molybdenum, or vanadium up to 5 per cent do not interfere. Up to 0.5 per cent chromium has no effect when the

tin is less than 2 per cent, but with larger amounts of tin only 0.25 per cent chromium can be tolerated. Interference from chromium can be eliminated in some instances by aliquoting the sample to reduce the amount of chromium present or by separating the tin as the sulfide. Telford [57] prefers to reduce the tin with sodium hypophosphite.[60] Since hypophosphite cannot be used in the presence of zirconium, the tin is isolated by a sulfide precipitation.

Procedure: Tin (Aluminum Reduction). A sample of Zircaloy is dissolved in an Erlenmeyer flask by warming it gently with HCl and HBF_4. The acid concentration is adjusted to 50 per cent HCl, and 15 ml of titanous chloride solution, prepared by dissolving 5 g of titanium in 250 ml of HCl and diluting to 500 ml, is added. The Ti^{+3} eliminates interference from possible incomplete exclusion of air during titration or oxygen dissolved in the KIO_3 reagent. The solution is heated to 70°C. If niobium is present, 25 ml of 60 per cent citric acid is added. About 1 g of aluminum turnings, sheet, or foil is added, and a two-hole stopper is inserted in the flask. Carbon dioxide is now passed through the solution at the rate of 3 to 4 bubbles per second until the end of the titration. The solution is boiled gently until the aluminum has dissolved, and boiling is continued for an additional 5 min. The solution is cooled to room temperature in an ice bath. Two grams of NaI is added, and the flask is shaken to dissolve the iodide. About 5 ml of 1 per cent starch solution is added, and the Sn^{+2} is titrated with a standard solution of KIO_3 to the blue end point.

In the event a source of CO_2 is not available, the air can be removed from the flask by the addition of 10 ml of 10 per cent $NaHCO_3$ solution or a lump of dry ice along with the aluminum.[62] The flask is stoppered and connected directly by means of a delivery tube with a 10 per cent $NaHCO_3$ solution during boiling and cooling. Just before titration the stopper is removed, and a small piece of dry ice is added to prevent the admittance of air.

Procedure: Tin (Hypophosphite Reduction). The sample solution is diluted to 300 ml with a total acidity of about 2 per cent. Tin is precipitated by passing H_2S through the solution at 80°C for 30 min. The mixture is allowed to stand for 3 hr, and the precipitate is filtered off using Whatman No. 42 paper. The precipitate is dissolved on the filter paper with $(NH_4)_2S$ solution. The $(NH_4)_2SnS_3$ solution is heated to boiling to remove most of the sulfide. About 5 ml of H_2SO_4 is added, and the solution is evaporated to fumes. If sulfur is present, 1 ml of HNO_3 is added and the fuming is repeated. The $Sn(SO_4)_2$ solution is diluted to 100 ml with HCl (1+1). About 0.1 g of NaH_2PO_2 is added to 10 ml of HCl (1+1) and 1 ml of 1 per cent $Hg(CN)_2$ solution in a small beaker. The mixture is boiled for 1 min and added along with 4 g of NaH_2PO_2 to the tin solution in a flask with a three-hole stopper. Carbon dioxide is now passed through the solution at the rate of 3 to 4 bubbles per second until the titration has been completed. The solution is boiled gently for 15 min and then cooled in an ice bath to about 20°C. A diluting solution containing 10 ml of 10 per cent KI solution, 20 ml of 50 per cent citric acid solution, 5 ml of 1 per cent starch solution, and 250 ml of H_2O is boiled gently for 10 min and cooled, and 3 g of $NaHCO_3$ is

added. The diluting solution is added to the sample solution through a funnel. The Sn^{+2} is titrated with standard KIO_3 solution. Care should be taken to prevent the admittance of air to the titrating flask at all times.

(5) *Polarographic Methods: Tin.* The well-defined polarographic wave produced by Sn^{+2} ions at -0.48 volt vs. S.C.E. in $1M$ HCl has been used for the analysis of Zircaloys.[63] It is essential that tin be in the stannous state. This can be assured by dissolving the alloy with a mixture of HCl, H_2SO_4, and HBF_4 under N_2, or by treating the oxidized solution of the alloy with powdered iron. If uranium is present, HNO_3 will be required for complete solution, and the use of iron reduction will be mandatory.

A direct polarographic method for tin and lead in the range of 10 to 200 ppm has been described for the analysis of zirconium and its alloys.[64] The wave produced by Sn^{+4} and Pb^{+2} at -0.42 volt vs. S.C.E. in HCl–NH_4Cl electrolyte is measured. Lead is coprecipitated as the sulfate with $BaSO_4$, and the wave height produced by tin alone is measured. Interference from copper or molybdenum in amounts up to 1 per cent is prevented by precipitation of these elements as ferrocyanides. Impurities such as aluminum, cadmium, chromium, copper, iron, magnesium, manganese, nickel, titanium, tungsten, vanadium, and zinc do not interfere. The method should be applicable to the determination of tin in Zircaloy.

Kallmann et al.[65] used the polarographic wave of Sn^{+4} at -0.25 volt in bromide–chloride medium following the isolation of tin by steam distillation with HBr. The procedure has been applied to a wide variety of zirconium-containing materials including Zircaloy, steel, bronze, brass, and ores. The HBr distillation separates tin from most elements with the exception of arsenic and antimony. Arsenic does not interfere in concentrations up to 10 times that of tin. The effect of antimony is insignificant for concentrations up to 5 times that of tin.

Bruce and Ashley [66] developed a rapid direct polarographic method for the determination of tin in Zircaloy. The alloy is simply dissolved with HBr and F^-, and tin is measured polarographically without reduction or separation. The deleterious effect of F^- on the capillary of the dropping-mercury electrode is avoided by using less than the stoichiometric amount of HF to aid dissolution of the alloy. Alternatively HBF_4 can be used instead of HF. The precision for samples containing about 15 mg of tin is ± 0.2 mg at the 95 per cent confidence level.

Procedure: Tin. A sample of Zircaloy containing not less than 2 mg of tin is dissolved in 50 ml of warm 48 per cent HBr. One milliliter of 48 per cent HF is added per gram of zirconium, or, alternatively 1 ml of 48 per cent HBF_4 is used. After solution is complete, 25 g of KBr and

5 ml of 0.2 per cent Triton X-100 solution are added, and the mixture diluted to 200 ml. The tin is determined from the polarogram recorded between 0 and −1.0 volt vs. S.C.E.

(6) *Polarographic Methods: Niobium.* A polarographic method has been described for the determination of niobium in zirconium-base alloys.[67] The method is applicable in the range of 1 to 5 per cent niobium and has been used for the analysis of Zircaloy and the zirconium–2 per cent niobium–2.5 per cent tin alloy with a standard deviation at the 95 per cent confidence limit of ±0.044 per cent for a single measurement.

Procedure: Niobium. A 0.5-g sample of alloy containing 1 to 5 per cent niobium is dissolved with 2 ml of H_2SO_4, 2ml of HCl, 2 ml of HBF_4, and 15 ml of H_2O. The solution is heated gently to accelerate dissolution. Then 14 5 ml of H_2SO_4 is added, and the solution is heated to fumes. The cooled solution is diluted to 50 ml with H_2O in a volumetric flask. The 6*M* H_2SO_4 sample solution is transferred to a thermostatted H type polarographic cell. The S.C.E. reference is isolated by a sintered-glass disk and a KCl agar bridge. The niobium peak at −0.950 volt is measured with a cathode-ray polarograph.

(7) *Spectrophotometric Methods.* Zircaloy can be dissolved in platinum ware with HNO_3 and HF. The solution is fumed [57] with H_2SO_4 to remove NO_3^- and F^-. The dissolution can be performed in glassware [58, 59] by heating with HCl and HBF_4. Reinhold [62] dissolves Zircaloy with 70 ml of (1+1) HCl and 3 ml of HF in glass and does not remove or complex the F^- with H_3BO_3 in a direct volumetric procedure for tin using aluminum as the reductant. The following procedure can be used in the volumetric analysis of tin by hypophosphite reduction and to prepare a solution that can be employed for the spectrophotometric determination of iron, nickel, and chromium.

Procedure. A 1-g sample is dissolved by heating with 25 ml of HNO_3 and slowly adding about 5 ml of HF. Then 10 ml of H_2SO_4 is added and the solution is evaporated to fumes twice in order to remove NO_3^- and F^-. If the sample does not contain uranium, the HNO_3 may be omitted. The sample is allowed to cool, and the salts are dissolved by adding 50 ml of H_2O and heating gently. The clear solution is transferred to a volumetric flask and made up to 100 ml with H_2O.

Iron. Iron is usually determined spectrophotometrically in Zircaloy or Zircaloy–uranium alloys. Zircaloy can be dissolved in HF. The excess F^- is complexed with H_3BO_3, and the zirconium, with ammonium citrate.[68] Alternatively the alloy can be dissolved with H_2SO_4 and HBF_4, the solution oxidized with a few drops of HNO_3, and boiled to expel NO_2^-.[69] Iron can be measured absorptiometrically as its thioglycollic complex in ammoniacal solution at 525 mμ. Up to 20 per cent tin or manganese, 10 per cent aluminum, 5 per cent copper or

vanadium, 2.5 per cent nickel, and 1 per cent chromium do not interfere.[69]

The method of Lawler [70] has been used for the analysis of zirconium, Zircaloy,[71] uranium–zirconium, and uranium–Zircaloy alloys.[72] The excess F is complexed with H_3BO_3, and the iron is measured absorptiometrically as the ferrous–1,10 phenanthroline complex in the presence of ammonium citrate at pH 3.5. Hydroquinone is used to reduce the iron.

The method of Center [73] has been satisfactorily used for the determination of iron in zirconium and Zircaloy.[74] The sample is dissolved with a mixture of HNO_3 and HF. The excess F^- is complexed with H_3BO_3, and the color developed with NH_4SCN is read at 480 mμ.

Procedure: Iron. An aliquot of the sample solution containing 50 to 500 μg of iron is transferred to a 100-ml volumetric flask. Five milliliters of 50 per cent tartaric acid, 1 ml of 10 per cent $NH_2OH \cdot HCl$, and 5 ml of 0.2 per cent 1,10 phenanthroline are added. The pH is adjusted to 5.5 to 6.0 with dilute NH_4OH and dilute HCl. The flask is heated in a hot-water bath at ~ 90° C for 10 min. The solution is cooled to room temperature and diluted to 100 ml; then the absorbance is measured at 505 mμ against a reagent blank.

Alternatively the color may be developed by treating an aliquot of the sample with $NH_2OH \cdot HCl$ and 1,10-phenanthroline, heating to near boiling, and adding NH_4OH dropwise until the first permanent precipitate of $Zr(OH)_4$ appears. Then acetic acid is added until a clear solution is obtained, and the absorbance is measured.

Nickel. The methods for the determination of nickel in Zircaloy or uranium–Zircaloy alloy are usually based upon the color complex formed between oxidized nickel and dimethylglyoxime. Bromine is the most commonly used oxidizing agent although the UKAEA laboratories [75, 76] prefer I_2 and Drushel et al.[77] describe the use of $K_2S_2O_8$. The nickel can be separated from as much as 100 mg of copper and cobalt,[78] which give colors with dimethylglyoxime, and from iron and uranium by $CHCl_3$ extraction of the nickel-dimethylglyoxime complex.[75, 76, 79] The nickel is back-extracted into HCl and determined spectrophotometrically using the major absorption peak of the oxidized nickel-dimethylglyoxime complex at 445 mμ.

The direct method, which is described here, is rapid, simple, and applicable over a wide range of nickel concentration.[80, 81] Iron and uranium in the presence of citrate or tartrate absorb very little above 500 mμ. Therefore, it is recommended that the measurement be made at 520 mμ, especially when uranium is an alloying element.

Procedure: Nickel. An aliquot of the sample solution containing 25 to 400 μg of nickel is transferred to a 100-ml volumetric flask. Ten milli-

liter of 10 per cent citric acid is added, and the pH is adjusted to 1.5±0.1 with NH_4OH. The solution is cooled in an ice bath, and 5 ml of saturated bromine water is added. After the solution has been 5 min in the ice bath, NH_4OH is added dropwise until the color of bromine is destroyed; then an excess of 5 ml NH_4OH is added. The flask is removed from the ice bath, 3 ml of 1 per cent dimethylglyoxime is added, and the solution is allowed to warm to room temperature for 15 min. The solution is diluted to volume with H_2O, and the absorbancy is measured within 30 min at 520 mμ in 2-cm cells against a reagent blank.

Chromium. Chromium is spectrophotometrically determined in Zircaloy by measurement of the intense reddish-purple complex of Cr(VI)-diphenylcarbazide at 540 mμ. The chromium can be oxidized by heating with $KMnO_4$.[82-85] The excess $KMnO_4$ is decolorized by the addition of sodium azide [82-84] or EDTA.[85] In the method described chromium is oxidized with $(NH_4)_2S_2O_8$ using $AgNO_3$ as a catalyst.[86-88] The excess persulfate is removed by boiling. Bauman [86] has used this oxidation procedure for samples dissolved with H_2SO_4 and HF. The excess F^- is complexed with H_3BO_3. Bane [86] removed the F^- by evaporating to fumes of SO_3.

Procedure: Chromium. An aliquot of the sample solution containing 5 to 15 μg of chromium is transferred to a 50-ml beaker. Five drops of 1 per cent $AgNO_3$ solution and 5 ml of 0.002 *M* $(NH_4)_2S_2O_8$ solution are added. The H_2SO_4 concentration should be ~0.2*N* to 0.4*N* in a volume of about 25 ml. The mixture is heated to boiling for 20 min and transferred to a 25-ml volumetric flask. The flask is cooled in an ice bath to about 15°C. One milliliter of 0.4 per cent ethanol solution of diphenylcarbazide is added, and the solution is diluted to volume with H_2O. The absorbance is measured at 540 mμ against a reagent blank within 10 min after the addition of diphenylcarbazide.

(d) *Zirconium–Aluminum Alloys.* The method of Freund and Miner [89] for the determination of small amounts of aluminum in zirconium is adaptable to zirconium–aluminum alloys. Zirconium is separated from aluminum by adsorption on a strongly basic anion-exchange resin, such as Dowex-1, from 0.06*M* HCl and 0.8*M* HF. Aluminum in the eluate can be determined gravimetrically by an oxine precipitation [90] or colorimetrically by the aluminon–thiogylcolic acid method. Iron is the most serious interference and requires a cupferron separation. Tin and vanadium also will interfere. The method was tested in the range of 0.001 to 3.8 per cent aluminum.

(e) *Zirconium–Thorium Alloys.* Milner and Edwards [91] have analyzed zirconium–thorium binary alloys over the composition range of 1 to 99 per cent thorium by complexometric titrations. For alloys containing more than 20 per cent thorium or 5 per cent zirconium, the sum of the constituents is obtained by adding an excess of EDTA and back-titrating with $Bi(NO_3)_3$ at pH 2.6 to 2.8 using xylenol orange

as indicator. The thorium is then masked with sulfate, and the liberated EDTA is titrated with $Bi(NO_3)_3$ at pH 1.2 to 1.3. For alloys containing less than 20 per cent thorium, the thorium is separated by precipitation as the fluoride using lanthanum as carrier before titration. For alloys containing less than 5 per cent zirconium, the zirconium is separated by precipitation with *p*-bromomandelic acid. The precipitate is dissolved, the organic matter is destroyed, and the zirconium is titrated.

(f) *Miscellaneous Zirconium Alloys.* Lead and antimony in the ternary alloys uranium–zirconium–lead and uranium–zirconium–antimony are separated and determined by electrolytic deposition. The lead is deposited as PbO_2 from HNO_3 solution. The antimony is deposited as the metal from H_2SO_4–HCl solution containing NH_2OH HCl.[92] Uranium in both alloys can be determined by redox titration in the solution remaining after electrolysis.

The ternary alloy uranium–zirconium–vanadium can be analyzed for zirconium [39] by precipitating with *p*-bromo(or *p*-chloro)mandelic acid and igniting to ZrO_2. Vanadium is separated as the cupferrate after the excess *p*-bromomandelic acid has been destroyed and then is ignited to V_2O_5.

Zirconium in the ternary alloy uranium–zirconium–molybdenum is determined [39] by precipitation with *p*-bromomandelic acid and weighed as ZrO_2. Molybdenum is determined in the original sample solution by differential spectrophotometry of the thiocyanate complex.

(g) *Trace Impurities in Zirconium and Its Alloys.* The analyst is referred to three comprehensive publications for the determination of impurities or minor alloying elements in zirconium or zirconium-base alloys.[69, 86, 87] Most of the basic chemical procedures for the determination of 23 elements in zirconium and Zircaloy metals were compiled by Read [86] in 1957. In a laboratory manual edited by Goward and Jacobs [87] in 1959, the methods were extended to cover recent zirconium alloys, new methods were added, and in some cases the existing methods were refined or modified. Both referee and production-control procedures with more emphasis upon spectrochemical analysis are included. In a recent book Elwell and Wood [69] cover the chemical analysis of 27 elements in zirconium and its alloys as used in the Imperial Chemical Industries Metals Division. In Chap. 11 of this book a survey of methods is given.

Topical reports by the Chemical Services Department, Operations Branch, Springfield, include methods for the determination of trace amounts of cobalt, copper, molybdenum, and tungsten. Cobalt within the range of 5 to 100 ppm in zirconium is directly determined absorptiometrically as the nitroso R-salt complex in HF, H_3BO_3, citrate solution. Cobalt in Zircaloy is separated by extraction with $CHCl_3$ from

HF solution as the potassium ethyl zanthate. The complex is destroyed by wet oxidation, and the cobalt is determined as the nitroso-R-salt complex.[93] Copper in uranium-Zircaloy alloy is reduced with $NH_2OH \cdot HCl$ in an HF, H_3BO_3, tartrate solution of the sample and extracted at pH 5 into $CHCl_3$ as the neo-cuproine complex.[94] The absorbancy is measured at 457 mμ within the range of 10 to 250 ppm copper. Molybdenum and tungsten in zirconium are determined absorptiometrically as dithiol complexes in the range of 10 to 50 ppm.[95] The molybdenum-dithiol complex is extracted with CCl_4 from an $HF–H_3BO_3$ solution in which the acidity has been adjusted to $2M$ to $3M$ with HCl. The acidity is increased to $5M$ to $8M$, the tungsten is reduced with Sn^{+2}, and the tungsten-dithiol complex formed at 90°C is extracted with CCl_4.

An X-ray fluorescence method has been suggested for the determination of microgram quantities of thorium in zirconium.[96] The thorium is precipitated as the fluoride using lanthanum as carrier. The thorium is adsorbed on a cation-exchange membrane and placed in the X-ray fluorescence spectrometer. The main thorium emission line, $ThL\alpha_1$, is counted. Bowell and Sandon [97] describe the determination of 10 to 400 ppm silicon in zirconium and Zircaloy. Silicon is measured absorptiometrically as the reduced silico-molybdic acid complex in an HF and H_3BO_3 solution of the sample.

5–1.3 Stainless-steel Alloy

Uranium has been combined with stainless steel to produce fuel elements that take full advantage of the corrosion resistance and heat resistance and desirable mechanical properties of stainless steel. The most important nuclear fuel component consists of a compact mixture of stainless steel and uranium oxide clad with stainless steel.

Titrimetric or gravimetric determination of uranium in stainless steel requires a prior separation of the uranium. Electrolysis with a mercury cathode is preferred as the most convenient and practical means of separating the components of stainless steel from uranium. Uranium is determined volumetrically by use of a Jones or lead reductor and a redox titration.

Uranium can be determined in a solution of the uranium oxide–stainless steel compact by X-ray emission spectrometry.[98] Although not quite so accurate as the chemical method, the X-ray procedure is more rapid and requires no chemical separation or processing other than solution of the sample.

When stainless-steel-clad fuel plates are formed by the hot-rolling technique used to produce the Borax V superheater plates, the thickness of the cladding is not uniform and varies over the area of the

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plate. Therefore, when analyses are required to determine the homogeneity of the fuel compact itself, the cladding must be removed from the sample sections of the fuel plates. There is no chemical method of removing the stainless-steel cladding that will not also attack the UO_2–stainless steel compact. Therefore a mechanical method of machining away the cladding is used. The surface of the specimen is milled until by visual inspection it is determined that the cladding has been completely removed.

(a) *Chemical Methods (Volumetric).* Mercury-cathode electrolysis is used to separate uranium from interfering ions such as iron, chromium, nickel, molybdenum, manganese, cobalt, copper, and tin. The elements vanadium, titanium, niobium, and tungsten are not removed by the mercury cathode and will interfere in the volumetric determination of uranium. If these metals are known to be present, they can be removed from the solution after mercury electrolysis by a cupferron–chloroform extraction.[99] The compact of UO_2–stainless steel, type 304, is dissolved with aqua regia and fumed with perchloric acid prior to separation in the mercury cathode. It has been reported that, when type 310 stainless steel is used, the compact will dissolve rapidly in perchloric acid alone. A 0.25-g sample is dissolved[100] in a few minutes by 10 ml of (1+1) $HClO_4$. The method is applicable over a wide range and has been used to determine from 5 to 20 per cent of uranium with a standard deviation of 0.2 per cent.

Procedure: Uranium. A sample of the UO_2-stainless steel compact weighing 1 to 4 g is heated with 10 ml of aqua regia per gram of sample in a 250-ml beaker. It may be necessary to add more aqua regia if the sample does not disintegrate completely. After reaction ceases, 5 ml of $HClO_4$ plus 5 ml excess per gram of sample is added, and the solution is heated until dense $HClO_4$ fumes appear. Fuming is continued for approximately 2 min at high heat until the chromium is oxidized and the solution is dark red. The beaker is allowed to cool until 10 ml of water can be safely added. The solution is boiled for about 1 min to eliminate chlorine. There is always a small residue remaining after dissolution of the Borax V fuel plates. This whitish residue is principally silica with traces of chromium and iron and an average of 50 μg of uranium. Marley and Kiley[101] report that an X-ray emission spectrographic examination of silica residues from similar samples shows that uranium is not adsorbed. Fifty milliliters of water and a few milliliters of filter-paper pulp slurry are added, and the solution is filtered through No. 41 Whatman filter paper into a suitable volumetric flask. The paper is washed thoroughly with hot distilled water and a few times with hot 2 per cent H_2SO_4. The solution is diluted to volume with water and mixed thoroughly. The size of the volumetric flask and the aliquot taken will depend upon the sample weight and the per cent of uranium.

An aliquot containing 60 to 90 mg of uranium is transferred to a mercury-cathode cell. When the standard sized Dyna-cath cell is used,

the solution is diluted to about 50 ml and electrolyzed for 45 min at 15 to 20 amp with the acid concentration in the range of 0.1*N* to 1.0*N*. At 15-min intervals the walls of the cell and the electrode probes are washed down with distilled water. With the current on, the solution is drained from the cell into a 400-ml beaker, and the cell is thoroughly washed out using 50 ml of water. After the volume has been reduced by evaporation, uranium in this solution is determined by the volumetric method described in Sec. 5–1.1(d)(2); see also Chap. 1.

If the electrolytic separation of the iron is not quantitative, the uranium results must be corrected by multiplying the per cent of iron determined colorimetrically by the factor 2.13 and subtracting from the per cent of uranium. Once the optimum electrolysis time has been determined for a specific set of conditions and equipment, the amount of iron remaining in solution is consistently below the level of significance. However, because of the magnitude of the iron interference, it is consistent with good laboratory practice to determine the iron by a rapid colorimetric method as a control on the efficiency of electrolysis and the chemical manipulations.

If interfering metals, such as vanadium, titanium, niobium, and tungsten are present, a few drops of HNO_3 is added to the solution from the mercury-cathode cell, and the solution is heated to boiling.[99] Ammonium hydroxide is added dropwise until precipitation is complete. The precipitate is filtered through No. 40 Whatman filter paper and washed with warm 2 per cent ammonium chloride solution. The precipitate is dissolved with hot (1+4) HCl, and the paper is washed free of acid with hot water. Ten milliliters of H_2SO_4 is added to the filtrate, and the solution is evaporated to strong SO_3 fumes, cooled, and diluted to about 100 ml with water. A slight excess of 2 per cent potassium permanganate is added until the solution is pink. The solution is cooled below 5°C and transferred to a separatory funnel. Twenty-five milliliters of 6 per cent cupferron solution is added, and the solution is shaken a few times. After the solution has stood for 3 to 4 min, 25 ml of cold chloroform is added, and the mixture is shaken vigorously. After separation of layers is complete, the chloroform is drained off and discarded. The extraction is repeated until the chloroform extract is colorless. Five milliliters of the 6 per cent cupferron solution is added. If the precipitate is white and remains white after standing a short time and does not impart a brown color to the chloroform extract, the extraction is complete. The aqueous layer is transferred to the original beaker, and 15 ml of HNO_3 is added. The solution is evaporated to strong fumes of SO_3 under an infrared lamp and fumed for 30 min. The solution is cooled, the sides of the beaker are washed down with 10 to 15 ml of water, and 1 ml of $HClO_4$ is added. The solution is heated and fumed four times, with a washing down of the beaker walls between each fuming, to completely remove the cupferron decomposition products and HNO_3. The uranium is now determined volumetrically.

(b) *X-ray Emission Spectrometry Methods.* A rapid X-ray emission spectrographic method for the determination of uranium in a solution of stainless steel, type 304, has been described by Silverman, Houk, and Moudy.[98] A perchloric acid solution of the uranium di-

oxide–stainless steel compact is prepared, and direct emission X-ray analysis is performed using strontium as an internal standard. No other processing or separation is required. The procedure was used to determine the homogeneity of uranium dioxide in the finished fuel plate prepared by encasing a mixture of UO_2 and powdered stainless steel in stainless-steel plates. No provision is made for removing the stainless-steel cladding prior to analysis. However, unless the cladding is known to be of uniform thickness, it will be necessary to remove the cladding. The accuracy of the uranium determination is approximately 99.5 per cent of the uranium dioxide present when strontium is used as the internal standard. An accuracy of about 95 per cent is obtained without strontium, using only the ratio of uranium to background. The method was applied to uranium dioxide–stainless steel compacts over the range of 15 to 25 per cent UO_2 with a standard deviation of 0.5 to 1 per cent of the UO_2 present. An X-ray spectrograph with a tungsten-target X-ray tube and a lithium fluoride analyzing crystal is used with a scintillation counter and scaler to detect and record the counts. A lead shield between the scintillation counter and the collimator prevents pickup of scattered radiation.

The working curve is prepared by measuring the time required to record 204,800 counts for the Kα line of strontium and the Lα line of uranium. The standard solutions contain 1.5 to 3.0 mg of UO_2 per milliliter and 2 mg of strontium nitrate per milliliter as the internal standard. A straight-line curve is obtained by plotting the ratio of counting times for the strontium to uranium against the concentration of UO_2 in milligrams per milliliter.

Procedure: Uranium. A sample of the UO_2–stainless steel compact weighing about 1 g is dissolved in 20 ml of aqua regia. Several drops of hydrofluoric acid and 15 ml of perchloric acid are added, and the solution is evaporated to dense fumes of perchloric acid. The solution is cooled and transferred to a 100-ml volumetric flask. Two milliliters of a strontium nitrate solution containing 100 mg of strontium nitrate per milliliter is added, and the solution is diluted to volume with water. Approximately 10 ml of this solution is used to fill the solution cell. The time required, 40 to 70 sec, to record 204,800 counts is measured for the Kα line of strontium and the Lα line of uranium. The ratio of counting time of strontium to uranium is calculated, and the concentration of uranium is obtained from the previously prepared working curve.

5–1.4 Molybdenum Alloys

The widespread use of molybdenum as an alloying metal in nuclear fuel assemblies has resulted in the application of a variety of techniques for the analysis of molybdenum alloys, particularly those with uranium. The gravimetric methods for molybdenum in uranium by

precipitation with alpha-benzoinoxime [102] or as lead molybdate [103] require a minimum of instrumentation and are particularly useful for the occasional analysis. Of special interest, when analyses for molybdenum and uranium are desired, is the separation of molybdenum as thorium molybdate followed by the volumetric determination of molybdenum and uranium.[104] Spectrophotometric methods have been used for molybdenum in uranium over the extreme range of trace amounts to over 90 per cent molybdenum.[105-108] The procedures are rapid, and, if use is made of differential measurement, the accuracy and precision rival the values obtained with gravimetric or volumetric methods.[105, 107] The spectrophotometric thiocyanate method has been applied without separation to ternary alloys of molybdenum with plutonium and uranium [109] and niobium and uranium.[110] A rapid polarographic procedure for the determination of uranium in the presence of molybdenum has been described.[111] X-ray absorption measures the molybdenum remaining in aqueous solution after solvent extraction of the uranium.[112] The technique of X-ray emission spectrometry from polished metal-alloy samples rapidly and directly determines molybdenum and ruthenium in uranium alloys.[113]

A nondestructive electrical conductivity test has been applied to the routine analysis of a uranium–molybdenum alloy.[114]

(a) *X-ray Absorption Methods.* X-ray absorption analysis has been applied to the determination of molybdenum in uranium–molybdenum alloys.[112] The method is reliable, reasonably accurate, and more rapid than the gravimetric methods. However, a separation of the bulk of the uranium is necessary. The alloy is dissolved with HNO_3 and the uranium is extracted with 35 per cent tributyl phosphate–Varsol solution from $8N$ HNO_3. The aqueous phase is transferred to a plastic absorption cell with an X-ray path of 1 in. The concentration of the molybdenum is determined by intensity measurement of the transmitted monochromatic X-ray beam at wave lengths on either side of the molybdenum K absorption edge. For alloys containing 2 to 5 per cent molybdenum, the limit of error for a single determination at the 95 per cent confidence level is ± 2.7 per cent.

(b) *X-ray Emission Spectrometry.* X-ray spectrometry has been used for the rapid, direct determination of molybdenum and ruthenium in uranium alloys without chemical dissolution or separation.[113] About 5 min is required for the surface preparation of the alloy specimen, and from 1 to 8 min counting time is required for measuring the intensities of the molybdenum and ruthenium K emission lines. The dispersion and resolving power of a topaz analyzer gives satisfactory resolution of molybdenum Kβ from ruthenium Kα and molybdenum Kα-ULβ_3 from ULβ_1. A lithium fluoride crystal is not adequate. In the range of 0.7 to 5.8 per cent molybdenum and 0.5

to 4.6 per cent ruthenium, the average absolute error for molybdenum is 0.03 per cent, with the maximum not exceeding 0.08 per cent; for ruthenium the average absolute error is 0.05 per cent, with the maximum not exceeding 0.11 per cent. The working curve is prepared by plotting the intensities of the K emission lines vs. chemically determined weight per cent of molybdenum or ruthenium. The intensities are corrected only by subtracting the background. When dealing with higher alloys of molybdenum and ruthenium the interelement effect becomes important, and a more complicated procedure, such as establishing a family of working curves, will be necessary to maintain a high level of reliability. The method is applicable to binary alloys with uranium.

Procedure: Molybdenum and Ruthenium. Slices are taken from the alloy ingot with an alundum cutoff wheel, and the surface is ground and polished. The polishing is finished with 22-μ silicon carbide paper. The prepared sample is held in a specimen holder under an aluminum plate secured by means of a spring clip. The plate has an aperture of $\frac{7}{8}$ in. Other sized apertures can be used provided the viewing area is constant with specimens of various sizes. The tungsten-target primary tube of the X-ray spectrometer is operated to give the optimum signal to background ratio. A collimator having parallel plates 4 in. long spaced 0.005 in. apart is used between the topaz crystal and a krypton-filled Geiger counter. The intensity of the ruthenium Kα line at 2θ angle of 27.47° is measured by recording the time to take 64,000 counts. The intensity of the molybdenum Kα line at 2θ angle of 30.35° is measured by recording the time to take 128,000 counts. In each case the intensity is corrected by subtracting the background intensity obtained from unalloyed uranium at the same angle.

The amount of molybdenum and ruthenium is read from the appropriate standard curve in which intensity in counts per second is plotted against weight per cent of the desired element.

(c) *Electrical-conductivity Method.* Cofield [114] adapted a nondestructive electrical-conductivity measurement to the analysis of binary uranium–molybdenum alloy in the range of 0 to 3 per cent molybdenum. With an eddy-current conductivity meter (ECC meter), operating in the frequency range of 75 to 85 kc, the 2 per cent molybdenum alloy agreed with the chemical analysis within a limit of error of ± 0.128 per cent molybdenum at the 95 per cent confidence level. The method is rapid, inexpensive, nondestructive, and precise. No chemical processing is required, and the analysis can be made with almost any shape object in 1 min or less. However, its use is economically limited to the analysis of large numbers of samples made under the same metallurgical conditions. The ECC meter must be calibrated with chemically analyzed standards that have the same metallurgical history as the test objects.

(d) *Gravimetric Methods.* (1) *Alpha-benzoinoxime for Molybdenum.* The alpha-benzoinoxime [102] precipitation of molybdenum from 5 per cent H_2SO_4, HCl, or HNO_3 solutions affords quantitative separation from uranium, zirconium, titanium, silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, aluminum, iron, Cr^{+3}, V^{+4}, cerium, nickel, cobalt, manganese, and zinc. The principal interferences that will contaminate the precipitate are Cr^{+6}, V^{+5}, tantalum, niobium, palladium, tungsten, and silicon. The precipitate, formed by molybdenum from a solution containing two to five times the theoretical amount of alpha-benzoinoxime, is dried, ignited directly to MoO_3, and weighed. In certain circumstances, when further purification of the precipitate is required or a more favorable gravimetric factor is desired, the precipitate is dissolved, and the molybdenum is precipitated and weighed as $PbMoO_4$.[103]

Procedure: Molybdenum. A sample of the uranium–molybdenum alloy is dissolved by reaction with HCl, and the dropwise addition of HNO_3, to produce a clear solution. Sulfuric acid is added, and the solution is evaporated to fumes of SO_3. An aliquot containing 50 to 150 mg of molybdenum is diluted to 200 ml and adjusted to 5 per cent H_2SO_4. If vanadium or chromium is present, 10 ml of 5 per cent ferrous ammonium sulfate solution is added to reduce vanadic or chromic acids. The solution is cooled to 5 to 10°C in an ice bath, and 10 ml of a 2 per cent alcohol solution of alpha-benzoinoxime for each 10 mg of molybdenum, plus 5 ml in excess, is slowly added with stirring. A slight excess of bromine water is added, and the beaker is allowed to stand in the ice bath for not longer than 10 min with occasional stirring. The bromine water and low temperature avoid the danger of reduction of the sexivalent molybdenum before it is precipitated. The precipitate is filtered onto Whatman No. 41 filter paper and washed with a cold solution prepared by diluting 50 ml of the 2 per cent alpha-benzoinoxime reagent and 10 ml of H_2SO_4 to 1 liter with water. Filtration may be aided by the use of filter pulp. The washed precipitate and paper are transferred to a platinum or procelain crucible and are carefully dried, charred without flaming, and ignited to MoO_3 at 500 to 525°C.

Somewhat more accurate results can be obtained,[102] particularly when the sample size is small, by weighing as $PbMoO_4$ with its more favorable gravimetric factor of 0.2613. The cooled MoO_3 is dissolved by warming with 10 ml of NH_4OH, and the solution is filtered through Whatman No. 40 filter paper. The paper is washed with hot NH_4OH (1+30), and the combined filtrate and washes are diluted to 100 ml. Hydrochloric acid is added to the color change of methyl orange. Fifty milliliters of 20 per cent ammonium acetate solution are added, and the whole is diluted to 250 ml with water. The solution is heated to boiling, and 10 ml of lead acetate solution containing 10 g of lead acetate and 1 ml of acetic acid per 100 ml of aqueous solution is added dropwise with stirring. The temperature is maintained at the boiling point for 3 min, and then the beaker and contents are allowed to stand for several hours or overnight. The solution is filtered through Whatman No. 42 filter paper containing

a little filter pulp. The beaker is rinsed, and the precipitate is transferred to the filter paper with 1 per cent ammonium nitrate solution. A single final wash with distilled water is made, and the paper with precipitate is dried in a tared porcelain crucible and ignited to $PbMoO_4$ at 700°C for 30 min. The ignition is repeated until constant weight is obtained.

(2) *Lead Molybdate for Molybdenum.* The precipitation of $PbMoO_4$ by the addition of lead acetate to a molybdenum containing solution can be applied directly to uranium–molybdenum alloys.[115] However, a double precipitation is required for quantitative results. The procedure has proved to be of most use for the analysis of a few alloys at a time with widely different molybdenum contents.

Procedure: Molybdenum. The uranium–molybdenum alloy is dissolved by treating with 10 ml of HCl plus 10 ml for each gram of sample. After the reaction has subsided, the slurry is heated, and HNO_3 is added dropwise until the solution is clear. The solution can also be cleared by the addition of 30 per cent H_2O_2. An aliquot selected to contain between 10 and 100 mg of molybdenum is diluted to 200 ml and heated to boiling, and a slight excess of 4 per cent lead acetate in 0.1 per cent acetic acid is added. One ml of 4 per cent lead acetate will precipitate about 0.01 g of molybdenum. If a precipitate of $PbMoO_4$ is formed, HNO_3 is added dropwise until the precipitate just dissolves. If no permanent precipitate forms, NH_4OH is added until the precipitate dissolves with difficulty. Twenty-five milliliters of a saturated solution of ammonium acetate is slowly added with stirring. The mixture is boiled for 10 min and then transferred to a steam bath for 30 min until the precipitate has coagulated and settled. Completeness of precipitation is checked by adding a few drops of lead acetate. The supernatant solution is decanted through a Whatman No. 42 filter paper; the bulk of the precipitate is retained in the beaker. The precipitate is washed with several portions of hot water; the washings are filtered. The filtrate and washes are discarded. The precipitate is dissolved by treating the precipitate in the beaker with hot 6*N* HCl and pouring it through the filter paper. The beaker is washed with several 10-ml portions of 6*N* HCl. The combined washes are diluted to 150 ml, 0.5 ml of 4 per cent lead acetate is added, and the solution is heated to boiling. Ammonium hydroxide is added until the precipitate dissolves with difficulty, and the molybdenum is reprecipitated by the slow addition of 25 ml of saturated ammonium acetate. The solution is boiled for 10 min and heated on a steam bath for 30 min. The solution is filtered through the same filter paper, and the precipitate is thoroughly washed with hot water. Filter pulp may be added to facilitate filtration. The paper and precipitate are carefully dried in a porcelain crucible and ignited at a low temperature until carbon is destroyed. The precipitate is ignited at 700°C to constant weight of $PbMoO_4$, and molybdenum is calculated using the gravimetric factor 0.2613.

(3) *Niobium.* Niobium is determined in a niobium–molybdenum–uranium alloy by separating the niobium and most of the molybdenum from the uranium by extraction into hexone from a 10*M* HF, 6*M*

H_2SO_4, and 2.2*M* NH_4F solution. The niobium and molybdenum are back-extracted into an aqueous peroxide solution and fumed with H_2SO_4. Niobium is separated from the bulk of the molybdenum by precipitation with NH_4OH; finally it is precipitated with tannic acid from 2*N* HCl solution and ignited to Nb_2O_5. Separation from molybdenum is necessary for, although molybdenum is not precipitated by tannic acid from 2*N* HCl, the niobium tannate precipitate carries down significant amounts of molybdenum giving niobium values as much as 10 per cent high with alloys containing equal amounts of niobium and molybdenum.

(e) *Volumetric Methods—Molybdenum and Uranium.* The titrimetric determination of molybdenum in uranium–molybdenum alloys is based upon the separation of molybdenum by precipitation as thorium molybdate followed by the reduction and titration of the molybdenum with ceric sulfate.[104] The procedure is rather lengthy but represents a unique combination of quantitative separation of molybdenum and uranium with volumetric analysis. Uranium can be determined in the filtrate remaining after separation of the molybdenum by reduction and titration with ceric sulfate. This is probably the simplest method available when analysis for both molybdenum and uranium is required. The method has been used for alloys in the range of 0.5 to 20 per cent molybdenum and is applicable to alloys of greater molybdenum concentration.

Procedure: Molybdenum. The alloy is disintegrated with as small a volume of (1+1) HCl as possible. The black residue of hydrated uranium dioxide is dissolved, and both uranium and molybdenum are oxidized to the hexavalent state by the dropwise addition of 30 per cent H_2O_2. The solution is boiled about 10 min to destroy the excess H_2O_2. It may be necessary to add a little HNO_3 to effect complete solution particularly for the higher molybdenum alloys. Aliquots containing 70 to 100 mg of molybdenum are placed in 400-ml beakers and diluted to 200 ml with water. Sixteen milliliters of glacial acetic acid are added to each sample and enough ammonium acetate, usually 1 g, to react with the mineral acid present. About 15 ml of thick filter-pulp slurry is added to each beaker, and the molybdate is precipitated as thorium molybdate by adding slowly with stirring a 25 per cent excess of thorium perchlorate solution, prepared by fuming purified thorium nitrate with perchloric acid to near dryness and diluting until 1 ml is equivalent to about 5 mg of molybdenum. The contents of the beaker are heated to boiling and filtered while hot through Whatman No. 42 filter paper. The precipitate is washed five to six times with hot (1+100) acetic acid. The precipitate and filter are returned to the original beaker, and 25 ml of HCl is added. The contents are stirred until the filter disintegrates. Seventy-five milliliters of water is added, and the mixture is heated to boiling and filtered while hot through Whatman No. 42 filter paper. Long boiling results in reduction of molybdenum and decomposition of the filter pulp. The

filter pulp, beaker, and filter are washed with hot (1+100) HCl. The filtrate, cooled to room temperature, is passed through an amalgamated-zinc Jones reductor into a fivefold excess of 10 per cent ferric alum containing 2 to 3 ml of H_3PO_4. The solution is titrated with 0.1*N* ceric sulfate using 2 drops of 0.025*M* ferroin as indicator. The end point is at the change from pink to colorless or light blue.

Procedure: Uranium. The filtrate from the separation of molybdenum as thorium molybdate is concentrated to a convenient volume, and an aliquot is selected to contain 100 to 125 mg of uranium. If nitric acid was used in dissolving the alloy, 10 ml of $HClO_4$ is added, and the solution is evaporated to fumes of $HClO_4$ several times to ensure complete removal of the nitrate ion. Uranium is determined volumetrically by reducing and titrating with ceric sulfate (see Chap. 1, Sec. 1–2).

(f) *Spectrophotometric Methods.* (1) *Peroxide: Molybdenum and Uranium.* Bacon and Milner[105] describe a high-precision spectrophotometric method for the determination of molybdenum in binary alloys with uranium. The absorbancy of the colored complex formed by molybdenum and hydrogen peroxide is measured differentially at 378 mμ in a solution of 1.5*M* H_2SO_4 and 0.18*M* H_2O_2. The procedure is direct and rapid compared with gravimetric methods. For alloys containing more than 2.5 per cent molybdenum, the precision is better than ± 1.0 per cent. The method is particularly suitable for alloys rich in molybdenum. With molybdenum contents greater than 90 per cent, an accuracy better than 99.9 per cent can be attained. However, since uranium contributes to the absorption, it is necessary to apply a correction factor, 1 per cent of uranium is equivalent to 0.0023 per cent molybdenum. Uranium is determined by differential spectrophotometry [116] in 4*M* H_2SO_4 at 430 mμ.

(2) *Thiocyanate: Molybdenum.* The spectrophotometric determination of molybdenum by direct measurement of the intense thiocyanate color at 500 mμ has been demonstrated to be satisfactory for the analysis of ternary alloys of plutonium–molybdenum–uranium.[109] No interference is observed with weight ratios of uranium to molybdenum and plutonium to molybdenum over the range of 0 to 5.5. The ternary alloy is dissolved by treatment with 6*N* HCl, followed by mixed HCl–HNO_3 with a little HF for alloys containing more than 50 per cent plutonium. The mixture is then fumed with H_2SO_4 to bring about complete solution and to remove nitrate. The determination of molybdenum as thiocyanate is made erratic by any nitrate ion remaining in the solution.

Milner, Barnett, and Bacon [110] adapted the direct thiocyanate spectrophotometric method to the determination of molybdenum in ternary alloys with niobium and uranium. The alloy is dissolved by HNO_3 and HF and fumed with H_2SO_4. Niobium is retained com-

pletely in solution upon dilution by the addition of oxalic acid. Absorbance measurements are made at 500 mμ by the differential method with a precision (1σ) of 0.5 per cent. The procedure is applicable over the range of 5 to 40 per cent molybdenum with a niobium content of 5 to 35 per cent.

A direct spectrophotometric–thiocyanate determination of molybdenum in uranium alloys which is rapid and accurate has been described for routine applications.[106] The alloy is dissolved in hydrochloric and nitric acids and then is fumed with perchloric acid. Ferric iron is added as an oxidation–reduction buffer, and the molybdenum thiocyanate color is developed by the addition of stannous chloride and sodium thiocyanate. Maximum color intensity is achieved when molybdenum is quantitatively in the five valence state.[117] The color is measured at 510 mμ, where the absorbance of uranium thiocyanate is negligible and the absorbance of the molybdenum–thiocyanate complex is still high enough for adequate sensitivity. Beer's law is followed at all concentrations. Investigation of the effect of certain impurities or alloying metals indicated that up to 5 per cent of aluminum, chromium, iron, manganese, nickel, tin, titanium, vanadium, and zirconium do not interfere. At the 1 per cent level, copper, niobium, and tungsten do not interfere. The method is applicable over the range of 0.50 to 11.6 per cent molybdenum. The range may be extended by the selection of proper aliquots.

Procedure: Molybdenum. A 0.5-g sample of the uranium alloy is treated with 10 ml of HCl (1+1) and heated gently. Nitric acid is added dropwise to oxidize and clear the solution. The cooled solution is transferred to a volumetric flask and diluted to volume. A 100-ml flask is used for alloys containing less than 3 per cent of molybdenum; a 200-ml flask, for alloys containing 3 to 6 per cent of molybdenum; and a 500-ml flask, for alloys containing greater than 6 per cent of molybdenum. To a 10-ml aliquot of the sample solution, 20 ml of an iron perchlorate solution (2.5 mg of iron per milliliter of $HClO_4$) and 5 ml of $HClO_4$ are added. If tungsten is present, 5 ml of H_3PO_4 is added to keep the tungsten in solution. The mixture is heated to strong fumes of $HClO_4$. The cooled solution is transferred to a 100-ml volumetric flask with the addition of 25 ml of water. Thirty milliliters of a mixture prepared by adding 1 part of a 10 per cent sodium thiocyanate solution to 2 parts of a 25 per cent stannous chloride solution is added, and the whole is immediately mixed by swirling. The solution is diluted to the mark with water, mixed, and allowed to stand for 10 min. If copper is present, the precipitate of copper thiocyanate is removed by filtering through a dry Whatman No. 42 filter paper. The absorbance is read at 510 mμ using 1-cm cells against an aqueous solution of all the reagents. The molybdenum is calculated from the factor, milligrams of molybdenum per absorbance unit, or from a standard curve prepared by carrying solutions of known amounts

of molybdenum in uranium through the colorimetric procedure. The standard molybdenum solution is prepared by dissolving 0.186 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 800 ml of water and diluting to 1 liter. This solution, containing approximately 0.1 mg of molybdenum per milliliter, is standardized gravimetrically.[118] The calibrating solutions are prepared by adding 0-, 1-, 2-, 3-, 4-, 5-, and 10-ml aliquots of the standard molybdenum solution to 100-ml flasks containing 50 mg of uranium.

(3) *Toluene-3,4-dithiol:Molybdenum.* Granger [107] describes a rapid, precise, direct spectrophotometric determination of molybdenum in uranium alloys using toluene-3,4-dithiol. The alloy is dissolved by treatment with HCl followed by the dropwise addition of 30 per cent H_2O_2 until the solution is clear. Excess peroxide is removed by evaporating to just dryness, and the residue is dissolved with HCl. A mixture of HCl and HNO_3 has been used to dissolve the alloy, and the nitrate ions have been removed by fuming [108] with H_2SO_4. The color is developed in 30 per cent *n*-butyl alcohol–aqueous 4.5*N* HCl solvent. The method has few interferences and is applicable over a wide range of molybdenum content. Measurement at 680 mμ by differential spectrophotometry gives a coefficient of variation of ±0.16 per cent with alloys containing 0.2 per cent or more of molybdenum. Absolute measurement of optical density permits determination down to 1 ppm. Variations of as little as 1 per cent in the molybdenum content of alloys can be detected with samples containing only 1 mg of molybdenum. With a modification of the dissolving procedure, the method is applicable to niobium alloys containing up to 10 per cent of molybdenum. The alloy is dissolved with HNO_3 and HF and evaporated to dryness. The residue is fused with potassium hydrogen sulfate, and the melt is dissolved in 50 per cent citric acid solution.

(g) *Polarographic Methods: Uranium.* The polarographic method of Susic, Gal, and Cuker [119] for the analysis without chemical separation of ores containing more than 0.01 per cent uranium was modified by Propst [111] for the determination of uranium in the presence of molybdenum. The procedure, originally developed for the analysis of highly radioactive solutions containing uranium, molybdenum, aluminum, mercury, and fission products, was studied over the range of 20 to 95 per cent of uranium with respect to molybdenum. Uranium is determined without interference from molybdenum, aluminum, iron, and mercury in a supporting electrolyte of potassium phthalate and ascorbic acid at pH 6. Molybdenum is not reduced at the dropping-mercury electrode in this buffer. Mercury(II) and Fe^{+3} are reduced by the ascorbic acid. Aluminum will precipitate after several hours; however, adequate time is available for the polarographic analysis. The method was tested with solutions containing 50 times as much aluminum as uranium and 3 times as much Hg^{+2}.

Susic reports that in the presence of ascorbic acid at pH 3.6 to 4.0 Mo^{+6}, V^{+5}, Cr^{+6}, Ti^{+4}, Cu^{+2}, and as much as 20 per cent of Fe^{+3} do not interfere in the polarographic determination of uranium. Propst, using the Susic method, found a positive bias of 10 per cent at molybdenum to uranium ratios of 0.5. However, increasing the pH to 6 with a phthalate–ascorbic acid buffer completely eliminated the molybdenum reduction wave.

In the phthalate–ascorbic acid buffer, the uranium gives a single wave with an $E_{1/2}$ of -0.47 volt vs. S.C.E. corresponding to a 1-electron reduction from U^{+6} to U^{+5}. The diffusion-current constant is 1.23. The diffusion currents and derivative peak heights are a linear function of the uranium concentration within the investigated range of 0.005 to 0.5 mg of uranium per 10 ml of electrolytic solution. A high-sensitivity polarograph (ORNL model Q–1338) is employed to record both normal and derivative polarograms.[120] Because of the distortion in the uranium diffusion-current wave due to the unfavorable ratio of diffusion to residual current, only the derivative peak heights are used when the uranium concentration is less than 0.05 mg per 10 ml. The precision of the analysis is 2.5 per cent, and duplicate analyses can be completed in 1 hr.

Procedure: Uranium. The uranium–molybdenum alloy is dissolved with HNO_3 (1+1). A 50-μl aliquot containing 0.05 to 0.3 mg of uranium is transferred to a 10-ml volumetric flask containing 200 μl of 1*M* potassium ascorbate and 9 ml of phthalate buffer prepared by dissolving 102 g of potassium acid phthalate and 10 g of KOH in distilled water, diluting to 1 liter, and adjusting to pH 6 by the addition of KOH or HNO_3 as required. The potassium ascorbate is prepared by dissolving 1.8 g of ascorbic acid in distilled water, neutralizing to pH 7 with KOH, and diluting to 10 ml. Neutral potassium ascorbate can be stored in glass for one week. The sample mixture in the 10-ml volumetric flask is diluted to volume with the phthalate buffer and transferred to a conventional polarographic cell. A slight lowering of the pH of the final solution has no effect on the analytical results. No molybdenum wave is observed down to pH 5.6. Nitrogen, which has passed through two chromous sulfate bubblers followed by a dilute caustic bubbler, is bubbled through the sample solution for 10 min to remove atmospheric oxygen. A high-sensitivity polarograph is used to record the normal and derivative polarograms using a dropping-mercury electrode at 0.1 volt per minute -0.2 volt to -0.8 volt vs. S.C.E. The temperature of the cell is maintained at 25 ± 0.1°C by means of a constant-temperature bath.

The uranium concentration is read from standard curves prepared from the diffusion currents and derivative peak heights obtained by the analysis of known samples. The diffusion current curve is usable down to 0.05 mg of uranium per 10 ml; the derivative peak heights are determinable to 0.002 mg of uranium per 10 ml.

5–1.5 Bismuth Alloys

Alloys or mixtures of bismuth with fissionable materials have received considerable attention as fuels for liquid-metal reactors. Most emphasis has been placed upon uranium–bismuth alloys although the feasibility of using slurries of uranium and thorium oxides or carbides in a bismuth matrix is under investigation. Analyses are required during the research and test phases in connection with corrosion studies of structural and containment materials. Studies of the effect of metal additives upon the solubility of uranium in bismuth and investigations relevant to putting the reactor into operation also require analyses. The same types of analyses will be necessary for the control and operation of a liquid-metal-fuel reactor. However, the analyses will be complicated by the presence of high levels of radioactivity and will not be considered here. Methods will be included for the analysis of pure uranium–bismuth alloys as well as those alloys containing magnesium, zirconium, and corrosion products, such as iron and chromium. Since the separation of uranium is of prime importance, the methods of analysis will be listed under the various separation techniques.

(a) *Methods of Separation.* (1) *Precipitation. 8-Quinolinolate.* A gravimetric method based on a procedure by Sen Sarma and Mallik [121] has been described for the analysis of uranium–bismuth alloys.[122] Quantitative precipitation of uranyl 8-quinolinolate (oxinate) from a solution at pH 5.5 complexed with ethylenediaminetetraacetic acid (EDTA) can be carried out in the presence of bismuth, iron(III), zirconium, thorium, rare earths, aluminum, copper, cobalt, nickel, zinc, cadmium, lead, manganese, and phosphate. The lower limit is 0.5 per cent of uranium with no less than 20 mg of uranium required per sample.

Bismuth can be determined after removal of the uranyl oxinate by hydrolyzing the bismuth–EDTA complex above pH 8 to give bismuth oxinate. The determination of both uranium and bismuth has been tested for alloys where the weight ratio of bismuth to uranium is 3 to 1 and 1 to 3.

Procedure: Uranium. The sample, dissolved in nitric acid, is converted to the chloride by two evaporations to dryness with hydrochloric acid. The residue is then dissolved in water, and an amount of EDTA equal to two times the sample weight is added. The solution (about 150 ml) is adjusted to pH 5.5±0.3 by the addition of ammonium hydroxide to the change of methyl red indicator. The solution may be turbid. One milliliter of (1+1) acetic acid is added (the solution should now be clear); then 25 ml of 20 per cent ammonium acetate solution is added. The solution is heated to about 60°C, and enough 4 per cent solution of 8-quinolinol (oxine) in ethanol is added to give

a sixfold excess in respect to uranium. The precipitate is allowed to stand for 10 min at about 30°C, and then it is filtered on a sintered-glass filter crucible. The precipitate is washed with warm water containing 25 ml of oxine solution per liter; it is then dried at 105°C for 1 hr and weighed as $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$.

Procedure: Bismuth. Oxine solution is added to the uranium-free filtrate from the above. The solution is heated to 50°C and made akaline with sodium hydroxide. The precipitate of bismuth oxinate is allowed to coagulate and is then filtered through hardened fluted filter paper. The washed precipitate is dissolved in hot hydrochloric acid (1+1). Two milliliters of oxine solution (4 per cent in ethanol) is added. The solution is heated to 60°C, and the bismuth oxinate is reprecipitated by adding ammonium hydroxide (1+1), 5 ml in excess of the quantity required just to form the precipitate. The beaker is set aside for 10 min at about 30°C, the precipitate is filtered, dried at 105°C and weighed as $Bi(C_9H_6ON)_3 \cdot H_2O$.

Phosphate. Uranium in the range of 1 to 20 per cent in bismuth alloys has been determined volumetrically after prior separation as uranyl ammonium phosphate from a solution complexed with EDTA.[123] Iron, chromium, copper, nickel, vanadium, cerium, neodymium, and bismuth do not interfere.

Procedure: Uranium. The solution of the sample containing 5 to 100 mg of uranium and a small excess of EDTA is buffered with acetate by adding ammonium hydroxide to the color change of methyl red and then adding sufficient buffer solution (0.1*M* in acetic acid and 0.1*M* in ammonium acetate) to restore the red color of the indicator. Two grams of diammonium phosphate is added, and the solution is heated to boiling for 2 to 3 min. The slurry is digested for 30 min at near the boiling temperature; then it is centrifuged, and the supernatant liquid is filtered through Whatman No. 42 filter paper. The precipitate is washed three times with hot 2 per cent ammonium chloride solution containing a small amount of diammonium phosphate. The precipitate is dissolved in the centrifuge tube with hot hydrochloric acid (1+3), and the solution is transferred to the original beaker. Any precipitate on the filter is dissolved and combined with the principal uranium solution. The uranium is determined by reduction in a lead reductor and titration with standard ceric solution in the presence of phosphoric acid using ferroin to indicate the end point.

Sulfide. Stoner and Finston [124] report a rapid quantitative separation of bismuth as the sulfide from uranium in the range of 10 to 1000 ppm uranium. Precipitation from a homogeneous solution with thioacetamide is utilized in 2*N* nitric acid at elevated temperatures. When applied to liquid-metal fuel,[125] the uranium is determined either polarographically in a sulfate-bisulfate supporting electrolyte at a half-wave potential of −0.24 volt vs. S.C.E. or spectrophotometically [126] by extraction of the uranium–dibenzoylmethane complex with amyl acetate and measurement of the absorbance at 412 and 426 mμ. Diaminocyclohexanetetraacetic acid (CHEL-600,

DTA) is added as a complexing agent to prevent interference from small amounts of bismuth in the latter procedure.

(2) *Solvent Extraction. Tributyl Phosphate.* Solvent extraction with tributyl phosphate (TBP) has been applied to the separation of uranium from thorium, bismuth, and various complex ores by Eberle and Lerner.[127] The separation from thorium is done from a 7*N* hydrochloric acid solution, and the separation from bismuth and ores containing no thorium or zirconium is done from a 4.7*N* nitric acid solution. Uranium is determined spectrophotometrically by extracting the separated uranium with 8-quinolinol (oxine)-chloroform and measuring the absorbance at 470 and 500 mμ. The procedure was tested at concentrations as low as 0.0005 per cent of uranium in bismuth. Although two extractions and multiple washes are required, Eberle and Lerner claim that an analysis can be completed within 45 min after the sample is in solution. The procedure has the advantage that a large number of diverse ions do not interfere.

This procedure with slight modification was adapted to the analysis of the majority of liquid-metal-fuel reactor-experiment project samples containing additives and corrosion products.[128] The range is 0 to 500 μg of uranium. A zirconium to uranium ratio of 4 to 1 at the level of 400 μg of zirconium shows no interference. Iron (III), copper, nickel, bismuth, rare earths, chromium (III), and cerium (IV) do not interfere. [See Chap. 1, Sec. 1–3.3(c)(1).]

Procedure. The sample is dissolved in nitric acid and the solution is transferred to a 250-ml separatory funnel and adjusted so that the volume is 50 ml and 4.7*N* in nitric acid. Twenty-five milliliters of TBP and 25 ml of ethyl acetate are added, and the separatory funnel is shaken for 1 min. The aqueous layer is allowed to separate and is discarded. The organic phase is washed with four 50-ml portions of 4.7*N* nitric acid. The separatory funnel is shaken for 1 min for each wash, and the washings are discarded. Uranium is transferred to the aqueous phase by extracting with 25-, 15-, and 15-ml successive portions of an ammonium acetate solution prepared by adding 430 ml of ammonium hydroxide to 369 ml of glacial acetic acid, diluting with 1 liter of water, adjusting to pH 7.6 with ammonium hydroxide, and diluting to 2 liters with water. The aqueous extracts containing the uranium are combined in a 150-ml beaker. Five milliliters of ammonium hydroxide is added, and the pH is adjusted to 7.6 by the dropwise addition of ammonium hydroxide. The solution is transferred to a 250-ml separatory funnel, and 25 ml of a 1 per cent solution of oxine in chloroform is added. The separatory funnel is shaken for 1 min. The cholorform layer is filtered through a Whatman No. 41 filter paper, and the absorbance is measured in 5-cm cells at 470 mμ and at 500 mμ against a blank treated in the same manner as the sample. With standard curves prepared at both 470 and 500 mμ, the efficiency of the separation can be determined by comparing the results calculated from the two curves.

Metal 8-quinolinolates (oxinates), such as those of bismuth, zirconium, and thorium, begin to absorb strongly at the lower wave lengths. When there are no interferences present, greater sensitivity is obtained at 470 mμ. If thorium is present, the procedure is modified after Eberle and Lerner [127] to include washing the sample with five 50-ml portions of 7*N* hydrochloric acid to remove thorium and any zirconium. The sample solution is then washed with five 50-ml portions of 4.5*N* nitric acid, and the uranium determination is completed as above. The method proved satisfactory with as much as 6 mg of thorium present. A standard deviation of 4.99 μg was obtained for 31 determinations at the 250-μg level of uranium.

Dibenzoylmethane. Since the presence of thorium greatly increases the analysis time in the procedure given under Sec. 5–2.1 (b)(1), another more rapid spectrophotometric method based upon extraction of the uranium–dibenzoylmethane complex [126] was adapted for routine applications in the presence of thorium.

Procedure. A 5-ml nitric acid solution of the sample sufficiently acid to prevent the hydrolysis of bismuth is transferred to a 125-ml separatory funnel. Five milliliters of a saturated ammonium chloride solution and 5 ml of 20 per cent diaminocyclohexanetetraacetic acid (CHEL-600, DTA) solution (prepared by dissolving 20 g of DTA in dilute sodium hydroxide and diluting with water to 100 ml with the pH adjusted to 5.2 with nitric acid) are added. The sample solution is adjusted to pH 4.5 with nitric acid and short-range pH paper. If bismuth precipitates, the sample is acidified and more DTA is added. Approximately 0.3 g of bismuth can be complexed by 5 ml of 20 per cent DTA. With the sample solution volume about 20 ml, 1 ml of a 1 per cent solution of dibenzoylmethane in ethyl alcohol is added. The liquid is mixed, and then 1 ml of 6*N* ammonium hydroxide is added with thorough mixing. The pH should now be 8. After the solution is allowed to stand for 15 min 5 ml of isoamyl acetate is added, and the separatory funnel is shaken for 1 min. The layers are allowed to separate for 15 min. The aqueous layer is drained, and the separatory funnel is shaken again. The solution is allowed to stand for 5 min, and any remaining aqueous layer is drained. The inside of the stem of the separatory funnel is dried with filter paper, and the acetate layer is filtered through a dry filter paper into a dry 1-cm cell. The absorbance of the uranium–dibenzoylmethane complex is measured at 430 mμ against a reagent blank.

Diethyldithiocarbamate. Milner and Edwards [129] describe a method for the analysis of ternary bismuth alloys containing 0.2 to 5 per cent uranium and 0.2 to 5 per cent neodymium or praseodymium which requires only 30 min after solution of the sample. Bismuth is separated by extraction with a chloroform solution of diethylammonium diethyldithiocarbamate from a 1*N* nitric acid solution. The solution is acetate buffered at pH 5.5 to 6.0, and the uranium is ex-

690–457 O—64——30

tracted with the same reagent. The absorbancy of the uranium–diethyldithiocarbamate complex in chloroform is measured spectrophotometrically. The neodymium or praseodymium is determined by an EDTA titration, with xylenol orange indicator at a pH of 5.6 to 5.8, of the aqueous solution remaining after the removal of the bismuth and uranium. Bismuth is determined by direct titration with EDTA at pH 1.5 with xylenol orange indicator. An estimate of the neodymium or praseodymium can be made by acetate buffering the solution to pH 5.6 after the direct titration of the bismuth, and again titrating with EDTA.

8-Quinolinol. Kirby and Crawley [130] have described methods for the determination of uranium, zirconium, magnesium, and iron in bismuth alloys. Zirconium and magnesium are added to improve the characteristics of the alloy, such as inhibition of corrosion and prevention of uranium oxidation. Iron enters the alloy from the containment system.

Uranium is determined in the range of 0.002 to 0.1 per cent by extraction of uranium 8-quinolinolate (oxinate) with chloroform from a solution complexed with EDTA and buffered at pH 7 with ammonium acetate. Uranium is determined spectrophotometrically by measuring the chloroform extract at 400 mμ. Incomplete extraction of uranium was experienced when a chloroform solution of 8-quinolinol (oxine) was used. It is recommended that the oxine be added in 5 per cent alcoholic solution before each of the chloroform extractions. Iron, magnesium, manganese, nickel, and bismuth do not interfere. A large excess of EDTA will eliminate any interference due to zirconium.

Magnesium is determined in the range of 0.005 to 0.06 per cent after removing interfering elements. The bulk of the bismuth is separated by extraction of bismuth iodide with methyl isobutyl ketone in acid solution. The elements uranium, zirconium, iron, nickel, manganese, and residual bismuth are separated by chloroform extraction of their oxinates at pH 6.5. Magnesium is finally precipitated with oxine at a pH greater than 10. The precipitate is dissolved in acid, and the oxinate solution is measured spectrophotometrically at 365 mμ.

Zirconium is determined by a modification of the Alizarin red S method. Nitric acid interferes; therefore the solution of the alloy is converted to perchlorate by evaporating and fuming at 200°C. The zirconium-Alizarin color is developed in 1.3*N* hydrochloric acid solution at boiling-water temperature for 3 min. The absorbance is measured at 560 mμ. The conditions of acidity and time of color formation are critical. Bismuth, uranium, magnesium, nickel, and

manganese do not interfere. No appreciable interference was observed with up to 500 μg of ferric iron.

Methyl Isobutyl Ketone. Iron is determined spectrophotometrically in the range of 0 to 80 ppm after extraction of the thiocyanate complex with methyl isobutyl ketone. Nitric acid is removed from the sample solution by fuming with perchloric acid. The solution is made about 1.2*N* in acidity by adding hydrochloric acid. Ammonium thiocyanate is added, and the iron thiocyanate complex is extracted with methyl isobutyl ketone. Bismuth does not interfere provided there is an excess of thiocyanate present. The bismuth thiocyanate remains in the aqueous phase. Uranium, magnesium, and zirconium do not interfere. Although cobalt thiocyanate will extract, its absorption peak occurs at a different wave length, and only large amounts would cause interference.

Acetylacetone. Kirshen and Freiser [131] suggest solvent extraction of uranium from bismuth using acetylacetone in the presence of EDTA. The procedure is applicable for as little as 0.02 per cent of uranium. The extraction of uranium is 98 per cent complete. Therefore, for results with an accuracy of ± 1 per cent, a correction factor must be applied. The method was tested over the range of 0.100 to 1 mg of uranium. The amount of bismuth in the sample is limited by the low solubility of EDTA, which must be present in 30-fold excess at pH 7.5.

Tris(2-Ethylhexyl) Phosphine Oxide. Heyn and Banerjee [132] have used the more soluble disodium salt of diaminocyclohexanetetraacetic acid (CHEL–600, DTA) as the complexing agent for bismuth. The chelates formed have greater stability constants than those formed with EDTA. They achieved a complete separation of 0.005 per cent uranium in bismuth by extraction with 0.1*M* tris(2-ethylhexyl) phosphine oxide (TEHPO) in cyclohexane at pH 5 in the presence of DTA. The uranium analysis was completed by measurement of the absorbance of the organic phase at 250 mμ.

(3) *Ion Exchange.* Ion exchange has proven to be a valuable technique for simplifying the quantitative separation of many elements, and procedures for separating uranium and thorium from bismuth have been described. Since the technique can easily be adapted to remote handling, it should be particularly attractive for the analysis of radioactive samples. Ion exchange has the disadvantage that any organic matter carried down from the resin column must be removed before subsequent determinations can be made. The presence of organic matter interferes in the uranium titration with ceric sulfate and obscures the end point in the EDTA titration of thorium. The removal of organic matter, e.g., by wet oxidation, necessarily lengthens the analysis time.

Milner and Edwards[133] propose an ion-exchange method of separating bismuth from binary alloys of uranium or thorium. It has been applied over the range of 0.001 to 10 per cent uranium and 0.05 to 10 per cent thorium. Bismuth in 10 per cent hydrochloric acid solution is retained on an anion-exchange resin of the strongly basic quaternary ammonium type. Uranium in the effluent is determined volumetrically with the lead reductor and ceric sulfate titration. For very low concentrations of uranium, a suitable colorimetric method may be preferred. Milner and Edwards also suggest the use of thoronol, the sodium salt of 1-(*o*-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid. The uranium is reduced in a lead microreductor, and the effluent is collected in a 25-ml flask, treated with 10 to 15 ml of acetone and 0.5 ml of 0.1 per cent aqueous thoronol solution, and then diluted to the mark with acetone. The absorbancy of the red complex is measured at 535 mμ against water as the reference.[134]

Thorium in the effluent in concentrations larger than 1 per cent is determined by titration with EDTA with pyrocatechol violet as the indicator. In the lower ranges the colorimetric method using thoronol is preferred.[135]

Bismuth ternary alloys containing 0.1 to 10 per cent uranium and thorium may be analyzed by selective elution from an anion-exchange resin.[136] Thorium is separated by elution with 5*M* hydrochloric acid, and the determination is made volumetrically with EDTA or absorptiometrically with thoronol. Uranium is then eluted with 0.2*M* hydrochloric acid and is determined volumetrically for amounts greater than 1 per cent. Smaller amounts are determined polarographically. Bismuth remains in the resin column.

Banerjee and Heyn[137] adapted the ion-exchange method of Fisher and Kunin[138] for the separation of uranium from bismuth in the range of 0.025 to 0.5 per cent uranium. This ion-exchange procedure differs from those mentioned previously in that the uranium is retained by the resin and the bismuth passes through the column. Uranium is then eluted with perchloric acid and determined colorimetrically.

Procedure. A sulfuric acid solution of the sample containing 50 to 200 mg of bismuth and 2 to 5 ml of sulfuric acid, respectively, is adjusted to pH 1.0 to 1.5 by the dropwise addition of 50 per cent sodium hydroxide solution to the ice-cold solution. The sample solution of 100 ml is passed through a bed of quaternary amine type anion-exchange resin (Dowex 1 X 10) in the sulfate form. The column is washed with dilute sulfuric acid (pH 1.0 to 1.5) until no bismuth is detected in the effluent by the iodide test. Washing is completed by passing through two 10-ml volumes of water. Uranium is eluted with 40 ml of perchloric acid (1+10), and the solution is evaporated to near dryness on a hot plate. The residue is dissolved in a minimum volume of water, and the uranium is determined spectrophotometrically with an alkaline peroxide method.[139] Rigid

control of temperature and volume of the sample solution is necessary to prevent hydrolysis of the bismuth. For each 200 mg of bismuth, 100 ml of solution containing 5 ml of sulfuric acid must be used. The pH adjustment is done in an ice bath, and the sample must be analyzed within 2 hr.

(4) *Volatilization. Bromide.* Milner and Barnett [140] have described a microvolumetric method for bismuth alloys containing 0.005 to 0.1 per cent uranium. The accuracy of the titration is ±1 per cent at the 100-μg uranium level; the lowest determinable amount is about 1 μg. Bismuth is separated by volatilization as the bromide from a solution containing hydrobromic acid and bromine. Iron, an interference in the titration, is eliminated by an ion-exchange separation. The uranium is reduced with a lead reductor and is titrated with ceric sulfate. The method is somewhat tedious and probably not too adaptable for routine analysis. There is no mention of any uranium lost during the volatilization step.

Wild [141] describes a polarographic method for the determination of as little as 10 ppm of uranium in 1 g of bismuth. At the 50-ppm level the coefficient of variation is 1.5 per cent. Bismuth is removed by volatilization of the bromide, and the uranium in the residue is determined polarographically in an acid tartrate medium. If other elements are present to the extent that they interfere with the polarographic measurement, a further separation is made by eluting uranium nitrate from a cellulose column. Although sensitive and accurate, the procedure is rather long for routine analysis. Wild warns that uranium can be lost during volatilization of bismuth bromide if heating is too long or carried out at too high a temperature.

A direct titration method for the determination of cerium in bismuth–uranium–cerium alloys has been described for the range 0.5 to 5 per cent cerium.[142] It is based upon the oxidation of Ce(III) to Ce(IV) by titration with potassium permanganate in a potassium pyrophosphate solution within the pH range of 5.7 to 7.0. The method is an adaption of one described by Marple, Przybylowicz, and Hume.[143] The end point is detected photometrically. Uranium in the range of 1 to 5 per cent is determined by separating the bulk of the bismuth as its volatile bromide and precipitating the uranium as uranyl ammonium phosphate in the presence of EDTA. The precipitate is dissolved in hydrochloric acid. The uranium is then reduced in a lead reductor and titrated with ceric sulfate. Bismuth is reduced to the metal in a lead reductor and therefore must be separated prior to the uranium determination.

(b) *Trace Elements.* Chemical methods have been described for the determination of the trace elements zirconium, iron, manganese,

silicon, phosphorus, carbon, chlorine, and oxygen in bismuth in the range that is of interest for bismuth-matrix liquid fuels.[128]

(c) *X-ray Emission Spectrometry.* X-ray fluorescence has been utilized for the analysis of dispersions of UO_2 in bismuth metal over the range of 2 to 30 per cent uranium.[144] The heterogeneous composition of the mixture precludes analysis in the solid state. The very strong HNO_3 required to keep bismuth in solution presents some hazard in containing the sample solution in a holder with thin Mylar film. Therefore the bismuth and uranium are precipitated with ammonia. The precipitate is dried at 300°C, powdered, mixed and transferred to the sample holder. The fluorescent lines $UL\beta_1$ and $BiL\alpha_1$ are measured and the bismuth/uranium intensity ratio is plotted on a log scale against the weight per cent of uranium. The X-ray spectrograph was equipped with a tungsten 50-kvp 40-ma excitation source and a scintillation counter as detector.

5–1.6 Fissium Alloys

(a) *Uranium–Fissium Alloys.* The Experimental Breeder Reactor-II (EBR-II), a sodium-cooled fast breeder reactor, is fueled with U^{235}. The reactor facility includes a fuel-recycling plant in which the spent fuel will be melt-refined in a pyrometallurgical process that removes the fission products. The fertile and fissionable materials are then refabricated into fuel plates. Only the fission products more volatile and more readily oxidized than uranium are removed. The more noble fission products of atomic numbers 40 through 46 will build up during repeated recycling to an equilibrium concentration; when this concentration is reached, the formation of the fission products is balanced by partial removal in processing, burn-up, and radioactive decay. So that the processing of an alloy that is changing in composition from cycle to cycle can be avoided, the reactor is started with an alloy containing nonradioactive fission elements in approximately equilibrium concentrations. The presence of these elements actually improves the metallurgical properties and radiation stability of the fuel. The alloy containing 0.2 per cent zirconium, 2.5 per cent molybdenum, 1.5 per cent ruthenium, 0.3 per cent rhodium and 0.5 per cent palladium is called 5 per cent fissium alloy. Element number 43, technetium, is not included in the start-up fuel alloy. Technetium, however, is one of the fissium elements, and its determination [145] is of interest in process experiments and as a means of determining fuel burn-up.

Molybdenum is determined by the thiocyanate–stannous chloride method. The Mo(V)–thiocyanate complex is extracted with butyl acetate, and the absorbance is measured at 470 mμ. The accuracy is ± 2 per cent at the 95 per cent confidence level.

Ruthenium is separated by distillation as the tetroxide and determined spectrophotometrically as perruthenate in dilute alkaline hypochlorite solution.[146] The accuracy is ±2 per cent at the 95 per cent confidence level.

Zirconium is separated by NH_4OH precipitation followed by *p*-bromomandelic acid precipitation. The determination of zirconium is made spectrophotometrically as the alizarin sulfonate lake.[147] The accuracy is ±2 per cent at the 95 per cent confidence level.

Rhodium is isolated by paper chromatography and determined by spectrophotometric measurement of the Rh(III) chloro complex formed in HCl–$SnCl_2$ solution.[148] The accuracy is ±3 per cent at the 95 per cent confidence limit. Karttunen and Evans[149] have reported a more rapid separation of rhodium that may be used to advantage for the routine analysis of uranium–fissium alloys. The ruthenium is removed by volatilization, and uranium is extracted with TBP in CCl_4. The rhodium is separated from the other elements by a cation-exchange resin.

Palladium is determined by extracting the palladium–nitroso naphthalate formed in slightly acidic solution and reading the absorbance at 370 mμ.[150] The metals iron, cobalt, nickel, copper, chromium, and zirconium and the platinum metals do not interfere. The accuracy is ±5 per cent at the 95 per cent confidence level.

Technetium is determined spectrophotometrically as the dithiol complex after separation of technetium by distillation.[145]

Procedure: Dissolution. A 4- to 5-g sample of uranium–fissium alloy in 25 ml of H_2O is dissolved with 50 ml of a solution containing 5 parts of HCl and 1 part of HNO_3 and 3 to 4 drops of HF. Heat is applied to hasten dissolution. If the alloy dissolves completely, the solution is diluted to 50 or 100 ml in a volumetric flask with 8*N* HCl. If solution is not complete, the sample is centrifuged, and the solution is poured off. The residue is washed with 8*N* HCl. Five milliliters of the (5+1) HCl-HNO_3 mixture is added to the residue, and the mixture is heated. If the residue dissolves, the solution is combined with the original solution. If solution is still incomplete, the residue is separated by centrifuging. The black residue, probably ruthenium, is treated with 2 ml of 2*N* NaOH plus 1 ml of hypochlorite solution prepared by mixing 15 parts of 1*N* NaOH with 1 part of 5 per cent sodium hypochlorite solution. It may be necessary to warm the mixture to complete the dissolution. The solution is acidified with dilute HCl, heated gently to completely decompose the excess hypochlorite, as evidenced by cessation of bubble formation, and is added to the original solution.

Procedure: Molybdenum. An aliquot of the sample solution from the dissolution step containing 20 to 180 μg of molybdenum (60 to 70 μg optimum) is treated with 3 ml of 9*M* H_2SO_4 and 2 ml of $HClO_4$ and heated to fumes. The walls of the beaker are washed down with H_2O. Ten milliliters of 9*M* H_2SO_4 is added, and the solution is evaporated and strongly fumed for 3 min to ensure complete removal of NO_3^- and Ru.

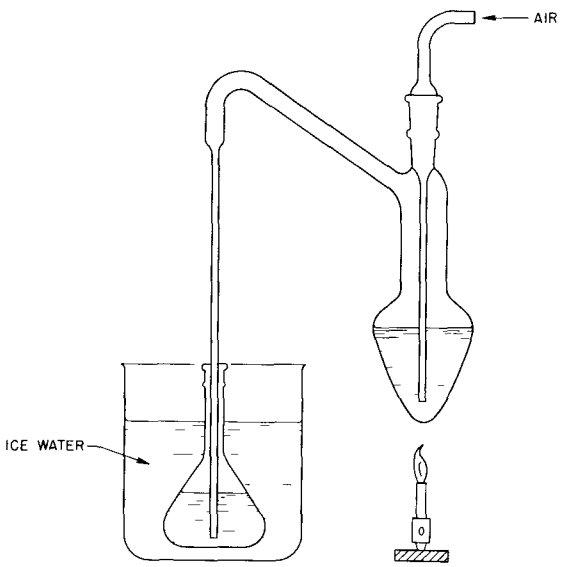


Fig. 5.1—Distillation setup for the determination of ruthenium in uranium–fissium alloys.

The solution is cooled, 10 ml of H_2O is added, and the solution is transferred to a 60-ml separatory funnel with two 5-ml portions of H_2O. The time is noted, and 1 ml of 0.025 *M* Fe $(NH_4)_2(SO_4)_2$ made up in 1 *M* H_2SO_4, 2 ml of 20 per cent KSCN solution, 3 ml of $SnCl_2$ solution (87 g of $SnCl_2$ dissolved in 25 ml of HCl and made up to 250 ml with H_2O), and 20 ml of butyl acetate are added. The mixture is shaken for 2 min. The phases are allowed to separate, and the lower aqueous phase is drawn off and discarded. The organic phase is transferred to a 25-ml volumetric flask. The separatory funnel is rinsed with butyl acetate. If the solution is slightly cloudy, 0.5 ml of anhydrous ethyl alcohol is added. The solution is made up to volume with butyl acetate. The absorbance is read 40 to 60 min after the addition of the $Fe(NH_4)_2(SO_4)_2$ at 470 mμ against a reference of butyl acetate.

Procedure: Ruthenium. An aliquot of the uranium–fissium alloy solution from the dissolution step containing 0.3 to 0.7 mg of ruthenium is treated with 1 ml of HCl and 0.5 ml of H_2SO_4. The solution is heated to fumes of H_2SO_4 to eliminate NO_3^-. The walls are washed with a few drops of HCl, and the solution is fumed again. The solution is cooled and transferred to the distillation flask, Fig. 5.1. A slurry of 0.5 g of $NaBiO_3$ in 5 ml of 6*N* H_2SO_4 is added to the sample. Air is bubbled through at the rate of 2 bubbles per second. The acidity should not exceed 6*N* H_2SO_4. The distillation flask is heated with a microburner, and 5 ml is distilled over in 8 to 10 min. The receiver is a 25-ml volumetric flask containing 1 ml of 5% sodium hypochlorite solution and 15 ml of 1*N* NaOH cooled in an ice bath. The receiving flask is lowered, and the delivery tube is washed with 1*N* NaOH. The distillate is warmed to room temperature and made up to 25 ml with 1*N* NaOH. The absorb-

ance is read at 385 mμ using 1-cm cells against a reference of 1 ml of 5 per cent sodium hypochlorite solution diluted to 25 ml with 1*N* NaOH.

Procedure: Zirconium. An aliquot of the sample solution from the dissolution step is taken containing 0.2 to 0.4 mg of zirconium. Three milliliters of HCl and 2 ml of H_2SO_4 are added, and the solution is heated to fumes of SO_3. The beaker walls are washed, and the fuming is repeated to ensure removal of NO_3^- and Ru. The solution is transferred to a 40-ml centrifuge tube and made slightly ammoniacal. The slurry is centrifuged, the supernate is removed, and the precipitate is dissolved with 10 drops of HCl and 10 ml of H_2O. If more than 30 mg of uranium is present, the ammonium hydroxide precipitation is repeated. Two milliliters of HCl is added, and the solution is made up to 10 ml with H_2O. Five milliliters of 2.9% *p*-bromomandelic acid solution is added and the precipitate is digested for 1 hr on a steam bath. A few milliliters of 1 per cent Aerosol OT is added to the cooled solution to prevent creeping. The solution is centrifuged, and the supernatant liquid is removed by aspiration. Eight drops of HNO_3, 25 drops of H_2SO_4, and 15 drops of $HClO_4$ are added to the precipitate of zirconium *p*-bromomandelate, and the solution is heated with a Cenco hot-cone heater to strong fuming until completely converted to sulfate. The solution is cooled, 20 mg of uranium is added, and the zirconium and uranium are precipitated with NH_4OH. The supernatant liquid is removed by aspiration. The precipitate is dissolved with 10 ml of 1.2*M* HCl and heat. The cooled solution is transferred to a 100-ml volumetric flask and diluted to about 80 ml with H_2O. Five milliliters of 0.05 per cent sodium alizarin sulfonate reagent is added, and the solution is made up to the mark with H_2O. After 1 hr the absorbance is measured in a 1-cm cell at 520 mμ against a reference containing 10 ml of 1.2*M* HCl and 5 ml of sodium alizarin sulfonate diluted to 100 ml with H_2O.

Procedure: Rhodium. An aliquot of the sample solution from the dissolution step containing 35 to 200 μg of rhodium (100 to 125 μg optimum) is transferred to a small beaker, and 3 to 4 drops of HCl and 2 drops of HNO_3 are added. The solution is evaporated as low as possible without going dry ~250 μl. The chromatographic paper, Eaton–Dikeman, grade 301, is 3 in. wide and 36 in. long. The paper is folded lengthwise, and a line is drawn 5 in. each way from the fold. The sample solution is spotted in the center section of one line (two samples can be chromatographed simultaneously). The beaker is washed twice with a few drops of 2*M* HCl, and the washes are spotted on either side of the sample. The paper is allowed to dry for 30 min. The paper is suspended in a covered 2- by 1-ft chromatographic jar with the center fold immersed in the solvent composed of 60 per cent hexone, 30 per cent HCl, and 10 per cent amyl alcohol. Diffusion is continued until the solvent wets three-fourths the length of the paper. The paper is marked ½ in. on either side of the pink rhodium band occurring approximately one-third of the distance from the origin to the solvent front. The paper is dried, and the marked area is cut out. The rhodium is leached from the paper by boiling with 60 ml of 4*M* HCl for 5 min. The slurry is filtered by suction through Whatman No. 42 paper, and the paper is washed with H_2O. The filtrate is evaporated to 5 ml. Five milliliters of HNO_3 is added, and the solution is evaporated to 3 ml. Two milliliters of H_2SO_4 and 3 ml of $HClO_4$ are added, and the solution is evaporated to strong fumes. The cover and sides are washed down with H_2O,

and the solution is fumed down to about 0.5 ml. The cover and sides are washed with HCl, and the fuming is repeated twice. Four milliliters of HCl is added, and the solution is heated to boiling. The solution is cooled, and 10 ml of 10 per cent $SnCl_2$ solution is added. The solution is brought to boiling and digested on a steam bath for 1 hr. The solution is cooled, transferred to a 50-ml volumetric flask, and diluted to volume with 2*M* HCl. The absorbance is read at 470 mμ in 5-cm cells against a reference of H_2O.

Procedure: Palladium. An aliquot of the sample solution from the dissolution step containing 10 to 50 μg of palladium (25 μg optimum) is transferred to a 60-ml separatory funnel and diluted to 30 to 40 ml with H_2O. Two milliliters of 3 per cent EDTA is added, and the pH is adjusted to 1 to 2. The NH_4OH present should not exceed 12 milliequivalents. If necessary the sample should be evaporated to reduce the acid concentration. One hundred microliters of a 1 per cent alcoholic solution of 2-nitroso-1-naphthol is mixed in the solution, and the mixture is allowed to stand 10 min. Ten milliliters of toluene is added, and the mixture is shaken for 1 min. The aqueous phase is discarded, and the organic phase is washed with 10 ml of 1*N* NaOH to remove excess reagent. The organic phase is transferred to a 1-cm cell. If the toluene is cloudy, it can be cleared by centrifuging for 1 min. The absorbance is measured at 370 mμ against toluene. A reagent blank is run through the entire procedure.

Procedure: Technetium.[145] The uranium–fissium alloy can be analyzed for as little as 0.001 per cent of technetium. An aliquot of the fissium alloy from the dissolution step is treated with HBr and H_2SO_4 and distilled. The fraction coming over above 155°C is collected. The technetium–dithiol complex is formed in 7*N* to 10*N* H_2SO_4 and is extracted into isoamyl acetate. The absorbance is read at 450 mμ against a blank carried through the procedure. The molar absorbance index of the yellow complex is approximately 19,000.

(b) *Uranium–Plutonium–Fissium Alloys.* Larsen and Seils[151] have described methods for the determination of uranium and plutonium in fissium alloys. The fission elements palladium, rhodium, and ruthenium are reduced to metals by the addition of magnesium to an HCl solution of the alloy and removed by filtration. The U(IV) is separated from the Pu(III) by extraction with tributyl phosphate–CCl_4 from 8*M* HCl solution. The uranium is stripped from the organic layer with 0.2*M* HCl, and converted to a HNO_3 medium, and the uranium is determined by an X-ray emission spectrometric method.[152] The uranium can be determined spectrophotometrically with somewhat less precision and accuracy. The uranium in the 0.2*M* HCl strip solution is precipitated with NH_4OH using lanthanum as carrier. The precipitate is dissolved in HCl, and the uranium is determined by the thiocyanate[153] or the acid–peroxide method.[154] Alternatively the uranium in the 0.2*M* HCl strip solution can be extracted and determined spectrophotometrically with dibenzoyl-

methane.[155, 156] The Pu(III) remaining in the aqueous phase is oxidized to Pu(IV) with $NaNO_2$ and extracted with TBP–Amsco-140. The plutonium is stripped from the organic phase with 0.2*M* HCl. The plutonium is precipitated by the addition of NH_2OH–HCl and NaOH. The $Pu(OH)_3$ is dissolved with 16*M* HNO_3, and the plutonium is determined by measuring the absorbance of the Pu(IV) nitrate complex at 475 mμ against a reagent blank.

If only the determination of plutonium is desired, plutonium can be separated from the alloy solution by coprecipitation of PuF_3 with LaF_3.[151] The PuF_3 is dissolved in a $Zr(NO_3)_4$–HNO_3 mixture, and the Pu(IV) nitrate complex is measured spectrophotometrically. Coefficients of variation for both the uranium and plutonium determinations are better than 1 per cent.

The uranium–plutonium–fissium alloy that is proposed as a recycling fuel contains 70 per cent uranium, 20 per cent plutonium, and 10 per cent fissium. This alloy can be dissolved as described for the uranium–fissium alloy, although the higher concentration of the relatively inert platinum metals lengthens the dissolution time. Alloys containing relatively large amounts of zirconium are very difficult to dissolve and require a three-step operation. The alloy is refluxed with a mixture of 5 parts HCl to 1 part HNO_3 for 2 hr. The residue is separated and treated with NaOH and NaClO to dissolve ruthenium. The residue is separated and treated with HNO_3 and HF, fumed to just dryness with $HClO_4$, and dissolved with dilute HCl.

The most convenient way to dissolve the alloy is in sealed quartz tubes at elevated temperatures, a technique originally reported by Wichers, Schlecht, and Gordon.[174] Smith[207] has used this method for dissolving plutonium alloys containing rhodium and platinum. A 0.5-g sample of uranium–plutonium–fissium alloy in an 8-mm-ID quartz tube with 2-mm walls is treated with 5 ml of HCl. When the reaction has ceased, 3 drops of $HClO_4$ or 5 drops of HNO_3 are added, and the quartz tube is sealed at a length of 11 to 12 in. The quartz tube is encased in a steel shell and heated as described for the dissolution of the UO_2–CaO–ZrO_2 ceramic in Sec. 5–2.1(b).

The alloying elements molybdenum, palladium, and ruthenium can be determined by the procedures described for uranium–fissium alloy. The separation of rhodium by paper chromatography as described for uranium–fissium alloy is not adaptable to plutonium alloys. Ion-exchange[208] is used to isolate the rhodium prior to the spectrophotometric determination as the Rh(III) chloro-complex. The zirconium is separated from plutonium by ion-exchange[157] and determined spectrophotometrically with sodium alizarin sulfonate.

Procedure: Rhodium. An aliquot of the uranium–plutonium–fissium alloy solution containing 50 to 150 μg of rhodium is transferred to a 40-ml centrifuge tube, and 200 μl of $HClO_4$ is added. The solution is heated to fumes. The solution is cooled, the sides of the container are rinsed with 500 μl of HCl, and the solution is heated until clear. The volume is increased to 5.5 ml with 8*M* HCl, and 0.5 ml of HNO_3 is added. The solution is heated until gas evolution occurs. Heating is discontinued, and the solution is allowed to stand 2½ hr. The solution is passed through a column of the strongly basic anion-exchange resin (Dowex 1 X 10). The column is washed with 8*M* HCl until a total volume of 45 to 50 ml has been collected. Two milliliters of H_2SO_4 is added, and the solution is evaporated to fumes. About 0.5 ml of $HClO_4$ is added to the hot H_2SO_4, and the fuming is continued for 1 to 2 min. The beaker is cooled, the cover and sides are rinsed with 8*M* HCl, and the solution is heated to copious fumes. The rinsing and fuming is repeated once more to ensure removal of ruthenium, NO_3^-, and organic matter. After the final fuming the volume should be about 0.5 ml of H_2SO_4. The determination is completed as described for uranium–fissium alloys.

Procedure: Zirconium. An aliquot of the uranium–plutonium–fissium alloy solution containing 40 to 100 μg of zirconium prepared as indicated in Sec. 5–1.6(b) is transferred to a small beaker. The acidity is adjusted to 10*N* with HNO_3, and the solution is allowed to stand overnight. The solution of the alloy is passed through the strongly basic anion-exchange resin, Dowex 1 X 10. The column is washed with 25 to 30 ml of 10*N* HNO_3. The eluate should contain less than 60 μg of plutonium as determined by alpha assay. The eluate is evaporated to 5 to 10 ml, and 5 drops of $HClO_4$ are added. The solution is fumed to remove ruthenium. After the solution has cooled, 200 μl of HNO_3 is added, and the solution is refluxed for 20 to 30 min to ensure complete dissolution of the zirconium. The solution is transferred to a 25-ml volumetric flask and diluted to 15 ml with H_2O. Five milliliters of 0.0125 per cent sodium alizarin sulfonate is added, and the volume is made up to the mark with H_2O. The well mixed solution is allowed to stand 1½ hr. The absorbance is measured in a 1-cm cell at 520 mμ against a reference of 0.12*N* HNO_3 containing sodium alizarin sulfonate.

5–2 CERAMICS

Ceramics inherently have the properties of dimensional stability, chemical inertness, and the ability to withstand high temperatures. The development of reactors designed to operate at elevated temperatures emphasizes the need for reactor materials with these qualifications. The use of ceramics may also result in a reduction of construction costs. One of the most economical nuclear fuel assemblies to fabricate is the cermet of aluminum–U_3O_8 clad with aluminum. This fuel plate is produced by hot extrusion of a mixture of aluminum and uranium oxide powders contained in an aluminum can. The nonmetallic uranium ceramic fuels are very stable and do not distort under intense radiation at high temperatures. The oxide fuels are not nearly so subject to corrosion by water as the metallic fuel elements

are. Therefore uranium oxide ceramics are suitable not only as fuels in high-temperature gas-cooled reactors but also in water-cooled or boiling-water reactors. The relatively poor heat-transfer characteristics of the oxide fuels has stimulated interest in materials of higher thermal conductivity, such as uranium carbide and uranium sulfide. Other systems are under investigation. One in particular that suggests interesting possibilities is a solution of uranium oxide in glass. Procedures for the determination of uranium and other major constituents are arranged under the various methods of dissolving the ceramics since the solution of the sample is in many cases the most difficult part of the entire analysis.

5–2.1 Methods of Dissolution

(a) *Acid.* (1) *Nitric Acid + Fluoride + Perchloric Acid: ThO_2–UO_2.* Thorium oxide–uranium oxide ceramics are dissolved in nitric acid containing a trace of fluoride ion. The fluoride ion, which acts as a catalyst in dissolving the thorium oxide, is added as hydrofluoric acid or sodium fluoride if platinum beakers are used. If glassware is used, fluosilicic acid or a fluosilicate is preferred to prevent etching. The sample solution is converted to perchlorate for the volumetric determination of uranium. The relative standard deviation of a single measurement is 0.08 per cent.[158]

If a significant amount of iron is present, as determined by colorimetric analysis using 1,10-phenanthroline,[159] the uranium result must be corrected.

The procedure has been applied to the analysis of the BORAX–4 fuel, a typical thorium oxide–uranium oxide ceramic containing nominally 6.35 per cent of UO_2 (93 per cent enriched).

> *Procedure: Uranium.* A sample of the pulverized thorium oxide–uranium oxide ceramic containing 100 to 125 mg of uranium is dissolved by heating with 6*N* nitric acid containing 0.01*M* to 0.03*M* fluoride. After the sample is completely dissolved, 10 ml of perchloric acid is added, and the solution is evaporated to fumes. The beaker is cooled, the walls are washed with water, and the fuming is repeated to ensure complete removal of nitrate. After it has cooled, the perchloric acid solution of the sample is diluted to 50 ml with 3*N* hydrochloric acid and passed through a lead reductor. The column is washed with 150 ml of 0.8*N* hydrochloric acid. Twenty-five milliliters of 12*N* sulfuric acid and 50 μl of ferroin are added to the combined eluates. An excess of standard 0.05*N* ceric sulfate is added from a weight buret, and the excess is back-titrated with standard 0.025*N* ferrous sulfate from a weight buret.

The ceramic containing 8.93 per cent of uranium dioxide (93 per cent enriched), zirconium oxide, and calcium oxide was used to spike

the Experimental Boiling Water Reactor (EBWR). This ceramic can be dissolved by the acid treatment outlined below. However, the sealed-tube method of dissolution described in Sec. 5–2.1(b) is recommended.

Procedure. A 1-g pulverized sample is treated with 25 ml of a mixture of 1 part hydrofluoric acid plus 4 parts nitric acid in a platinum beaker, and the solution is evaporated to near dryness on a steam bath. After repeating the mixed-acid treatment and evaporation, 15 ml of perchloric acid is added, and the solution is heated to fumes on a hot plate. The cover and walls of the beaker are washed with water, and the fuming is repeated to ensure removal of fluoride. Fifty milliliters of water is added, and the solution is heated to boiling. If any insoluble material remains, it is filtered off, ignited, and dissolved by treatment with hydrofluoric acid and fuming with perchloric acid; then the resulting solution is added to the filtrate. Procedures for the determination of uranium, zirconium, and calcium are given in Sec. 5–2.1(b).

(2) *Nitric Acid+Hydrochloric Acid: La_2O_3–UO_2.* The ceramic lanthanum oxide–uranium oxide is dissolved with a mixture of nitric and hydrochloric acids. The solution is converted to chloride, and the lanthanum and uranium are isolated by ion exchange. Lanthanum is determined either gravimetrically or volumetrically as the oxalate, and uranium is determined volumetrically by cerate oxidimetry. If only uranium is to be determined, the ion-exchange separation can be omitted.

The procedure, applicable over a wide range, was used for the analysis of samples containing 25 to 95 per cent of uranium for phase-equilibrium determinations.

Procedure: Lanthanum. A pulverized sample of the lanthanum oxide–uranium oxide ceramic containing about 100 mg of lanthanum is dissolved by heating it with 10 ml of aqua regia (1 part nitric acid to 3 parts hydrochloric acid). After the sample is completely dissolved, 5 ml of hydrochloric acid is added, and the solution is evaporated to dryness on a steam bath. The residue is dissolved with 20 ml of 9*N* hydrochloric acid. A 16-mm-ID ion-exchange column 11 cm in length, containing about 20 ml of Dowex 1 X 10, 200 to 400 mesh, chloride form, is prepared by washing the column with 9*N* hydrochloric acid. The sample solution is passed through the column at the rate of 2 to 3 ml per minute. The column is washed with 75 ml of 9*N* hydrochloric acid in 10- to 15-ml portions. The effluent containing the lanthanum is evaporated to dryness on a steam bath. The residue is dissolved with 10 ml of water; the solution is then heated to near boiling, and 50 ml of hot 1*N* oxalic acid is added slowly with stirring. The mixture is heated to boiling for a few minutes and allowed to stand for at least 2 hr, or preferably overnight, at room temperature. The column is freed of uranium in preparation for the next sample by eluting the uranium with 100 ml of 1*N* hydrochloric acid. The lanthanum in the

oxalate precipitate is determined by a gravimetric or a volumetric method.

Gravimetric Method. The supernatant liquid is filtered through a No. 42 Whatman filter paper or equivalent containing a mat of filter pulp prepared by filtering a water slurry of filter pulp through the paper. After the bulk of the supernatant has been filtered, the precipitate is slurried with a small amount of filter pulp and transferred to the filter by washing with 20 ml of 1*N* oxalic acid. The filtrate must be absolutely clear and should be closely observed for the presence of any lanthanum oxalate that might have passed through the filter. The paper, plus precipitate, is dried, charred, and finally ignited to La_2O_3 in platinum at 800 to 850°C.[160]

Volumetric Method. The precipitate of lanthanum oxalate is filtered onto a fritted-glass crucible of fine porosity and washed very thoroughly with 300 ml of water at room temperature.[160] Methyl orange is added to the last portions of the filtrate to determine whether all absorbed oxalic acid has been removed. The color produced should match that formed by the addition of methyl orange to the wash water. The lanthanum oxalate is dissolved on the filter with hot sulfuric acid (5+95). The precipitate is broken up and stirred while successive portions of the acid solution, totaling 100 ml, are drawn through the filter. The solution is cooled to 30°C, and the oxalate is titrated with standard 0.05*N* potassium permanganate. Approximately 90 per cent of the titrant required is added. The solution is heated to 60°C, and the titration is completed to a faint pink color that persists for 30 sec.

Procedure: Total Uranium. A sample selected to contain 80 to 100 mg of uranium is dissolved with 10 ml of aqua regia or 5 ml of perchloric acid. If aqua regia is used, 5 ml of sulfuric acid is added, and the solution is taken to vigorous fuming twice to remove the nitrate ion. The perchloric or sulfuric acid solution is diluted with 50 ml of 3*N* hydrochloric acid, and the uranium is determined volumetrically as described in Sec. 5-2.1(a)(1).

It is imperative to know the uranium to oxygen ratio when determining the equilibrium phase diagram for the lanthanum oxide–uranium oxide system. Although accurate total uranium, lanthanum, and oxygen analyses will provide this information, a simpler approach is to determine the tetravalent uranium.

Procedure: Uranium as U^{+4}. A weighed sample containing about 100 mg of uranium is dissolved by treating it with a measured excess of standard 0.05*N* ceric sulfate and 25 ml of 6*N* sulfuric acid in a flask with a ground-glass joint. The integrity of the ceramic is preserved by submitting the samples in sealed glass ampoules. The ampoule is broken beneath the surface of the ceric sulfate solution by striking it with a glass rod. The flask is attached to a reflux condenser and the mixture is heated to boiling and refluxed until the sample is completely in solution. The condenser is washed down, and the solution is cooled to room temperature. The excess ceric sulfate is titrated with standard 0.025*N* ferrous sulfate using ferroin indicator. The U^{+4} is calculated

from the difference between the original amount of ceric sulfate and the ceric sulfate remaining after complete solution of the sample.

(3) *Hydrofluoric Acid + Nitric Acid: UO_2–Glass.* Uranium oxide–glass mixtures to be analyzed for sodium and calcium are dissolved by treatment with hydrofluoric acid and nitric acid. Sodium is determined by precipitation with magnesium uranyl acetate. Calcium is determined by titration with ethylenediaminetetraacetic acid (EDTA) after an ion-exchange separation of the uranium.

Procedure: Sodium. A pulverized sample of the UO_2–glass is dissolved by treatment with hydrofluoric acid and nitric acid in a platinum beaker. The solution is evaporated to dryness, the residue is dissolved in water, and the solution is transferred to a volumetric flask. The solution should be free of silica and fluoride ion. An aliquot containing 10 to 20 mg of sodium is evaporated to less than 5 ml, and the sodium is precipitated and weighed[161] as $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2 \cdot (C_2H_3O_2)_2\, 6\frac{1}{2}H_2O$.

Procedure: Calcium. An aliquot of the nitric acid solution of the sample prepared for the determination of sodium is evaporated several times with hydrochloric acid to convert all salts to chlorides. The residue after the final evaporation is dissolved with 9*N* hydrochloric acid, and the uranium is separated by ion-exchange as described in Sec. 5–2.1(a)(2). The effluent is evaporated to dryness and dissolved with 50 ml of boiling water containing 5 drops of hydrochloric acid. Five milliliters of 1*M* KOH containing 1 g of KCN per 100 ml is added. The cyanide will mask any iron or copper that may be present. The pH should be above 12. About 10 mg of modified Calcein indicator[162] mixture, prepared by grinding together 0.2 g of Calcein, 0.12 g of thymolphthalein, and 20 g of KCl, is dissolved in the solution. The calcium is titrated with standard 0.01*M* EDTA solution, with vigorous stirring, to the color change of green to purple.

(4) *Hydrofluoric Acid + Perchloric Acid: UO_2–Glass.* Uranium oxide–glass is prepared for the analysis of potassium by dissolving with hydrofluoric acid and perchloric acid. Potassium is determined by the perchlorate method.

Procedure: Potassium. A pulverized sample of UO_2–glass is treated in a platinum beaker with 10 ml of hydrofluoric acid and 10 ml of perchloric acid. The mixture is heated to fumes of perchloric acid, boiled almost to dryness to remove excess perchloric acid, and cooled. If the mixture is not completely soluble in 25 ml of water, the treatment with hydrofluoric acid is repeated. When complete dissolution is achieved upon the addition of 25 ml of water, 5 ml of perchloric acid is added, and the fuming almost to dryness is repeated to eliminate traces of fluoride. Potassium is determined by the perchlorate method.[163]

(5) *Sulfuric Acid: US and ThS.* The refractory inorganic sulfides of uranium and thorium are analyzed for insolubles, sulfide

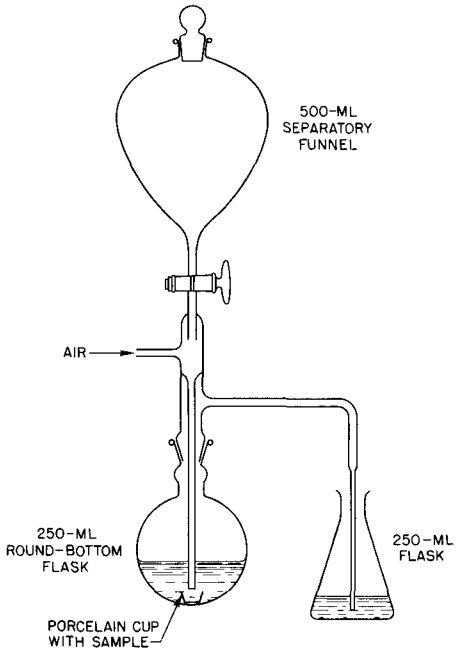


Fig. 5.2—Distillation setup for the determination of sulfide sulfur in US and ThS.

sulfur, total sulfur, and either uranium or thorium. Sulfide sulfur is determined by measuring the hydrogen sulfide evolved when the sample is dissolved with sulfuric acid.[164] An insoluble residue at this stage is usually indicative of oxygen contamination in the original sulfide. The dried residues from uranium sulfide samples show the characteristic X-ray diffraction patterns of UO_2, UOS, and uranium alone or in combination. Uranium or thorium is determined in the sulfuric acid solution of the sample by volumetric or gravimetric methods.

Procedure: Sulfide Sulfur. A sample of uranium or thorium sulfide weighing 50 to 100 mg and contained in a small porcelain cup is placed in the round-bottom flask shown in Fig. 5.2. The end of the delivery tube is immersed in the solution in the receiving flask which contains 10 ml of 0.1*N* standard silver nitrate, 30 ml of 6*N* ammonium hydroxide, and 50 ml of water. Air is slowly bubbled through the system to provide stirring and to sweep evolved gases into the receiving flask. Approximately 100 ml of 10 per cent sulfuric acid (~3.6*N*) is added to the round-bottom flask from the separatory funnel. This flask is heated with a Meker burner, and the solution is boiled vigorously to evolve all the hydrogen sulfide. Boiling is continued until the steam passing over into the receiving flask has heated the solution thereby aiding in the digestion of the precipitated silver sulfide and causing it to coagulate. This should require 15 to 20 min. The receiving flask is lowered, and

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the steam is allowed to condense a minute or two longer to wash the inside of the delivery tube. The silver sulfide is filtered off through Whatman No. 40 filter paper and washed with hot water. The filtrate is cooled and acidified with 30 ml of concentrated nitric acid, and 2 ml of 20 per cent ferric alum is added as indicator. The excess silver nitrate is titrated to a faint orange color with standard 0.1*N* potassium thiocyanate using a 10-ml buret.

Procedure: Insoluble Residue. The residue remaining in the round-bottom flask after volatilization of the sulfide sulfur is determined by filtering the sulfuric acid solution of the sample through a tared 15-ml sintered-glass crucible of fine porosity. The residue is washed with water, dried at 110° C, and weighed.

Volumetric Procedure: Uranium. After removal of any insoluble residue, the sulfuric acid solution of the sample is evaporated to approximately 2 or 3 ml and diluted to 50 ml with 3*N* hydrochloric acid. Uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

Gravimetric Procedure: Uranium. A gravimetric determination of the uranium may be preferred as for example in the analysis of an occasional sample. The sulfuric acid solution is evaporated to about 100 ml. Uranium is precipitated by the addition of a slight excess of carbonate-free ammonium hydroxide to the hot solution. The precipitate is digested 10 to 15 min or until the precipitate has coagulated. The solution is filtered through Whatman No. 42 filter paper. The precipitate is washed with hot ammoniacal 2 per cent ammonium nitrate and ignited to constant weight as U_3O_8 at 850°C.

Procedure: Thorium. The filtered solution from the round-bottom flask is evaporated, and the excess sulfuric acid is carefully fumed off. The residue is dissolved with 0.4*N* hydrochloric acid, and the thorium is precipitated as the oxalate and ignited to ThO_2.[165]

Thorium can also be separated from the excess sulfuric acid by precipitation with ammonium hydroxide. Either the precipitate is dissolved with dilute hydrochloric acid and the thorium precipitated as the oxalate or the precipitate is ignited directly to ThO_2. If the thorium hydroxide is ignited, then a reprecipitation of the thorium hydroxide is recommended. The thorium hydroxide carries down sufficient sulfate ion in the first precipitation that prolonged ignition at high temperature is required to reach constant weight of ThO_2.

(6) *Nitric Acid + Bromine: US and ThS.* Total sulfur is determined in uranium or thorium sulfide by dissolving the sample with an oxidizing mixture of nitric acid and bromine. The solution is converted to chloride, and the sulfate is precipitated, ignited, and weighed as barium sulfate.

Procedure: Total Sulfur. A sample of uranium or thorium sulfide weighing 150 to 200 mg is treated with 10 ml of a bromine–potassium bromide mixture prepared by dissolving 16 g of potassium bromide in a minimum amount of water, adding 10 g of bromine, and diluting to 100 ml with water.[166] After the solution has stood for 15 min in a cold-water bath with occasional swirling, 15 ml of nitric acid is added,

and the mixture is allowed to stand for an additional 15 min at room temperature. The beaker is heated gently on a steam bath until the reaction has ceased and the bromine has been volatilized. The solution is evaporated to dryness. Ten milliliters of concentrate hydrochloric acid is added, and the solution is again evaporated to dryness to remove nitrate ion. The residue is dissolved with 2 ml of hydrochloric acid and diluted to 200 ml with hot water. The solution is heated to boiling, and a 1 to 2 ml excess of a 10 per cent solution of barium chloride is added dropwise with constant stirring. The barium sulfate precipitate is digested for at least 1 hr on a steam bath. The solution is filtered through a tared porcelain filtering crucible of fine porosty. The barium sulfate is washed with warm water until 25 ml of washings tested with silver nitrate is only faintly opalescent. The crucible and contents are dried at 110°C and finally heated at approximately 850°C to constant weight.

(7) *Nitric Acid + Sulfuric Acid: UO_2–MgO and U_3O_8–MgO.* The ceramic UO_2–MgO or U_3O_8–MgO is dissolved with nitric acid. If only uranium is to be determined, 5 ml of sulfuric acid is added, and the solution is fumed to remove the nitrate ion. The uranium is determined volumetrically as described in Sec. 5–2.1(a)(1). Uranium and magnesium are determined by separating the uranium by a double ammonium hydroxide precipitation in the presence of sufficient ammonium chloride to prevent precipitation of the magnesium. The precipitate is filtered off and either ignited and weighed as U_3O_8, or dissolved and the uranium determined volumetrically. Magnesium is determined in the filtrate by precipitation as magnesium ammonium phosphate and ignition to pyrophosphate.[167] Magnesium can also be determined volumetrically by titration with EDTA.[168]

UO_2–Nd_2O_3 and UO_2–Al_2O_3. The ceramics UO_2–Nd_2O_3 and UO_2–Al_2O_3 are dissolved by treating the pulverized sample with nitric acid and fuming with sulfuric acid until all the nitrate ion has been removed. Uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

UO_2–BeO. The highly refractory fuel pins composed of pellets fabricated from a mixture of nearly equal amounts of UO_2 and BeO which are then extruded and sintered at 1500 to 1900°C are difficult to dissolve. The most efficient method is a two-solution treatment, first with nitric acid to dissolve the UO_2 and then with sulfuric acid to dissolve the separated BeO.[169] The sealed-tube technique described in Sec. 5–2.1(b) for dissolving the UO_2–CaO–ZrO_2 ceramic can be used to advantage for this ceramic.

If only uranium is to be determined, the volumetric procedure described in Sec. 5–2.1(a)(1) is followed. The procedures given here include the separation and determination of uranium and beryllium. Brinton and Ellestad[170] separated beryllium from uranium by precipitating the bulk of the beryllium as the basic carbonate with ammo-

nium carbonate and then precipitating the beryllium remaining in the filtrate with ammonia in the presence of hydroxlyamine. Beryllium is weighed as BeO, and uranium is weighed as U_3O_8 after acidifying the solution, boiling, and precipitating with NH_4OH. Although quite satisfactory results can be obtained with this procedure, it requires a double precipitation of the beryllium. The more rapid procedure adapted from the method of Kolthoff and Sandell [171] for the separation of aluminum and beryllium which requires only a single precipitation with 8-hydroxyquinoline will be described.[172] Uranium is precipitated and weighed as $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$, and beryllium is precipitated as the phosphate and weighed as $Be_2P_2O_7$.

This procedure is superior when less than 100 mg of sample is available because of the favorable gravimetric factors. Beryllium pyrophosphate, unlike beryllium oxide, is not hydroscopic and consequently is a more suitable weighing form. The method was used for the analysis of UO_2–BeO ceramic pins over the range of 20 to 60 per cent of UO_2.

Procedure: Uranium. The UO_2–BeO sample containing not more than 100 mg of either oxide is treated with hot (1+1) nitric acid until most of the UO_2 is dissolved leaving a BeO skeleton. The uranium solution is decanted, and the BeO is dissolved in (1+9) sulfuric acid by heating under reflux. Several hours may be required to effect complete solution. The combined acid solution is neutralized with ammonium hydroxide until the solution is only weakly acid. The volume is adjusted to about 100 ml, and the solution is heated to 70 to 80°C. About 15 ml of a 5 per cent 8-hydroxyquinoline in 2*N* acetic acid is added, and uranyl oxinate is precipitated by the slow addition of 2*N* ammonium acetate. After a permanent precipitate is formed, 15 ml more of the 2*N* ammonium acetate is added to ensure complete precipitation. The precipitate is allowed to settle and is then filtered through a weighed sintered-glass crucible. The uranyl oxinate is washed with 2 per cent ammonium acetate solution, dried to constant weight at 120°C, and weighed as $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$. The relative error is 0.80 per cent over the range of 24 to 70 mg of uranium.

Procedure: Beryllium. The filtrate remaining after removal of the uranium oxinate is evaporated to near dryness, and the organic salts are destroyed by repeated additions of nitric and hydrochloric acids followed by evaporation. The solution is diluted to 250 to 300 ml, and 5 g of ammonium chloride is added. Beryllium hydroxide is precipitated by adding ammonium hydroxide until alkaline to methyl red (pH 6.3). Ten to fifteen milliliters of 10 per cent ammonium dihydrogen phosphate solution is added, and the solution is made acid to methyl red (pH 4.2). The solution is heated on a steam bath or hot plate for 1 to 2 hr until the amorphous precipitate of $Be(OH)_2$ has changed to finely crystalline $BeNH_4PO_4 \cdot xH_2O$. The supernatant solution is adjusted to pH 6.3 using methyl red indicator without agitating the precipitate. Digestion is continued until the supernatant solution is clear.

The cool solution is decanted through a Whatman No. 42 filter paper, and the precipitate is washed with a hot 1 per cent solution of ammonium nitrate made basic to methyl red with a few drops of ammonium hydroxide. The precipitate is ignited at 900°C and weighed as $Be_2P_2O_7$.

(8) *Nitric Acid + Perchloric Acid: UO_2–CaO.* The ceramic UO_2–CaO is dissolved with nitric acid and fumed with perchloric acid to remove the nitrate ion. The perchloric acid solution is diluted with 3*N* hydrochloric acid and the uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

(9) *Nitric Acid + Hydrofluoric Acid + Sulfuric Acid: UO_2–ZrO_2.* A pulverized sample of the ceramic UO_2–ZrO_2 is dissolved in nitric acid plus a few milliliters of hydrofluoric acid. When dissolution is complete, 5 ml of sulfuric acid is added, and the solution is fumed to ensure removal of fluoride and nitrate ions. Uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

(10) *Hydrochloric Acid + Nitric Acid + Sulfuric Acid: Al–U_3O_8.* The cermet fuel used in the Argonne Naught Power Reactor (Argonaut) is composed of a mixture of 39 per cent uranium oxide (20 per cent U^{235}) and aluminum clad with aluminum. The cermet is dissolved with hydrochloric acid, nitric acid, and sulfuric acid. Uranium is determined volumetrically. A nondestructive density method is used to determine the uranium content of a whole fuel plate.

This cermet is prepared with cladding by the hot extrusion of a mixture of aluminum powder and uranium oxide contained in an aluminum cylinder. Even though the core is quite uniform in composition, the thickness of the cladding varies considerably over the area of the plate. Therefore, chemical determination of uranium with samples from different parts of the plate varies widely and cannot be correlated with the uranium content of the whole plate. A density method [173] for calculating the total uranium of each plate was used to verify the composition of each plate prior to loading the reactor. The calculation is based upon the theoretical density of aluminum and uranium oxide and the measured density of the fuel plate. The density of the fuel plate was determined from its weight and volume. The volume was obtained from the increase in volume of a container of water when the plate was suspended completely immersed in the water. The validity of the uranium values obtained by the density method was verified by measuring the density of specimens punched from the fuel plates and then dissolving the entire specimen and determining the uranium by chemical analysis.

Procedure: Uranium. The cermet of aluminum-uranium oxide is dissolved by treating with hydrochloric acid in a beaker until the

reaction is substantially complete and then adding nitric acid to complete the dissolution of the uranium oxide. Five milliliters of sulfuric acid is added to the sample solution or to an aliquot containing 0.2 to 0.3 g of uranium. The solution is heated to fuming and cooled, the walls of the beaker are washed down with water, and the fuming is repeated to ensure complete removal of nitrate. The uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

(b) *Sealed Tube: UO_2–CaO–ZrO_2.* The sealed-tube technique of Wichers, Schlecht, and Gordon [174] greatly simplifies the solution of the ceramic UO_2–CaO–ZrO_2 for analysis. The ceramic is completely dissolved in hydrochloric acid solution from which aliquots can be taken for the determination of uranium, calcium, and zirconium. The acid dissolution method described in Sec. 5–2.1(a)(1) is long and tedious involving repeated evaporations and fumings to effect complete solution of the ceramic. Therefore, if facilities are available, the sealed-tube method of dissolution is recommended.

Procedure: Uranium. A sample of the pulverized UO_2–CaO–ZrO_2 ceramic weighing 1 to 2 g is transferred to a well-annealed pyrex glass tube. The tube is 15 cm long, has a 15-mm bore and 2.5-mm wall thickness, and has a stem 8 cm long with a 4-mm bore and 2-mm wall thickness. Ten to twelve milliliters of hydrochloric acid is added, and the open end of the stem is heated with an oxygen-gas flame to produce a gastight seal. The sample tube is placed in a steel cylinder along with enough solid carbon dioxide to produce a compensating gas pressure of ~3500 psi during heating. The steel cylinder is capped immediately to produce a gastight seal, and the tube is heated overnight at 300°C. The steel cylinder is removed from the furnace and allowed to cool to room temperature before being opened. (When plutonium is present, if evidence of a leak from the pyrex tube is shown on opening the steel tube, the tube is recapped, and the entire unit is disposed of in the manner prescribed for contaminated material.) The pyrex tube is frozen in liquid nitrogen before it is removed from the shell and opened by making a scratch around the tube just below the stem and applying the molten end of a glass rod to the scratch. The contents of the tube are transferred to a 50-ml volumetric flask and diluted to volume. When a 2-g sample is dissolved, a precipitate will often be present in the tube after the reaction has been completed. However, the precipitate is readily soluble in water.

Uranium is determined in an aliquot of the sample solution by the volumetric method described in Sec. 5–2.1(a)(1).

Procedure: Calcium. Calcium is isolated from an aliquot of the sample solution by precipitation of calcium oxalate.[175] The determination may be completed either by igniting the calcium oxalate and weighing as calcium oxide or by titrating the calcium oxalate with permanganate.

Procedure: Zirconium. Zirconium is determined in an aliquot of the sample solution by precipitating the zirconium and uranium with ammonium hydroxide to separate from calcium. The precipitate is dissolved with 10 per cent sulfuric acid, and the zirconium is precipitated with cupferron.[176] The zirconium precipitate is filtered off, washed, dried, and ignited in platinum and weighed as ZrO_2.

Zirconium can also be separated from an aliquot of the sample solution by precipitation with *p*-bromomandelic acid; it is determined[177] by igniting and weighing as ZrO_2.

(c) *Fusion.* (1) *Pyrosulfate: UO_2–ZrO_2.* The ceramic UO_2–ZrO_2 which is soluble in acid, can also be dissolved by fusion with potassium pyrosulfate.[178] The analyst may prefer the fusion method because it is rapid and does not involve any evaporation or fuming. The UO_2–ZrO_2 ceramic is fused with 10 times its weight of potassium pyrosulfate preferably in a clear quartz or Vycor crucible to permit observation of the fusion process. When a clear melt is obtained, the crucible is cooled, and the contents are dissolved in dilute sulfuric acid. Uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

UO_2–Al_2O_3. The ceramic fuel element UO_2–Al_2O_3 is prepared for analysis by fusion with potassium pyrosulfate. The fusion melt is dissolved, and the uranium is determined by X-ray emission spectrography.[179]

Consalvo and Rynasiewicz[180] use a semi-micro volumetric method for determining uranium in the UO_2–Al_2O_3 ceramic. The dissolved pyrosulfate fusion melt is passed through a Jones reductor, and the uranium, after aeration, is titrated with potassium dichromate. These methods are particularly useful when the sample size is necessarily small, e.g., the measurement of the homogeneity of reactor fuel by the analysis of individual strips or sectioned pieces from a fuel-element strip.

Procedure: Uranium, X-ray Emission Spectrography. A sample of the UO_2–Al_2O_3 fuel element is fused with potassium pyrosulfate. The melt is dissolved in distilled water to which a few drops of sulfuric acid have been added. The solution is diluted to contain 0.94 mg to 1.28 mg of uranium per milliliter. An aliquot of the sample solution is excited by X-rays in an X-ray spectrometer set at 50 kvp and 40 ma. The uranium $L\alpha_1$ emission lines diffracted by a lithium fluoride single crystal are collimated by flat parallel nickel foils spaced 0.005 in. apart, ratio 800 to 1. Detection is accomplished by a thallium-activated sodium iodide scintillation crystal mounted on a photomultiplier. The signal is preamplified, and passed through a linear amplifier, and the pulses are fed into an electronic scaling circuit and recorded on a high-speed electronic counter. The time required to accumulate 128,000 counts is measured. The concentration of uranium is read from a calibration curve prepared by plotting counts per second vs. concentration on linear paper. Chemical preparation of the sample requires about 40 min. The counting time is of the order of 2 min. There is a negative error of about 1 per cent if the molar ratio to uranium is 50 for aluminium and 10 for iron.[181] The standard deviation is 1.8 per cent as determined from twelve measurements on standard solutions.

Procedure: Uranium, Volumetric. A sample of the UO_2–Al_2O_3 ceramic containing 8 to 20 mg of uranium is fused with sodium pyrosulfate. The

cool melt is dissolved in 25 ml of water acidified with 1.5 ml of sulfuric acid. The sample solution is passed through a Jones reductor column ⅝ by 5 in. The column is washed with 25 ml of 5 per cent sulfuric acid and 25 ml of water. The effluent is aerated for 15 min by bubbling air through the solution. Five milliliters of a freshly prepared 4 per cent ferric chloride solution is added plus 4 ml of a phosphoric acid–sulfuric acid mixture prepared by mixing 35 ml of phosphoric acid with 15 ml of sulfuric acid. Two drops of diphenylamine sulfonate indicator are added, and the solution is titrated to a permanent purple color with 0.027*N* potassium dichromate.

Iron is likely to be present as an impurity and is titrated along with the uranium. For the amount of iron normally present, it is more rapid and accurate to correct the per cent of uranium calculated from the titration by subtracting the product of 2.13 times the per cent of iron determined independently by a colorimetric method. If the iron is very high, the separation of the iron by mercury-cathode electrolysis prior to the titration is preferred.

The determination of uranium in the range of 8 to 20 mg in UO_2–Al_2O_3 ceramic fuel sections has an absolute error of ±0.1 mg of uranium.

(2) *Sodium Carbonate: UO_2–Glass.* Uranium oxide in various glass matrices can be prepared for analysis by a carbonate fusion and acid dehydration procedure. Silica is determined in the acid-insoluble dehydration residue by ignition to SiO_2 and volatilization with hydrofluoric acid. Uranium is determined volumetrically in the filtrate remaining after the removal of the silica.

Procedure: Silica. A pulverized sample of UO_2–glass containing 100 to 200 mg of silica is fused for 30 min using a blast burner with 10 g of sodium carbonate in a covered platinum crucible. The melt is cooled and disintegrated by 50 ml of water in a beaker. Fifty milliliters of perchloric acid is slowly added, and the silica is determined by the perchloric acid dehydration method.[182]

Procedure: Uranium. The filtrate remaining from the silica determination is fumed until salts begin to precipitate to remove excess perchloric acid. The salts are dissolved with 50 ml of 3*N* hydrochloric acid, and the uranium is determined volumetrically.

(d) *Ashing.* (1) *UO_2–Graphite.* A dispersion of uranium oxide in graphite is used as fuel for the TREAT reactor (Transient Reactor Test), an irradiation facility for the testing of fast reactor fuels. The fuel, containing less than 0.5 per cent enriched uranium, is analyzed for total ash, impurities, and uranium. The sample is prepared for analysis by ashing at 850°C.

Procedure: Ash. A sample of the uranium oxide–graphite fuel is weighed in a tared platinum dish and placed in a muffle furnace. The temperature of the furnace is raised to 850°C and maintained at this temperature until ignition is complete. Ashing may require from several hours to overnight depending upon the sample size and ignition

conditions. Ashing can be accelerated by passing a slow flow of air or oxygen through the furnace. The platinum dish is cooled in a desiccator and weighed. The sample is heated again to 850°C for 10 min, cooled, and weighed to ensure complete ashing.

Procedure: Metal Impurities. Metal impurities in the fuel are determined spectrographically. The oxide residue from the determination of total ash is analyzed by a carrier-distillation technique[183] (see Chap. 12).

Procedure: Uranium, Volumetric. Uranium is determined by dissolving a weighed amount of the residue from the total ash determination with nitric acid. Any insoluble material is separated and fused with pyrosulfate. The melt is dissolved with water acidified with sulfuric acid and is combined with the nitric acid solution. Five milliliters of sulfuric acid is added, and the solution is heated to strong fuming. The beaker is cooled, the walls are washed down with water, and the solution is fumed again to ensure complete removal of nitrate. The uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

Procedure: Uranium Colorimetric. If the amount of sample available is insufficient for a volumetric uranium determination, the colorimetric thiocyanate method is used.[184] The ash remaining from ignition of the uranium oxide–graphite sample is dissolved as described for the volumetric uranium determination except that the addition of sulfuric acid and the fuming are omitted. An aliquot of the solution of the ash containing about 1 mg of uranium is transferred to a small flask. One milliliter of hydrochloric acid and 0.5 ml of sulfuric acid are added. The solution is heated to dense white fumes of sulfur trioxide, cooled, diluted with a few milliliters of water and transferred to a 25-ml volumetric flask. One milliliter of 10 per cent stannous chloride and 15 ml of acetone saturated with ammonium thiocyanate are added and mixed well after each addition. The solution is diluted to volume with distilled water and mixed thoroughly. The absorbance is measured at 375 mμ using stoppered 1-cm quartz cells against a blank prepared in the same way as the samples. The standard deviation for routine applications is ±0.75 per cent. When more care than usual is exercised, a standard deviation in precision and accuracy of ±0.5 per cent can be achieved.[185]

(2) *UO_2–Polystyrene.* Dispersions of uranium oxide in polystyrene are analyzed for ash, impurities, and uranium as described in the procedure for uranium oxide–graphite dispersions with the exception of the ashing procedure. The uranium oxide–polystyrene dispersion is heated at 200 to 300°C until the volatile material has been removed. The temperature is then increased to 850°C. The ignition at 850°C is generally complete in 30 min.

(3) *UC.* Uranium carbide is analyzed for carbon by combustion in oxygen and absorption of the carbon dioxide in Ascarite. Uranium is determined in the residue from the carbon determination by either weighing directly as U_3O_8 or dissolving the residue and determining the uranium volumetrically. Uranium can also be determined by

dissolving the uranium carbide in hydrochloric acid and employing the volumetric method described in Sec. 5–2.1(a)(1).

Procedure: Carbon. Approximately 0.5 g of uranium carbide in a platinum boat is introduced into a quartz tube. Oxygen is passed through the tube, and the sample is burned at 1000°C. The carbon dioxide is caught in a weighing tube containing Ascarite and weighed.[186]

Procedure: Uranium. If the uranium carbide is known to be free of significant amounts of metal impurities, uranium can most easily be determined by weighing the uranium oxide remaining in the platinum boat from the carbon determination. The platinum boat is removed from the tube and heated in air for several minutes at 850°C. The boat and contents are cooled in a desiccator and weighed as U_3O_8.

If there is any question of the purity of the uranium carbide, the residue remaining in the platinum boat from the carbon determination is dissolved with nitric acid. Five milliliters of sulfuric acid is added, and the solution is taken to vigorous fuming. The beaker is cooled and the walls are washed down with water. The fuming is repeated to ensure complete removal of nitrate. The uranium determination is completed volumetrically as described in Sec. 5–2.1(a)(1).

5–3 PLUTONIUM ALLOYS

5–3.1 Plutonium–Aluminum Alloy

Various methods have been proposed for the separation of plutonium and the determination of aluminum in plutonium–aluminum alloys. Cleveland and Nance [187] separated the plutonium by precipitation and extraction as plutonium cupferrate and spectrophotometrically determined the aluminum as the oxine complex in $CHCl_3$. A coefficient of variation of 2.6 per cent for a 1 per cent aluminum alloy was obtained. Smith [188] precipitated the plutonium as the iodate and determined the aluminum colorimetrically with aluminon. In the 0.2 to 0.4 per cent aluminum range, the coefficient of variation is 6.4 per cent. Miner et al.[189] quantitatively separated the plutonium by retention on a strongly basic anion-exchange resin. The aluminum can be determined by a gravimetric oxine method with a coefficient of variation of 2.2 per cent for a 1 per cent aluminum alloy, by a volumetric oxine method with a coefficient of variation of 1.6 per cent, or by EDTA titration with a coefficient of variation of 2.0 per cent. Evans [190] found when using the EDTA titration of aluminum as described by Miner [191] that he could not get consistent results unless the column eluate was wet oxidized with $HClO_4$ and HNO_3 to remove organic matter in solution. Evans prefers to determine the aluminum after the ion-exchange separation by the rapid method of Watts [192] in which the aluminum is measured by titrating the hydroxide released by the addition of F^- to a basic solution of sodium aluminate. Jones

and Phillips [193] utilized the ion-exchange separation but determined the aluminum colorimetrically with oxine in the range of 0.1 to 1 per cent aluminum. Atkins and Jenkins [191] determined 1 per cent or more of aluminum in plutonium–aluminum alloys by EDTA titration after an ion-exchange separation of the plutonium.

The ion-exchange separation is preferred because it is easier to perform in the glove-box facilities required when handling plutonium samples. The colorimetric procedures are not as precise as the gravimetric or volumetric methods and are useful only for low aluminum alloys or when the sample size is small. The volumetric methods are comparable in accuracy to the gravimetric and considerably less time consuming.

(a) *X-ray Emission Spectrometry.* Plutonium–aluminum alloys can be analyzed for plutonium by X-ray spectrography with about the same precision as the uranium–aluminum alloys. Samples must be prepared within a completely enclosed system, such as a glove box, and precautions must be taken to prevent contamination of the X-ray instrument. The intensity of the plutonium $L\alpha_1$ fluorescence is measured.

> *Procedure: Plutonium.* Alloys of plutonium-aluminum are analyzed for plutonium by essentially the same technique described for uranium–aluminum alloys. The samples are cut, ground, and polished within a completely closed glove-box system. Each prepared specimen is wrapped and sealed in two layers of 0.00025-in.-thick Mylar film before being transferred to the X-ray unit. This very thin but tough film has no effect on the intensity of the plutonium $L\alpha_1$ fluorescence and prevents contamination of the instrument.

(b) *Spectrophotometric Methods: Aluminum.* Jones and Phillips [193] describe an absorptiometric determination of aluminum in plutonium–aluminum alloys in the range of 0.1 to 1 per cent aluminum. The alloy is dissolved with a minimum of HCl. Plutonium (IV) is adsorbed on a strong basic ion-exchange resin (Dowex 1 or De-Acidite FF) from $8M$ HNO_3. The effluent is fumed with $HClO_4$. Any ion present is extracted as the 8-hydroxyquinaldine complex into $CHCl_3$ at pH 9.2. Hydrogen peroxide is added to complex traces of plutonium remaining, and the aluminum is extracted as the 8-hydroxyquinoline complex into $CHCl_3$. The absorbancy is measured at 390 mμ. Jones and Phillips suggest that alloys of higher aluminum content would not require ion-exchange adsorption of most of the plutonium. Masking of plutonium could be entirely achieved by complexing with peroxide.

Atkins and Jenkins [191] have analyzed plutonium-aluminum alloys containing 1 per cent aluminum or more by separating the plutonium

by ion exchange and titrating the aluminum with EDTA. Plutonium is measured by differential spectrophotometry.[194]

Procedure: Aluminum. The alloy is dissolved with (1+1) HCl and made up to a convenient volume with 1*M* HCl or HNO_3. An aliquot containing at least 25 mg of aluminum is made up to 25 ml with HNO_3 to a final acid concentration of 7*M*. The solution is passed through a column of strongly basic anion-exchange resin (De-Acidite FF or Dowex-1). The eluate is fumed with $HClO_4$ to remove HNO_3. Any aluminum perchlorate is dissolved by adding 20 ml of dilute HCl. A 10 per cent excess of a 0.1*M* EDTA solution is added, and the solution is made just alkaline to methyl red. The solution is boiled for 2 min and then cooled, and 3 g of ammonium acetate is added. The pH should be 6.5. The excess EDTA is titrated with standard 0.1*M* $FeCl_3$ using 0.2 g of salicylic acid as indicator.

Procedure: Plutonium. The plutonium is eluted from the resin column with 5 ml of 1*M* HNO_3 followed by 15 ml of 10 per cent $NH_2OH \cdot HCl$ solution. The solution is allowed to stand overnight at 25°C. The Pu(III) is measured by differential spectrophotometry[194] against a suitable plutonium standard at 565 mμ. Alternatively the plutonium in the solution of the alloy may be measured directly by differential absorptiometry without separation from the aluminum. However, there is a small negative correction for the aluminum. The direct method is particularly suited to alloys of high plutonium content.

5–3.2 Plutonium-Iron Alloys

Atkins and Jenkins[195] have applied the colorimetric 1,10-phenanthroline method for iron to plutonium–iron alloys containing less than 5 per cent iron. No separation is required. If the measurement is made differentially, the precision is comparable to that obtained by volumetric methods. For plutonium alloys containing more than 5 per cent iron, the plutonium is removed by absorption on a strongly basic anion resin. The iron is eluted with 7*N* HNO_3, fumed with $HClO_4$ to remove NO_3^-, reduced in a lead reductor, and titrated with $Ce(SO_4)_2$.

5–3.3 Plutonium-Thorium Alloy

Differential spectrophotometry of Pu(III) in hydroxylamine-hydrochloride solution has been applied to the determination of plutonium in plutonium–thorium alloys without separation.[196] The absorbancy of the alloy in 1*M* HCl and 5 per cent $NH_2OH \cdot HCl$ solution is measured at 565 mμ against an accurately known plutonium standard solution. Milligram amounts of plutonium can be determined with a precision (1σ) of ± 0.05 per cent.

5–3.4 Plutonium–Titanium Alloy

Bergstresser [197] has applied the colorimetric determination of titanium with H_2O_2 to the analysis of plutonium–titanium alloys containing 0.1 to 1.0 per cent titanium. When H_2O_2 is added to a $HClO_4$ solution of the alloy, the yellow colored titanium complex and a precipitate of plutonium are formed. The insoluble PuO_4 is removed by centrifuging, and the titanium–peroxy complex is measured at 410 mμ against 1.5N H_2SO_4. For samples containing 50 mg of plutonium and 50 to 500 μg of titanium, the standard deviation is 2 μg. Milligram amounts of thorium do not interfere, but uranium and niobium do interfere. Other elements that normally interfere with the titanium–H_2O_2 method [198] will also cause difficulty.

5–3.5 Plutonium Binary Alloys with Zirconium, Molybdenum, or Cerium

Buchanan et al.[199] have reported the feasibility of applying ion-exchange separation to binary alloys of plutonium with zirconium, molybdenum, or cerium. The plutonium is absorbed on a strongly basic anion resin, and zirconium is eluted with 10N HNO_3, precipitated with NH_4OH, and ignited to ZrO_2. The molybdenum is eluted with 8N HNO_3, precipitated from acid–acetate solution with oxine, and weighed as MoO_2 $(C_9H_6ON)_2$. The cerium is eluted with 12N HNO_3, precipitated with NH_4OH, and ignited to CeO_2.

Bergstresser [200] uses the precipitation of zirconium by p-bromomandelic acid to separate zirconium from plutonium. The determination is completed by igniting and weighing as ZrO_2. In addition to the elements that have been reported as noninterfering [193] may be added molybdenum, lanthanum, and plutonium(III). In the range of 9 to 15 mg of zirconium, the range for the standard deviation is 0.05 to 0.17 per cent. The recovery of zirconium from solutions containing 5 to 12 mg of zirconium and 10 to 20 mg of plutonium is 99.9 $\pm$0.3 per cent at the 95 per cent confidence limit. The direct weighing of zirconium p-bromomandelate is not applicable in the presence of plutonium. The effect of plutonium is similar to that of iron, aluminum, and titanium as reported by others.[191, 193]

The spectrophotometric determination of zirconium by measurement of the color produced with Alizarin sulfonate [194] can be used for plutonium–zirconium alloys provided plutonium is present [200] as Pu(III). The mercaptoacetic acid which removes the interference of iron by reducing it to Fe(II) will also reduce the plutonium to Pu(III). Although relatively rapid, the precision is considerably less than that of the gravimetric method.

Procedure: Zirconium. A plutonium–zirconium alloy containing less than 50 per cent plutonium is fused with 1 to 2 g of fused $NaHSO_4$, and the melt is dissolved in water. If the alloy contains more than 50 per cent plutonium, the alloy is heated with 6*N* HCl to dissolve as much plutonium as possible before fusing the metal residue with $NaHSO_4$. The solution of the sample is diluted to 25 ml, and an aliquot is selected to contain about 10 mg of zirconium. The aliquot is adjusted to 15 ml, 3.2*N* to 4.0*N* with respect to HCl. About 0.2 g of $NH_2OH \cdot HCl$ is added, and the mixture is heated on a steam bath for several minutes to ensure reduction to Pu(III). To the hot solution 15 ml of 0.1*M* *p*-bromomandelic acid is slowly added. Heating is continued for 30 to 45 min. The precipitated zirconium *p*-bromomandelate is transferred to a tared 7-ml porcelain filtering crucible using a wash solution of 0.1*N* HCl and 0.01*M* *p*-bromomandelic acid. A final wash of H_2O is made. The precipitate is dried at 110 to 130°C and ignited at 900 to 950°C for 20 min. The zirconium is weighed as ZrO_2.

5–3.6 Uranium–Plutonium Alloys

Milner and Edwards [201] describe the instrumentation and procedure for the determination of plutonium in uranium–plutonium alloys by controlled-potential coulometry. Uranium does not interfere; however, a small correction for iron is necessary. The method was applied to alloys in the range of 0.1 to 12 per cent plutonium, with concentrations of plutonium from 100 μg to 1 mg. The coefficient of variation is ± 0.14 per cent for a pure plutonium solution at the 1 mg level.

The uranium–plutonium alloys can be analyzed for uranium and plutonium by the methods indicated for uranium–plutonium–carbon in Sec 5–3.7.

5–3.7 Plutonium Carbides

(a) *Determination of Carbon.* The carbides of plutonium and uranium–plutonium can be analyzed for carbon by conventional combustion methods. The sample is burned in O_2, and the CO_2 is measured by absorbing in Ascarite and weighing. When the sample size is small, the CO_2 is measured with a capillary-trap manometer.[202]

(b) *Dissolution.* Plutonium monocarbide is easily dissolved with HCl to give a clear solution. However, occasionally a black residue of carbon is obtained. This is believed to be unchanged powdered graphite used in the production of the PuC. In this case it is necessary to add HNO_3 and fume with $HClO_4$ to obtain a clear solution. Drummond et al.[203] report that acid hydrolysis products of the higher carbides, Pu_2C_3 and PuC_2, contain a hydrocarbon wax-like material. The uranium–plutonium carbide is disintegrated with HCl, and a clear solution is obtained by the dropwise addition of HNO_3.

(c) *Determination of Plutonium.* Plutonium in Pu–C or U–Pu–C is most easily determined by amperometric titration [204] of Pu(VI) with Fe(II). The HCl or HNO_3 solution of the carbide is fumed with H_2SO_4. The acidity is adjusted to 0.5*N* H_2SO_4, and the plutonium is oxidized to Pu(VI) with AgO. The excess oxidant is destroyed by heating, and the Pu(VI) in 5*N* H_2SO_4 is titrated with 0.05*N* $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The end point is detected amperometrically by measuring the current generated by excess titrant at a rotating platinum microelectrode vs. a saturated Hg_2SO_4 electrode. The elements uranium, iron, cobalt, and aluminum do not interfere. Such elements as cerium, chromium, vanadium, and manganese, which are oxidized by Ag(II) and reduced by Fe(II), will interfere. The precision and accuracy of the method have a coefficient of variation of 0.06 per cent for a single determination in the 10- to 20-mg range. In the 100 to 200 μg of plutonium range, the coefficient of variation is 0.4 per cent. The method has been applied over the range of 5 to 80 per cent plutonium in U–Pu–C.

Plutonium can also be determined by differential absorptiometry after separation of the uranium by ion exchange.[195]

(d) *Determination of Uranium.* Uranium in U–Pu–C or in binary alloys with plutonium is determined by redox titration after a prior separation of the plutonium. The plutonium can be separated by ion exchange [205] or by solvent extraction.[206] It is imperative in both methods that the plutonium be present in the monomeric form as Pu(IV). Polymerization of plutonium is unlikely if the plutonium solution has been kept at an acid concentration of 0.1*M* or greater. The polymerized form of plutonium can be converted to the normal extractable or exchangeable form by heating [206] the solution for several minutes with HNO_3. Reducing the plutonium quantitatively to Pu(III) and then oxidizing to Pu(IV) ensures the correct valence state for plutonium. The HCl–HNO_3 solution of the alloy is adjusted to 1*N* acidity, and $NH_2OH \cdot HCl$ equal to 10 times the weight of plutonium is added. The mixture is heated to about 80°C for 5 min to complete the reduction to Pu(III). The plutonium is now oxidized to Pu(IV) by adding $NaNO_2$ equal to 25 times the weight of plutonium. The mixture is allowed to stand until gas evolution ceases. Separation of the plutonium and uranium can be made by ion exchange or solvent extraction.

(1) *Ion-exchange Separation.* The sample solution is made 7*N* in HNO_3 and passed through a strongly basic anion-exchange resin.[195, 205] The uranium is eluted with 7*N* HNO_3. The NO_3^- is removed by fuming with $HClO_4$, and the uranium is determined volumetrically as described in Sec. 5–2.1(a)(1). The plutonium is

stripped from the resin by washing with one column volume of $1N$ HNO_3 and then with a 5 per cent solution of $NH_2OH \cdot HCl$. The plutonium can be determined by differential absorptiometry of the blue Pu(III) solution.[196]

(2) *Solvent-extraction Separation.* The plutonium in the $1N$ HNO_3 sample solution is separated from the uranium by making two extractions with $0.5M$ 2-thenoyltrifluoroacetone (TTA) in $CHCl_3$. Moore and Hudgens [206] make the extraction with $0.5M$ TTA in xylene. The aqueous layer containing the uranium is washed with $CHCl_3$ to remove traces of TTA and then fumed with H_2SO_4 or $HClO_4$. The uranium is determined volumetrically as described in Sec. 5–2.1(a)(1).

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CHAPTER 6

EXPENDED REACTOR FUELS

By G. L. Booman and J. E. Rein*

Although the types of nuclear reactor fuels proposed or under study number in the hundreds, relatively few have been used as cores in operating nuclear reactors. The number of different major analytical programs involving expended fuel is therefore small. The main plant programs are: (1) separation of plutonium from irradiated natural uranium; (2) processing of spent fuels for recovery of unspent fissionable material; (3) evaluation of large-scale pilot-plant prototype reactors; and (4) evaluation of irradiated fuels. Under the latter category, a large number of experimental fuels have been tested for radiation stability in such reactors as the Materials Testing Reactor and the Engineering Test Reactor at the National Reactor Testing Station in Idaho and the Low Intensity Test Reactor at the Oak Ridge National Laboratory. The postirradiation examination of these fuels usually includes metallurgical tests and chemical analyses; the latter mainly involve radiochemical determinations to establish the degree of fission or burn-up which has occurred. Only a limited discussion of irradiated-fuel programs is included in this chapter because, aside from handling and sampling techniques, conventional radiochemistry is involved.

The unique problem associated with expended-reactor-fuel analysis is the high level of radioactivity involved. This affects analytical programs in two ways. First is the need for personnel protection; such protection requires specially designed facilities and apparatus for shielding and atmosphere control (Sec. 6–1).

In such facilities samples with activity levels that, under present tolerances,[1] would restrict the analyst to less than 1-sec exposure if handled in a conventional laboratory are routinely analyzed.

Second, but more important from the viewpoint of analytical chemistry, is that samples from expended fuels with high activity levels contain fission products in sufficient concentration levels to act as interferences in the methods employed. This is shown in Fig. 6.1, where the upper number in each block indicates the mole ratio (in per cent) of fission product to the uranium present after a 50 per cent burn-up followed by a 100-day cooling period.[2] The lower number in each block indicates the mole ratio (in per cent) of fission

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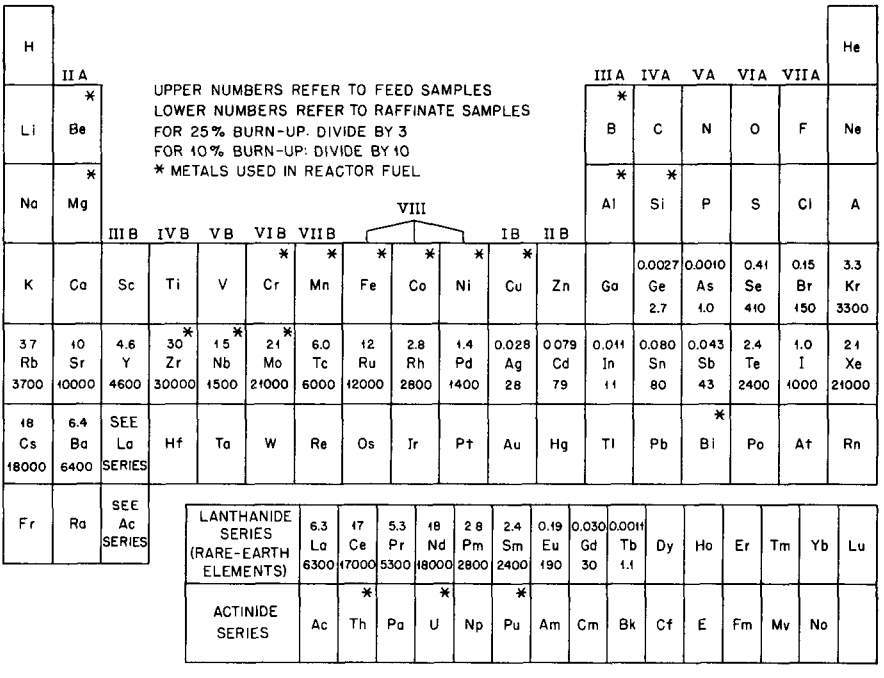


Fig. 6.1—Fission product to uranium mole ratio (in per cent) after 50 per cent burn-up and 100-day cooling period.[2]

product to the uranium that is present in the raffinate after the bulk of the uranium has been extracted. As can be seen there are many elements present in large enough concentrations to interfere with the determination of the uranium. The degree of interference will depend on the method used. This effect of fission products is further complicated because many exist in multioxidation states unknown in process samples and exhibit complex chemistry.

Another analytical difficulty is indicated in Fig. 6.1 Many elements are used as alloying constituents (see Chap. 5) and in the case of enriched-uranium fuel are the major components. Other diverse ions are added in high concentrations in recovery processes. Even the determination of acidity, usually considered a simple analysis, is made difficult by high concentrations of varied hydrolyzable ions, a characteristic of fuel-element process samples.

The authors, realizing that analytical programs for irradiated fuels in the literature are outdated, requested the analytical chemists of various Atomic Energy Commission contractor laboratories concerned with the analysis of irradiated fuels to provide current information with emphasis on proven methods. Their cooperation is gratefully acknowledged.

6–1 TECHNIQUES, FACILITIES, AND APPARATUS

6–1.1 Techniques

Four basic approaches [3] have been developed for the analysis of samples containing high levels of radioactivity: dilution of sample, separation of desired constituent, remote analysis, and in-line analysis.

(a) *Dilution of Sample.* The simplest plan of analyzing samples is based on cutting off a small amount of solid sample or diluting a small volume of liquid sample and then transferring and analyzing aliquots of below-tolerance activity level on the open bench. The only shielded or remote-handling apparatus required in this method is some type of mechanical cutting or coring apparatus or a pipet and a transfer mechanism.

The dilution technique is limited to the determination of those constituents for which sensitive methods are available. A major application is the determination of fission products by radiochemical methods.

(b) *Separation of Desired Constituent.* The technique second in simplicity and economy is based upon separation of the desired constituent. This has been used for the separation of uranium; plutonium; inert materials, such as anions and gaseous elements; and certain fission products.

Liquid–liquid extraction has been used extensively, and ion exchange has been used to some extent for separating the unfissioned uranium and plutonium. For accurate results the recovery should be quantitative; however, conditions that give high recoveries tend to cause carry-over of one or more fission products. Hence a compromise is often made between the recovery and the degree of decontamination. The isotope-dilution technique, which provides a yield correction, circumvents this difficulty. The application of this technique to the determination of uranium is described in Sec. 6–3.2.

The separation of inert material and certain fission products has been essentially limited to those which can be volatilized. Typical examples are: the pyrohydrolysis of fluoride; the distillation of ammonia from alkaline aqueous samples; the high-temperature evolution of such gases as hydrogen, nitrogen, oxygen, Xe^{133}, and Kr^{85} from metal specimens; and the distillation of such fission products as iodine, bromine, and ruthenium after chemical treatment to obtain volatile valence states.

(c) *Remote Analysis.* The technique of confining the entire analytical procedure to a shielded enclosure is termed remote analysis. These enclosures vary in complexity from a lead-brick barricade in a hood with simple tongs to multimillion dollar installations with

thick concrete walls, viewing windows, elaborate manipulators, and push-button controls. For economic feasibility the high initial cost of such installations must be offset by reduction of hazards from radioactivity, increased production, and the improved accuracy obtainable with larger sized samples.

(d) *In-line Analysis.* The ultimate goal for the analysis of highly radioactive streams is in-line process control. In addition to the usual advantages of continuous surveillance and efficiency, in-line analysis decreases radiation hazards. Transporting and handling of high-level samples are not required, and the need for remote facilities is less. The newness and complexity of the processes and the need for maintenance-free equipment make the application of this technique to process plants difficult. In spite of these difficulties, the advantages are so great that an increasing number of projects are being undertaken in this field.

6–1.2 Facilities

Small mobile shielded facilities, commonly called "junior caves," have been used extensively for such analytical purposes as sampling and diluting and for simple analyses. Apparatus within the cave is usually specially designed for remote control from without and for easy operation with simple tong-like manipulators. The adaptation of junior caves at the Savannah River Laboratory for pipetting, preparing dilutions, determining specific gravity by the falling-drop technique, and titrating for acid in the presence of as much as 25 curies (1 Mev) of radiation is described by Leith.[4] Larsen, McCown, and Sovereign [5] describe the use of junior caves capable of handling 10 curies of 1-Mev gamma radiation for a wide variety of analytical operations at Argonne National Laboratory. These authors discuss the opening of sealed irradiation cans, the cutting and trimming of metal fuel elements by electrolytic dissolution, the separation of rare gases and other volatile fission products, and the liquid–liquid extraction separation of uranium and plutonium. The above is indicative of the operations performed.

Junior caves are limited in shielding capabilities to about 25 curies of 1-Mev gamma radiation. For levels higher than this, cells with heavier shielding, permanent in location, are required. Typical high-level facilities used for remote analytical operations are summarized in Table 6.1. The main reference sources for this table are reprints of papers from each annual Hot Laboratories and Equipment Conference. Papers presented at these meetings cover every facet of remote operation from the sampling of radioactive streams to the examination of large process apparatus and comprise the major source

of this type information. Ten meetings have now been held: the first was in 1953 and the tenth was held in November 1962.

The number of high-level facilities designed exclusively for analytical use is relatively small. Most installations have a series of cells, varying up to about nine in number; one or two of these may be used for analytical purposes. The majority of the cells are used for examination of irradiated materials and for various metallurgical tests.

The specific design of a high-level facility for analytical purposes is governed by the types and frequencies of analyses. A versatile facility, which can be changed rapidly from one analytical measurement to another, is best suited for a research installation. Commercial laboratory equipment is used with master–slave manipulators. Almost all the facilities listed in Table 6.1 are this type. For routine process control in a production plant, a facility with specialized apparatus for each analysis is well suited; such apparatus is designed for operation by push-button control from outside the shielding. Simple tong-like manipulators, less expensive than master–slave manipulators, can be used. The main example of this type facility is the remote analytical facility at the Idaho Chemical Processing Plant (see Table 6.1).

A comprehensive review [19] describing glove boxes and shielded caves was published in 1958. The most complete coverage of enclosures and accessory equipment for hot-laboratory operation is that of Stang.[20] Shielded enclosures, high-level cells, portable caves, mobile shields, unshielded glove boxes, and hoods are described along with the following accessories: filters, plastic cubicles, viewing equipment (windows and lens systems), manipulators, in-process fluid-transfer devices, and apparatus for reactions, filtration, ion exchange, heating, mixing, weighing, and monitoring.

One session of the Sixth Hot Laboratories and Equipment Conference was devoted to safety aspects of high-level facilities. Stout and Stearns [21] discussed plutonium handling; Hungerford [22] surveyed fire protection; Smith and Conboy [23] covered safety alarm systems, cell-entry problems, and training programs; Hale [24] surveyed ventilation; and Engle [25] discussed high-efficiency air filters.

The problem of decontamination of both cells and apparatus was extensively surveyed by Watson.[26]

The economics of operation in an analytical laboratory concerned with radioactive samples was discussed by Christopherson.[27]

6–1.3 Apparatus

(a) *Sampling Apparatus.* A shielded pipet is almost universally used for liquid samples. The Hanford pipet [28] is an adaptation of

Table 6.1—TYPICAL REMOTE-CONTROL HIGH-LEVEL FACILITIES USED FOR ANALYTICAL PURPOSES

Facility	General features	General functions	Analytical functions	Refs.
Atomics International, Canoga Park, Calif.	Nine cells; model 8 manipulators; 42-in. magnetite concrete shielding	Disassembling of large objects, such as fuel elements, control rods, and pumps; physical testing; metallography	Dissolution; radiochemistry for burnup; density of solids; gamma scan on solid samples	6
Hanford High-level Radiochemistry, Hanford, Wash.	Three large cells; sampling lines connect to operating areas; General Mills crane between cells for equipment transfer; model 8 manipulators; 48-in. concrete shielding	Primarily designed for chemical research of a broad nature	Not stated but versatility should permit any desired function	7
Los Alamos Intermediate-level Radiochemistry, Los Alamos, N. Mex.	One kilocurie high alpha level samples; one cell with five model 8 manipulators and three stations; end stations equipped with dry boxes; center station for disassembly and for supplying the end stations	Preparing radiochemical samples from various mechanical assemblies and fuel elements; performing bench chemistry operations behind shielding	Essentially radiochemical analysis	8
Los Alamos Alpha–Gamma	Sixteen cells laid out in two groups of eight, back to back, with common transfer area; sealed enclosures placed inside cells; each cell shielded for 100,000 curies of 0.1-Mev gamma radiation; two height positions for model 8 manipulators; construction began in late 1959	Examining irradiated uranium and plutonium fuels; includes metallurgical tests	Facility designed for versatile use of commercial equipment	9

Pratt & Whitney, Livermore, Calif.	Five cells; 1-ton in-cell cranes; model 8 manipulators; chemical operations; cell can handle 1000 curies of 1-Mev gamma activity	Examining large equipment; machine shop; metallurgical examination	Sampling of both solids and liquids; can do complete remote analysis, although low-level aliquots are usually removed for analysis	10
Argonne EBR–2 Junior Cave, NRTS, Idaho	Six caves; 20 curies of 1-Mev gamma activity; model 8 manipulators	Designed for analytical use; uses commercially available equipment	Designed to provide analyses for fast-breeder reactor operation and its fuel-reprocessing cycle as described in Sec. 6–7	11 12
Oak Ridge National Laboratory High-level Analytical, Oak Ridge, Tenn.	Eight cells; model 8 manipulators; 3 ft of concrete shielding; two conveyers for transfer between cells; lead drawers on front face for supply and reagent transfer	Designed for analytical use; uses both commercial and custom-designed equipment	Used for analyses of HRE samples; one cell equipped for emission spectrography	13 14 15
Idaho Chemical Processing Plant, NRTS, Idaho	Two parallel lines of 16 boxes each; simple Castle manipulators; supply and reagent dumbwaiter connected to a conventional laboratory above; electric dolly for transfer between boxes	Designed for analytical use; uses custom-designed equipment	Designed for routine operations; each box specially equipped for a separate analytical determination	16 17 18

the Gilmont ultramicroburet, which consists of a reservoir and plunger in conjunction with a micrometer screw. It has a capacity of 0.1 ml, with each revolution of the dial micrometer gauge corresponding to a delivery of 10 μl. Fluorothene, which is nonwettable, is used instead of glass for the pipet stem. This minimizes contamination and permits ready maintenance. At Hanford this pipet is often installed with the delivery end behind lead brick and glass barricades. For completely remote operation a position-displacement servo-operated pipet was introduced by workers at Oak Ridge.[14] The pipet used at the Idaho Chemical Processing Plant (ICPP) is described by Dykes.[18] In this pipet a 12-position rotary switch controls delivery. Two 50-μl, seven 100-μl aliquots, or any combination to a total of 950 μl can be delivered with a standard deviation of 0.4 μl for a single delivery over the entire range.

Sampling of solids is often accomplished by anodic dissolution to minimize dispersion of particulate activity. Both nitric acid [29] and sulfuric acid [30] have been used as electrolytes with rather simple apparatus. Results, usually for fission products, are often expressed in terms of a uranium ratio, negating the need for quantitative sampling. Mechanical samplers, such as cutters, lathes, and drills, are used. After complete dissolution of the sample, an aliquot of the resulting solution is taken for analysis.

Samples from process streams and tanks are commonly obtained by a recirculating air-lift sampler; [31] the sample bottle, fitted with a self-sealing neoprene cap pierced with stainless-steel inlet and outlet probes, forms part of the recirculating system. A specially shielded sampling gallery is required. After the bottle has been filled, the probes are withdrawn, and the capped bottle is transferred to the high-level cell by means of conveyers or hydraulic lift trucks fitted with lead pigs.

(b) *Apparatus for Analysis.* As described previously the majority of high-level cells are equipped with master-slave manipulators and commerical analytical apparatus. Minor modifications in the apparatus are made to facilitate operation. For certain applications where equipment is installed for long-term use, the controls are modified for remote operation. Apparatus in which the sensing elements are physically separable from the measuring systems are often installed with the measuring systems outside the shielding. Examples are automatic titrimeters, pH meters, polarographs, and spectrophotometers. Examples of installation and operation of specific analytical equipment are given in most of the references listed in Table 6.1. Of particular interest are the descriptions of the apparatus used in the high-level facility at Oak Ridge National Laboratory [14] (ORNL) and in the remote-control analytical facility at the ICPP.[16] Also of in-

terest are the comparison of apparatus designed for the same analytical functions in various high-level facilities,[3] the description of the emission-spectrograph installations at ORNL,[15] and the discussion of the adaptation of commercial equipment in the analytical caves at Argonne National Laboratory (ANL) for a fused-salt fuel-reprocessing process.[12] The last reference also describes the use of a single-pan balance, adapters for commercial glass macro- and micropipets, extraction and ion-exchange apparatus for remote separation, a mercury-cathode electrolysis setup, and adaptation of such apparatus for final analytical measurements employing the Beckman Model B spectrophotometer, a titrimeter, a polarograph, and a flame photometer.

(c) *In-line Equipment.* As implied previously the use of in-line analytical apparatus is severely hampered by both the relative newness of the field and by the requirement of maintenance-free operation. According to Brouns and Alkire,[32] five basic requirements must be met for a successful in-line program in a plant processing radioactive material: (1) it must be known that fresh sample is continually supplied to the instrument; (2) provision for periodic calibration of the instruments must be built in; (3) instruments must be simple and ruggedly constructed of corrosion-resistant material since operational reliability with consequent low maintenance is more economical in the long run than low initial cost; (4) justification for an in-line program should be based on improved operational efficiency, not on decreased analytical costs; (5) prototype models must be tested under conditions similar to the proposed plant installation, preferably in pilot plants, for relatively long periods.

Maintenance, perhaps the major economic factor, is severely affected by high-level contamination. The affinity of various materials for a typical mixture of fission products is described by Axtmann.[33] He found that there appears to be no correlation between the types of material and the contamination; this is attributed to the many phenomena, such as adsorption, electrolytic reduction, monomolecular-layer formation, and chemical reactions many which contribute to radioactive contamination of the surfaces. Lucite was found to have the lowest contamination index of the plastics studied, and Boltaron has one of the highest. It is of interest that stainless steel, which has a high corrosion resistance, has one of the poorer contamination indices.

Many in-line instruments in production plants measure only one physical property, such as specific gravity, pH, liquid level, temperature, or conductivity. The major analytical techniques that have been most successfully used are colorimetry, turbidimetry, the counting of alpha and gamma radiation present in the plant streams, and

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gamma absorptiometry. A great deal of research and development has also been expended on electroanalytical measurements, such as polarography,[34-36] for uranium monitoring and conductivity and radio frequency oscillometry for acid analysis.

Scott and Van Meter [37] described the first Hanford filter photometer model for monitoring streams for uranium or potassium dichromate. Some outstanding features of this instrument are as follows: use of simple optics, easy replacement of the cell, which is the only component coming in direct contact with the high-level sample, use of cerium oxide-stabilized glass for the cell (conventional glass darkens when exposed to radiation); and protection of the light bulb and filters by disks of radiation-resistant glass. Improvements in a later model [32] of this instrument consisted of a mechanical arrangement permitting placement of two interference filters with different transmittance bands in the optical path. One filter transmits light that the stream component being measured absorbs, and the other filter transmits a nonabsorbing wave length.

Standardization is made automatically about twice an hour with the nonabsorbing filter. In this way compensation is made not only for changes in the measuring circuits but also for such variables as darkening of the optical windows and the accumulation of dirt inside the cell.

Prohaska [38] describes a flow colorimeter for measuring the uranium concentration in process streams of uranyl nitrate solutions. Although the instrument was basically designed for high-concentration streams (of the order of 50 g of uranium per liter), lower concentrations can be measured by changing the length of the optical path and the electronic gain. A 3 per cent precision, based on comparison with grab samples, was obtained over a four-month operational period.

An in-line turbidimeter for monitoring the immiscible organic content of aqueous streams is described by Colvin.[39] It is designed for the range of 0 to 1 per cent organic solvent in water. A dual-beam optical system is used with the two beams transversing different path lengths. The ratio of the two intensities is measured which corrects for light-source fluctuation and provides compensation for fouling or radiation darkening of cell windows.

Continuous monitors for low levels of beta and gamma contamination in flowing streams are described by Wingfield [40] and by Kelley and Susano.[41] Wingfield [42] has also developed a continuous alpha monitor for aqueous streams in which the flowing stream comes in direct contact with a scintillation screen. The scintillations are viewed by a photomultiplier and are indicated by a count-rate meter.

Wingfield's instrument has no moving parts, hence requires little maintenance. The detection limit is 3.3×10^{-10} curie/ml.

Gamma absorptiometry, the absorption of low-energy (0.06 to 0.1 Mev) gamma photons, was first proposed by Miller and Connally [43] for continuous monitoring of the concentration of transuranic elements. Americium-241 with a 462-year half life is now used at Hanford and at Savannah River as the gamma-emitting source. Thurnau [44] describes the simple and rugged Savannah River instrument, which is used by nontechnical operators. The range of 50 to 100 g of uranium per liter is covered with a standard deviation of 0.05 per cent.

6–2 SEPARATION PROCESSES FOR URANIUM AND PLUTONIUM

The natural-uranium fuels are usually unalloyed uranium metal or dioxide. A common cladding material is aluminum, although others are used. The initial process step is either mechanical decladding or special treatment for dissolution of the cladding. This section does not cover these special treatments.

Two processes are used almost exclusively to recover and purify uranium and plutonium from irradiated natural-uranium fuel on a large scale. The Redox process [45] involves a methyl isobutyl ketone (4-methyl-2-pentanone) extraction with aluminum nitrate as a salting agent and an oxidation–reduction control of plutonium with ferrous sulfamate and chromium (VI). The Purex process [46] uses tributyl phosphate (TBP) in a kerosene type diluent as the extractant with nitric acid as the salting agent. The oxidation and reduction of plutonium are controlled by nitrite and ferrous sulfamate. The newer Purex process has the advantages of safety and economy. The TBP–kerosene solvent has a higher flash point and lower volatility than methyl isobutyl ketone, and the nitric acid salting agent is recoverable by distillation. The latter decreases both material and waste-storage costs.

The simplified flow sheets (Figs. 6.2 and 6.3) show the parallelism of the two processes. The four main steps are: (1) simultaneous separation of the uranium and plutonium from the fuel cladding and fission products; (2) separation of the uranium and plutonium; (3) further decontamination and recovery of plutonium; (4) further decontamination and recovery of uranium. Each process includes solvent recovery, and the Purex process, as indicated, has a nitric acid recovery step.

The conditions, as indicated on the flow sheets, vary slightly from one installation to another. Process and analytical data in this section are based mainly on Hanford information.[47, 48]

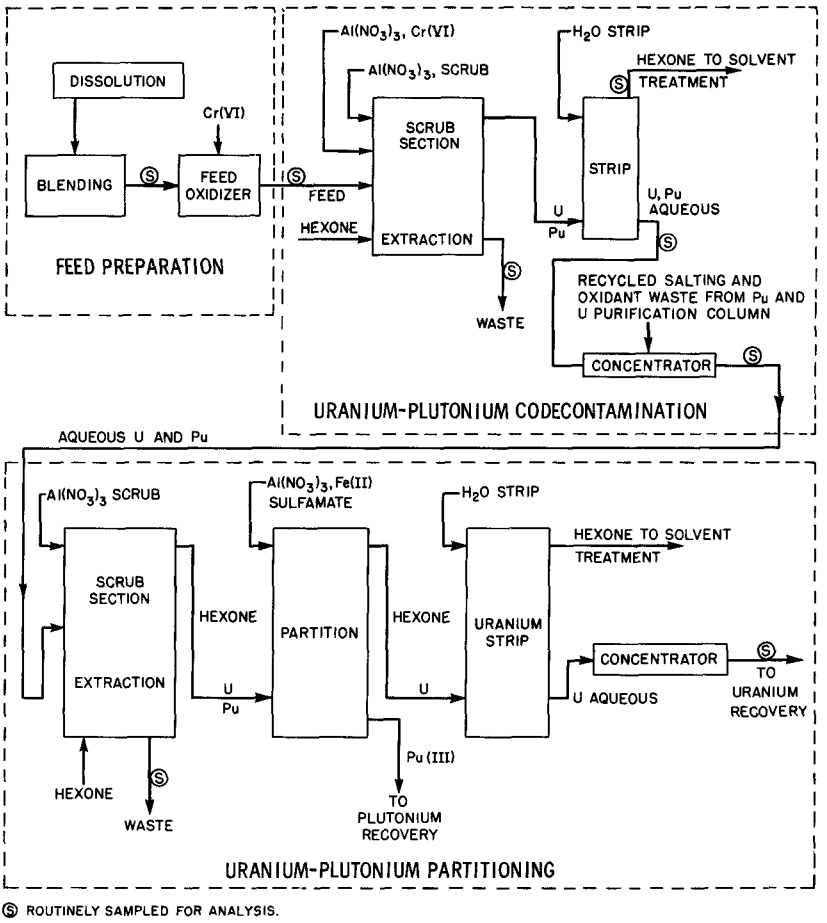


Fig. 6.2—Flow sheet for Redox recovery process.

Rather simple shielded facilities are used for handling highly radioactive samples at the two United States plants, Hanford and Savannah River. Junior caves equipped with ball-and-socket manipulators are used for such operations as delivering small aliquots or separating uranium or plutonium from fission products. Much work is done from behind lead-brick barricades in conventional laboratory hoods with simple hand-operated tongs. Samples containing large amounts of plutonium are handled in glove boxes. One of the few analyses done remotely is the determination of specific gravity by the falling-drop technique (Sec. 6–10.5).

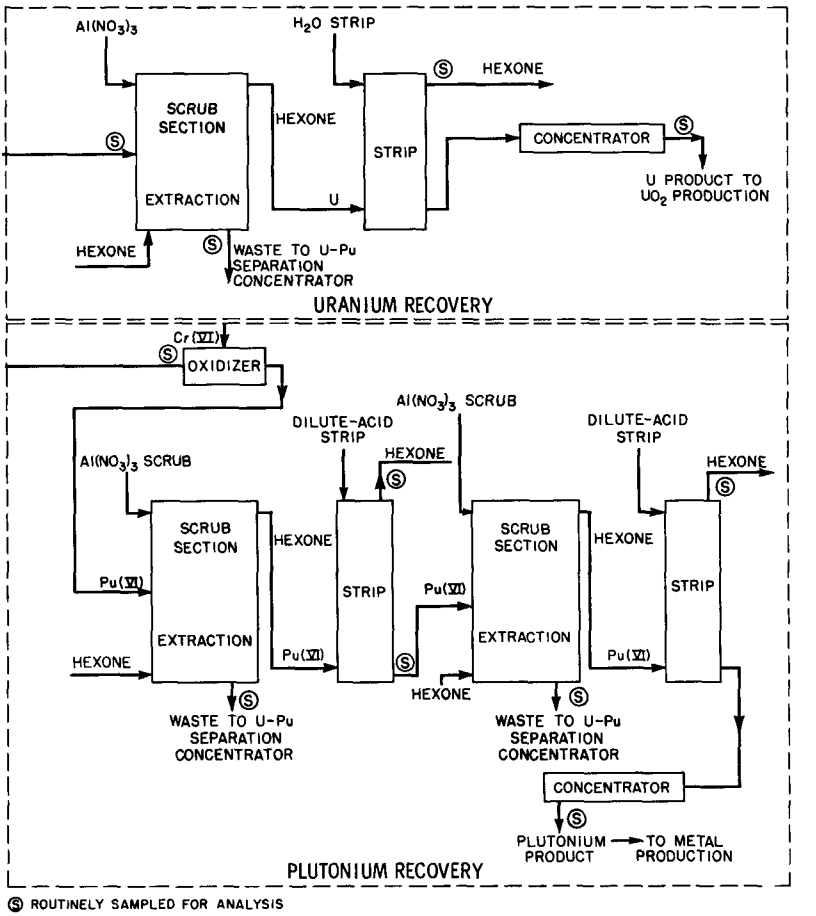


Fig. 6.2—(Continued).

6–2.1 Types of Samples

The analytical program for both the Purex and Redox processes is summarized in Table 6.2.

6–2.2 Discussion of Methods

(a) *Specific Gravity.* The falling-drop method, discussed in Sec. 6–10.5, is used to determine the specific gravity of highly radioactive samples. Other samples are analyzed by a conventional pycnometer method.

(b) *Acidity.* Three methods are used to determine acidity, depending on sample composition. These are direct determination of pH, coulometric titration, and acidimetric titration after complexing with oxalate ion. These methods are discussed in Sec. 6.10.1.

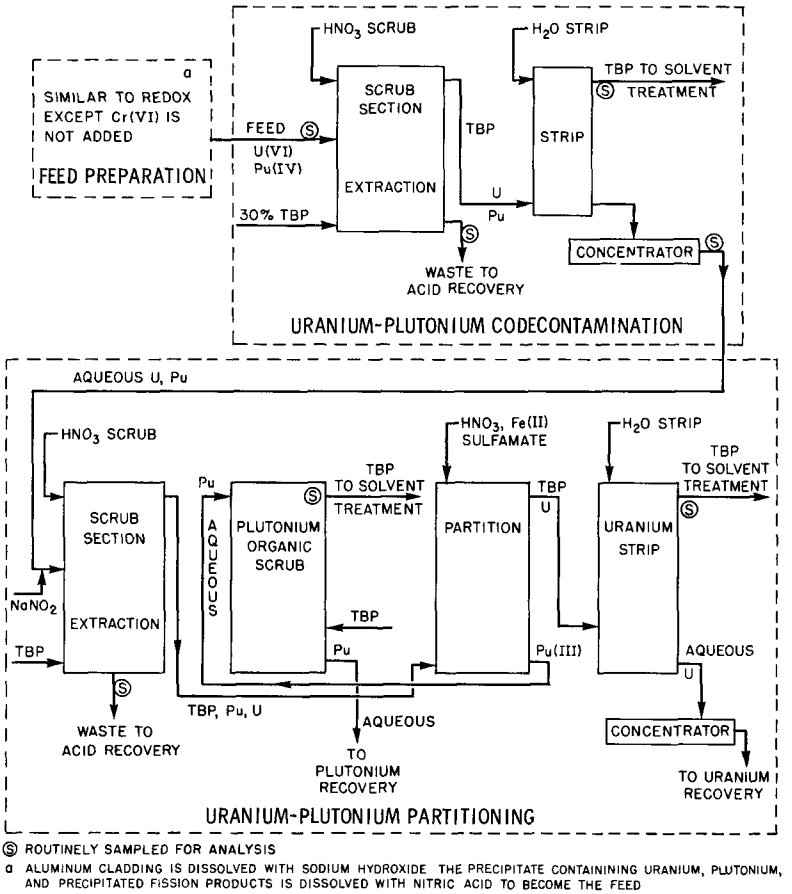


Fig. 6.3—Flow sheet for Purex recovery process.

(c) *Uranium.* The highly radioactive solutions, such as the dissolver solution, containing large amounts of uranium are analyzed for uranium by an indirect measurement of density. This technique is limited to fairly pure solutions. Dissolver solutions, in which the compositions are not consistent, are analyzed by X-ray absorptiometry after separation of the uranium by liquid–liquid extraction. Uranium, normally present in low concentrations in waste and plutonium streams, is determined by fluorophotometry. See Sec. 6–10.2 for a discussion of these methods.

(d) *Plutonium.* Alpha counting, the most sensitive method for the determination of plutonium, is routinely used for lean plutonium samples, such as waste streams. It is also used for highly radioactive samples so that small aliquots can be analyzed. Direct counting, of course, is simplest and is used whenever applicable. Thus minute

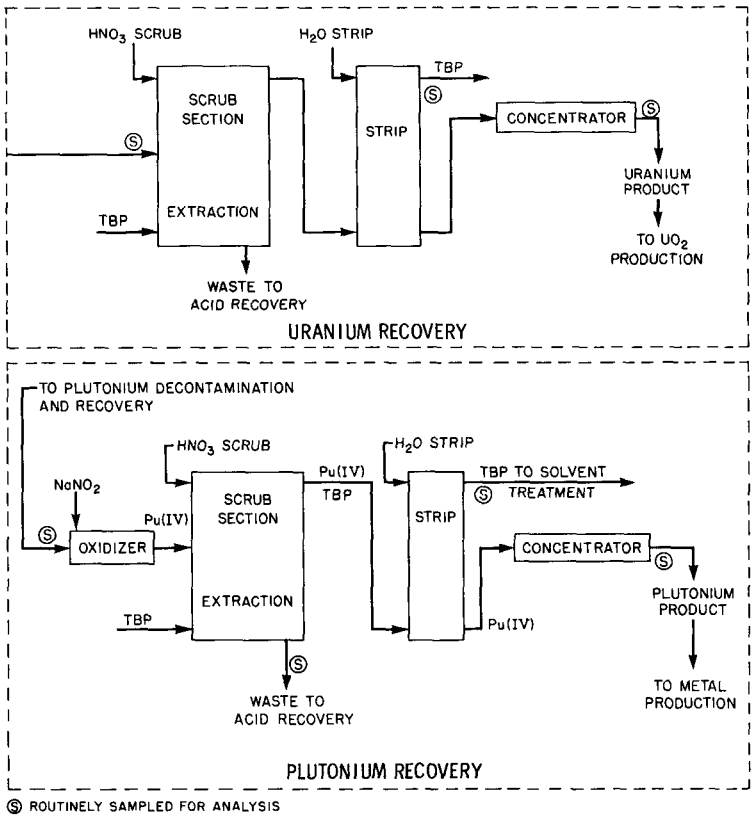


Fig. 6.3—(Continued).

aliquots of the metal-solution blend streams, the codecontamination feed, and the feed to the plutonium-recovery section are analyzed for plutonium by direct alpha counting. Corrections for other alpha emitters and the effect of the isotopic distribution or specific activity of the plutonium are discussed in Secs. 6–10.4, 6–2.2(e), and 6–2.2(d).

A separation of plutonium in samples containing high salt or high fission-product concentrations and low plutonium levels is necessary prior to alpha counting. This is characteristic of waste- and uranium-stream samples. Both the thenoyltrifluoroacetone (TTA) extraction and the lanthanum fluoride carrier methods are employed.

For streams in the plutonium-recovery cycle with low uranium concentration, such as the Redox second-cycle feed and the product, X-ray absorptiometry is the selected method for the determination of plutonium.

A ceric titration method is used for assaying plutonium metal. After dissolution of the sample (about 500 mg) in hydrochloric acid, pluto-

Table 6.2—REDOX AND PUREX ANALYTICAL PROGRAM

Sample	Approximate composition		Routine determinations	Usual method
	Redox	Purex		
Metal–solution blend	$2M$ U(VI) $<0.3N$ acid. $0.1M$ $Al(NO_3)_3$.	$1.8M$ U(VI) $1N$ acid.	Total alpha (Pu) U Specific gravity Acidity Am, Cm	Direct alpha counting. Density caculation. Falling drop. Oxalate potentiometric. Extraction, alpha counting.
Feed to codecontamination	As above with $0.2M$ Cr(VI).	As above	Total alpha (Pu) Acidity Am, Cm	Direct alpha counting. Oxalate potentiometric. Extraction, alpha counting.
Various column waste streams throughout the entire process (both organic and aqueous streams analyzed to establish column operation).			Variable (usually) U Pu Specific gravity Acidity	Fluorimetric. Extraction, alpha counting. Falling drop (high-level activity). Pycnometric. Varies, depending on sample.
Feed to partitioning	$1.3M$ U(VI) $1.1M$ $Al(NO_3)_3$. $0.2N$ acid-deficient. $0.06M$ Cr(VI).	$1.8M$ U(VI) $1N$ acid. $0.03N$. $NaNO_2$.	U Pu Acidity Specific gravity Cr(VI), Redox only Total gamma activity	X-ray absorptiometric. Alpha counting. Oxalate potentiometric. Falling drop. Colorimetric. Counting.

Feed to uranium recovery	2.6*M* U(VI) 0.2*N* acid-deficient.	1.5*M* U(VI) 0.3*N* acid. 0.014*M* ferrous sulfamate.	U Pu Acidity Gamma ratio	Density calculation. Alpha counting. Oxalate potentiometric. Counting.
Uranium product	2.1*M* U(VI) 0.1*N* acid.	2.1*M* U(VI) 0.1*N* acid.	U Pu Specific gravity Gamma ratio Metal impurities Gamma scan Beta ratio	X-ray absorptiometric. TTA* separation, alpha counting. Pycnometric. Counting. Emission spectrographic. Multichannel spectrometric. Counting.
Uranium trioxide product	UO_3	UO_3	U Metal impurities Pu Gamma ratio Beta ratio U^{235} S Physical characteristics.	Gravimetric. Spectrographic. TTA* separation, alpha counting. Counting. Counting. Mass spectrometric. Turbidimetric.
Feed to plutonium recovery.	1*M* Al $(NO_3)_3$ 0.2*N* acid. 0.2*M* Cr(VI).	2.7*N* acid 0.07*N* Na^+. 0.01*M* $Fe_2(SO_4)_3$.	S Acidity Total alpha (Pu) Gamma activity Cr(VI), Redox only	Fluorimetric. Oxalate potentiometric. Direct counting. Counting. Colorimetric.
Feed to second-cycle plutonium recovery.	0.9*M* $Al(NO_3)_3$ 0.2*N* acid.	Not applicable	U Pu Acidity Gamma activity	Fluorimetric. X-ray absorptiometric. Oxalate potentiometric. Counting.

Table 6.2—REDOX AND PUREX ANALYTICAL PROGRAM—Continued

Sample	Approximate composition		Routine determinations	Usual method
	Redox	Purex		
Plutonium product	6*N* acid	Same as Redox	U	Fluorimetric.
			Pu	X-ray absorptiometric.
			Acidity	Oxalate potentiometric.
			Specific gravity	Pycnometric.
			Fe	Colorimetric.
			Total alpha activity	Direct counting.
			Gamma activity	Counting.
			Metal impurities	Spectrographic.
			Specific activity	Alpha counting and chemical analysis.
Plutonium-metal product			Pu	Ceric titrimetric.
			Metal impurities	Spectrographic.
Condensates and cooling water.			Total alpha activity	Direct counting.
			Beta activity	Counting.
Recovered acids			Acidity	Titrimetric.
			Specific gravity	Pycnometric.
			U	Fluorimetric.

*TTA indicates thenoyltrifluoroacetone.

nium is reduced to the (III) valence state with excess titanous chloride and titrated with standard Ce(IV) in a nitrogen atmosphere. The titer between the first end point, representing the excess Ti(III), and the second end point of Pu(III) to (IV) is used to compute the plutonium concentration. A correction for iron, based on a separate colorimetric determination, is required.

A controlled-potential coulometric method [49] has been reported based on the work of Booman, Holbrook, and Rein [50] which appears superior to the above ceric titration method.

(e) *Americium and Curium.* The Am^{241} and Cm^{242} activities significantly affect the direct alpha count of the metal-solution blend stream and would cause high bias for plutonium if not corrected. An independent analysis [51] is made for these activities involving both tributyl phosphate (TBP) and TTA extractions.

Tetra and higher valence plutonium and U(VI) are extracted into 30 per cent TBP-xylene from a 2*M* nitric acid solution. Trivalent americium and curium have negligible extraction coefficients at this acidity and remain in the aqueous phase. The pH is adjusted to 4.5, and the americium (III) and curium (III), along with any residual uranium, neptunium, and plutonium, are extracted into 0.5*M* TTA-xylene. Tributyl phosphate is then added to the separated organic phase, and the americium and curium are stripped with 0.5*M* nitric acid; the tetra and higher valence states of the other three transuranic elements remain in the organic phase. The nitric acid strip solution is alpha counted. In addition to procedural details, the referenced work [51] includes an excellent summary of extraction coefficients of zirconium (IV), rare earths, and various oxidation states of the transuranic elements in TBP-xylene and of the transuranic elements in 0.5*M* TTA-xylene under various extraction conditions.

(f) *Chromium(VI).* The two streams analyzed in the Redox process, (1) feed to partitioning and (2) feed to plutonium recovery, are sufficiently low in activity that they can be used in conventional bench-top analytical procedures. The classical diphenylcarbazide colorimetric method is used.

(g) *Gamma-counting Measurements.* Gross gamma counting serves as a measure of fission-product contamination at various steps of the processes. Beta-activity measurements are less pertinent since the fission products, which have prescribed limitations in the products, are gamma emitters. Gamma counting is also more readily accomplished, especially by scintillation spectrometry.

The gamma ratio is a comparison of the gamma count of the sample through an 8.9 g/cm^2 lead absorber to that of natural uranium similarly measured. The absorber is used to discriminate against the

relatively low U^{237} gamma energies. Corrections are made for the residual U^{237} count and for loss in fission-product counting rates. An alternate Hanford method employs a 1.7 g/cm² lead absorber with a 0.45-Mev cutoff. At Hanford, if the gamma ratio exceeds a value of 2 in the uranium product, a gamma scan is made for identification of fission products. The advantages of multichannel spectrometers for complex-mixture identification such as this are discussed in Sec. 6–10.6.

(h) *Beta-counting Measurements.* The relative unimportance of beta measurements has been mentioned in the preceding section, and only an after-the-fact analysis is made of the final trioxide product. A 50-mg sample is counted with an end-window Geiger tube counter with a 25 mg/cm² gold absorber for U^{237} discrimination. A calculated contribution of uranium daughters is subtracted, and the result is compared with the counting rate of natural uranium similarly counted.

(i) *Specific Activity.* The specific activity must be known in order to convert total alpha measurements to plutonium-assay values. The specific-activity factor, called the F factor at Hanford and defined as grams of plutonium per alpha count per minute, is determined on a daily basis by combining alpha measurements and chemical analyses of plutonium products. Normally plant feeds are blends of known and consistent isotopic composition in order that an estimated F factor based upon the total alpha to uranium ratio can be used and revised slightly by the daily F-factor determination. Should fuels of varying irradiation history be processed, isotopic plutonium analysis is required. The isotopes Pu^{239} and Pu^{240} are determined by a thermal-ionization mass spectrometer, and Pu^{238} is determined by alpha pulse-height counting (Sec. 6–10.4). A 100-mg quantity of plutonium from the metal-blend solution is isolated by anion-exchange separation for this isotopic analysis.[52]

(j) *Metal Impurities.* The line-rich spectra of plutonium and uranium require separation of the impurities either prior to or during the spectrographic excitation period. The carrier-distillation method serves the latter purpose, and liquid–liquid extraction or ion exchange, the former. For a discussion of the merits of these various techniques see Chaps. 2 and 12.

Iron in the plutonium-metal product is determined by the classical *o*-phenanthroline colorimetric method (see Chap. 2).

(k) *Uranium Trioxide Powder Analyses.* The uranium assay is based on ignition of the uranium trioxide to U_3O_8 for 30 min in an air atmosphere at 900 to 950°C. The gravimetric result is corrected for the spectrographically determined impurities.

A mass spectrometer using uranium hexafluoride is used for U^{235} analysis (see Chap. 13).

Total sulfur, principally present as sulfates, is determined by a reduction to sulfide, distillation, and iodimetric titration. The reductant is a mixture of hydrochloric acid, hydriodic acid, and hypophosphorous acid.

The physical characteristics determined are density and particle size, the latter by standard screens.

(l) *Miscellaneous Determinations.* A considerable number of supporting analyses for process reagents and for special constituents in process samples and in the recycled extractant are, of course, required. The recycled extractant analyses are empirical and are designed to evaluate the extractant for various extraction coefficients. The methods are discussed in Sec. 6–10.3. Classical methods are used for process reagents and special constituents.

6–3 NITRIC ACID RECOVERY PROCESS FOR ALUMINUM–URANIUM FUEL

A typical example of an aluminum–uranium fuel is that of the Materials Testing Reactor (MTR) located at the National Reactor Testing Station in Idaho. The fuel element consists of parallel plates about 70 mils thick and several feet in length. The alloy is approximately 18 wt. % uranium and 82 wt. % aluminum with about 215 g of 90 per cent enriched uranium per element. The cladding is type 2S or 61S aluminum about 20 mils thick. Fuels from testing reactors such as the MTR are highly burned up, on the order of 20 to 30 per cent; therefore the concentration of fission products is high and must be considered for diverse ion effects in analytical methods, as previously discussed.

A simplified flow sheet of the recovery process used with this type fuel is given in Fig. 6.4. The solvent is nitric acid containing mercuric nitrate as a catalyst. The extractant is methyl isobutyl ketone (tributyl phosphate is also used); the aluminum nitrate formed from the dissolved aluminum serves as the salting agent. At the top of the extraction column is an aluminum nitrate scrub section. The strip solution used is dilute nitric acid. After evaporation the uranyl nitrate is processed through two more similar cycles.

6–3.1 Types of Samples

Routine analyses are made on dissolver solutions, on the aqueous raffinate streams from all three cycles, and on the final product. In addition, nonroutine samples are analyzed from the scrub column, first- and second-cycle products, and recycled organic solvent. The

Table 6.3—ALUMINUM–URANIUM FUEL ANALYTICAL PROGRAM

Sample	Approximate composition	Constituent determined	Usual method
Dissolver	1.5*M* $Al(NO_3)_3$	Acidity	Oxalate potentiometric.
	0*M* HNO_3.	U	Isotope dilution, mass spectrometric.
	1.4 mg/ml U(VI).		
	0.002*M* Hg(II).	Specific gravity	Falling drop.
	0.3 mg/ml fission products.	Fission products	Radiochemical.
First-cycle extraction column aqueous raffinate.	Same as dissolver but with less than 1×10^{-3} mg/ml U(VI).	U	Extraction, fluorimetric.
Various column waste streams in process cycle.	Both aqueous and organic samples	U	Extraction, fluorimetric.
		Radioactivity	Radiochemical.
Final product	1.5*M* U(VI)	U	Gravimetric (direct ignition).
	0.2*M* HNO_3.	Metal impurities	Extraction, emission spectrographic.

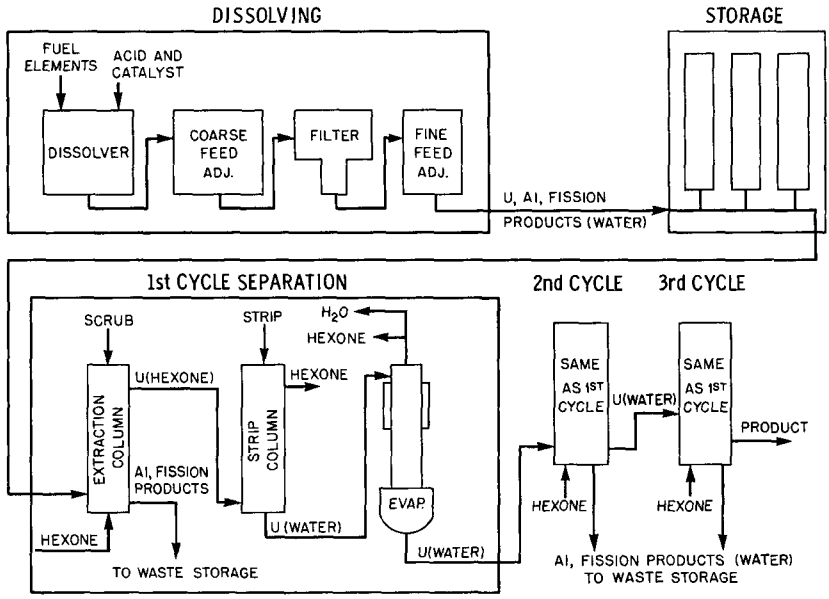


Fig. 6.4—Flow sheet for aluminum–uranium fuel recovery process.

high-level radioactive samples from the dissolver and the first-cycle aqueous raffinate are analyzed in the facility described by Dykes, Fletcher, Turk, Rein, and Shank.[16] The radiation level of these samples is about 100 rem/hr at a 6-in. distance. The analytical program [53] of the ICPP is summarized in Table 6.3.

6–3.2 Discussion of Methods

(a) *Uranium in Dissolver Solution.* The isotope-dilution mass-spectrometric method proposed by Inghram [54] and further developed by Goris, Duffy, and Tingey [55] has three decided advantages for high-activity samples. The first advantage is that, in the separation of uranium from the fission products for subsequent analysis, quantitative recovery is not necessary; hence the separation procedure can be tailored for high decontamination. The second advantage is that this method simultaneously yields total uranium concentration and uranium isotopic distribution. In the processing of highly enriched fuel, plant balances are made with respect to U^{235} which requires an isotopic analysis of the (dissolver) plant input stream. The third advantage is that, when a surface-ionization mass spectrometer is used, a few hundred micrograms of uranium is sufficient, requiring the handling of only a small sample. The mass spectrometer used at the ICPP is described by Echo and Morgan.[56]

The separation method for uranium is based on the uranium selective liquid–liquid extraction system of Maeck, Booman, Elliott, and Rein,[57] which is discussed in Sec. 6–10.2. The salting strength is decreased to increase total beta and gamma decontamination to about 1×10^4 at the expense of about a 10 per cent uranium loss. In fuel that has been cooled for four months, the only fission products to accompany uranium in any significant quantity are Ru^{103} and Ru^{106}. Uranium-233, not present in expended enriched-uranium fuel, is the added isotope. It is obtainable in 99 per cent purity from the Isotopes Division at the Oak Ridge National Laboratory.

Procedure. The procedure is as follows: 0.5 ml of a 1.00 mg of U^{233} per milliliter solution and 4 ml of 2*N* acid-deficient 2.0*M* aluminum nitrate are placed in a test tube. In the remote facility a 0.5-ml sample aliquot is delivered to the tube, and the solution is mixed until it is homogeneous; then 2 ml of methyl isobutyl ketone is added. The phases are mixed for 1 min, and about 1 ml of the organic phase is poured into a centrifuge tube, which is then transferred to a conventional chemical laboratory.

For a sample with an original radiation level of 50 rem/hr at 6 in., the radiation level in the centrifuge tube will now be on the order of 1 to 5 mrem/hr at 6 in. The sample is centrifuged, and the organic phase, now virtually free of activity, is pipetted into a clean tube. The uranium is simultaneously stripped from the methyl isobutyl ketone and precipitated by shaking for 5 min, by hand or by mechanical means, with 2 ml of 30 per cent hydrogen peroxide. Polyethylene stoppers are used since organic matter leached from neoprene stoppers causes interference in the mass spectrometer. The supernatant is decanted, and the peroxide precipitate is washed with an acetone–water (1+1) solution to remove traces of methyl isobutyl ketone, which also interferes. In the mass-spectrographic laboratory, the precipitate is dissolved with a minimum volume of warm nitric acid. The resulting solution is transferred onto a tantalum filament and then evaporated. Details of the mass spectrometer operation are given by Duffy, Wheeler, and Morgan[58] and in Chap. 13.

(b) *Uranium in Aqueous Raffinate Samples.* Liquid–liquid extraction separation followed by fluorophotometry (Sec. 6–10.2) is used to determine uranium in aqueous raffinate samples. Either the methyl isobutyl ketone extraction system of Maeck, Booman, Elliott, and Rein [57] or a tributyl phosphate system is used. The extracted fission-product ruthenium in the methyl isobutyl ketone system, even though minuscule, is objectionable if platinum dishes are employed for the fusion because a nonleachable alloy forms and with repeated use the dishes build up a sizable radiation level.

(c) *Acidity.* The oxalate-complexing titrimetric method [59] used to determine acidity is discussed in Sec. 6–10.1.

(d) *Activities and Fission Products.* Usually gross gamma and gross beta activities are determined on various samples to establish column operation performance. A 200- to 400-fold dilution of the sample is made. Aliquots are evaporated on watch glasses for beta proportional counting. Gamma counting is made in a high-pressure ion chamber. Because the samples contain a wide diversity of fission products, some with incompletely known decay schemes, gamma-counting results are reported in terms of radium equivalent.

For specific fission products conventional radiochemistry, simplified when possible by multichannel gamma scanning, is used.

(e) *Specific Gravity.* The falling-drop method, which is used to determine the specific gravity of high-level samples, is discussed in Sec. 6–10. Specific gravity on samples with low activity levels is determined on a conventional Westphal balance.

(f) *Final Product.* The concentration of total metal impurities is on the order of 1000 ppm. A direct ignition to U_3O_8, followed by a spectrographic determination of metal impurities, is used.

Aliquots of about 5 g are delivered into tared platinum crucibles; a small amount of filter-paper pulp and hydrofluoric acid are added; evaporation to dryness is carried out under infrared lamps; and the uranyl nitrate is converted to constant weight U_3O_8 in a muffle furnace at 900°C. The gravimetric uranium result is corrected for the metal impurities.

For the impurity determination, uranium is separated by extraction into 20 per cent tributyl phosphate in *n*-hexane, and cobalt–molybdenum internal standard is added to the aqueous phase, which is spectrographically analyzed by the porous-cup technique of Feldman.[60]

6–4 HYDROFLUORIC ACID RECOVERY PROCESS FOR ZIRCONIUM–URANIUM FUEL

6–4.1 Types of Samples

Navy submarine high-zirconium–low-uranium content irradiated fuel has been processed at the ICPP. A typical flow sheet [61] for a 1 per cent uranium alloy is shown in Fig. 6.5. The process involves dissolving the irradiated fuel in a Monel dissolver vessel with hydrofluoric acid, adding Cr(VI) to oxidize U(IV) to U(VI), complexing free fluoride with excess aluminum nitrate, adjusting the concentration to optimize solubility and extractability, extracting with 10 per cent tributyl phosphate in a kerosene diluent in a pulse column, and stripping with dilute nitric acid. This head-end treatment is followed by two methyl isobutyl ketone extraction cycles. Only the

690–457 O—64——34

Table 6.4—ZIRCONIUM–URANIUM FUEL ANALYTICAL PROGRAM

Sample	Approximate composition	Constituent determined	Usual method
Dissolver	1.6*M* Zr(IV)	Zr	Cupferron amperometric.
	7.4*M* total F^-.	Acidity	Oxalate potentiometric.
	0.8*N* acid.	U	Isotope dilution, mass spectrometric.
	1.5 mg/ml U(IV).		
		Specific gravity	Falling drop.
		Fission products	Radiochemical.
Column feed	0.55*M* Zr(IV)	As above, plus	As above.
	2.5*N* acid.	Al	Fluoride complexing pH titrimetric.
	0.5 mg/ml U(VI).		
	0.01*M* Cr(VI).	F	Pyrohydrolytic, thorium conductometric.
	4.1*M* total NO_3^-.		
	0.75*M* Al(III).		
	3.0*M* total F^-.	U	Extraction, fluorimetric.
Column raffinate	Same as column feed but with less than 1×10^{-3} mg/ml U(VI).		
Column product	1.0*M* U(VI)	U	Isotope dilution, mass spectrometric.
	0.6*N* acid.		
		Fission products	Radiochemical.
Extractant collection tank	10% TBP–kerosene with less than 0.1 mg/ml U(VI).	% TBP	Acid saturation.
		Fission products	Radiochemical.

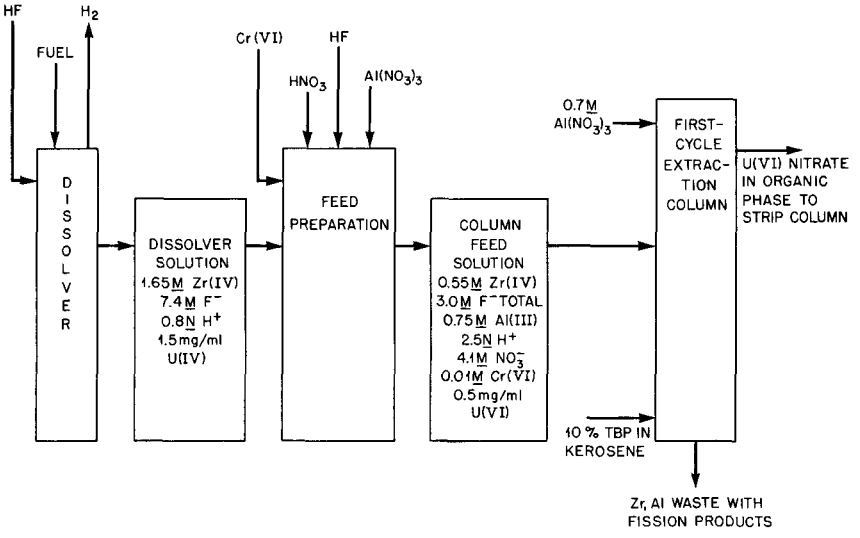


Fig. 6.5—Folw sheet for zirconium-uranium fuel recovery process.

analytical program for the head-end treatment [62] is described here (Table 6.4) since the second and third cycles are substantially as given in Sec. 6–3 for aluminum–uranium fuel.

6–4.2 Discussion of Methods

(a) *Uranium in Dissolver and Column Feed.* The isotope-dilution mass-spectrometric method as discussed in Sec. 6–3 for aluminum fuel is used with one modification for the dissolver sample. A small amount, 0.1 ml, of chromium(VI) is added to ensure oxidation of uranium to the extractable (VI) valence state.

(b) *Zirconium.* The amperometric method, with cupferron as the titrant, of Olson and Elving [63] was adapted to remote analysis. This method is directly applicable to fluoride-containing samples, and neither aluminum nor uranium interferes. The concentration of fission-product zirconium is negligible compared with that of the fuel alloy.

An aliquot of the sample containing about 0.09 millimole of zirconium is titrated with standard 0.05*M* cupferron with a dropping-mercury electrode at a reduction potential of −0.84 volt vs. the saturated calomel electrode. An important pretreatment is heating the sample before titration in 18*N* sulfuric acid to dissociate polymeric zirconium species that are sufficiently stable to prevent stoichiometric reaction with cupferron.

(c) *Aluminum.* The pH method of Hays [64] was modified by Paige, Elliott, and Rein [65] especially for the column feed samples. Fluoride is removed from a sample aliquot containing 5 to 11 mg of aluminum by a single fuming with sulfuric acid. Aluminum in the residue is dissolved with sodium hydroxide, the pH is adjusted to 10.5 to 10.6, potassium fluoride is added, and a back-titration is made to the same pH value (10.5 to 10.6) with standard hydrochloric acid. The added fluoride complexes the aluminum and releases an equivalent amount of hydroxyl ions according to the reaction

$$AlO_2^- + 6F^- + 2H_2O \longrightarrow AlF_6^{-3} + 4OH^-$$

Under actual conditions the ratio of hydroxyl ions released per aluminate ion is nearer 3.9 than 4.

(d) *Fluoride.* Pyrohydrolysis with an aluminum oxide accelerator followed by a conductometric titration with thorium nitrate is used for the determination of fluoride.[66] The procedure consists in three distinct steps: (1) pipetting the sample into a nickel boat partially filled with aluminum oxide; (2) pyrohydrolyzing at 1000°C; and (3) titrating. Each operation is performed in a separate remote-operation box.

(e) *Tributyl Phosphate (TBP).* Dykes [67] modified the acid extraction method for TBP determination of Allen and DeSesa [68] from a potentiometric to a bromthymol blue indicator end point. Uranium up to 5 g per liter does not interfere; above this concentration a preliminary strip with carbonate is made. The procedure involves the titration of nitric acid extracted into the TBP diluent after three equal-volume contacts with 8*M* nitric acid. An advantage of the indicator end point is that, as the last traces of acid are extracted from the organic phase by the standard base titrant, a clear warning is given.

6–5 SULFURIC ACID RECOVERY PROCESS FOR STAINLESS STEEL–URANIUM FUEL

Two stainless-steel-clad stainless steel–uranium dioxide reactor fuels, the North American Aviation Organic Moderated Reactor Experiment (OMRE) and the Navy Submarine Intermediate Reactor (SIR), were processed at the ICPP in 1959. The process, which is similar to that used with the zirconium–uranium fuel, consisted in a special head end treatment (Fig. 6.6) involving dissolution and one tributyl phosphate extraction cycle followed by two methyl isobutyl ketone extraction cycles. The dissolution is a two-step process made in a Carpenter-20 stainless-steel vessel. Sulfuric acid is first added to dissolve the bulk of the stainless steel. The final result is a slurry of uranium dioxide and small quantities of insoluble stainless-steel com-

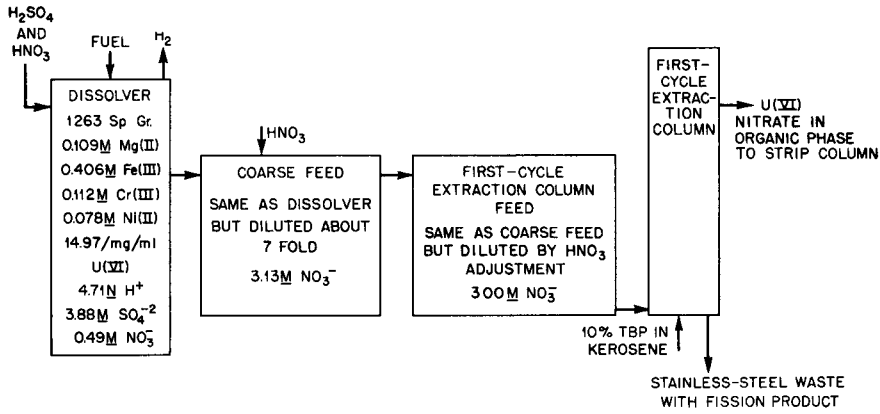


Fig. 6.6—Flow sheet for stainless steel–uranium fuel recovery process.

ponents. Nitric acid is then introduced primarily to dissolve the uranium dioxide. It also serves to passivate the surface of stainless-steel vessels in subsequent processing stages. A ball of steel wool is inserted in each fuel rod prior to dissolution to initiate the reaction. The dissolver is washed with water between batches to remove nitrate which would passivate the next fuel loading.

6–5.1 Types of Samples

The analytical program [69] for the head-end treatment only is discussed here because the second and third extraction cycles are similar to those used for aluminum–uranium fuel (Sec. 6–3).

Table 6.5 summarizes the analytical program. Again, many of the methods are the same as those used for the aluminum–uranium fuel and zirconium–uranium fuel and are discussed only if modified.

6–5.2 Discussion of Methods

(a) *Uranium in Dissolver and Coarse Feed.* The isotope-dilution mass spectrometric method for uranium as described for aluminum fuel (Sec. 6–3) provides the official plant result but is time consuming, requiring about 2 hr. The passivation effect and a criticality problem that would exist if double batching should occur require a rapid uranium result. The rapid-extraction spectrophotometric method of Maeck, Booman, Elliott, and Rein [70] was adapted. This method, specific for uranium, involves an extraction of the trinitratouranyl complex of tetrapropylammonium nitrate from an acid-deficient aluminum nitrate salting solution into methyl isobutyl ketone followed by a direct absorbance measurement at 452 mμ.

Table 6.5—STAINLESS STEEL–URANIUM FUEL ANALYTICAL PROGRAM

Sample	Approximate composition	Constituent determined	Usual method
Dissolver	0.40*M* Fe (III)	Fe	Dilution, spectrophotometric.
	0.11*M* Cr (III).	U	Isotope dilution, mass spectrometric.
	0.08*M* Ni (II).		
	0.11*M* Mg (II).		Extraction, spectrophotometric.
	4.7*N* acid.	NO_3^-	Spectrophotometric.
	3.1*M* SO_4^{-2}.		
	0.50*M* NO_3^-.		
	15.0 mg/ml U(VI).		
Dissolver wash	Decreasing concentrations of dissolver	Acidity	Titrimetric.
Course feed	Same as dissolver but diluted about sevenfold with HNO_3 and a final NO_3^- concentration of 3.1*M*.	U	Isotope dilution, mass spectrometric.
			Extraction, spectrophotometric.
		NO_3^-	Spectrophotometric.
		Acidity	Oxalate potentiometric.
		SO_4^{-2}	Lead amperometric.
		Specific gravity	Falling drop.
		Fission products	Radiochemical.
Column feed	Same as course feed but adjusted to 3.0*M* NO_3^-.	NO_3^-	Spectrophotometric.
Column raffinate	Same as column feed but less than 1×10^{-3} mg/ml U(VI).	U	Extraction, fluorimetric.
Column product	1*M* U(VI)	U	Isotope dilution, mass spectrometric.
	0.8*N* acid.		
		Fission products	Radiochemical.
Extraction collection tank	10% TBP–kerosene with less than 0.1 mg/ml U(VI).	% TBP	Acid saturation.
		U	Fluorimetric.

In practice a test tube containing 6 ml of the $2N$ acid-deficient $2.8M$ aluminum nitrate salting solution, and 3 ml of methyl isobutyl ketone is transferred to the remote facility. A 0.75-ml sample aliquot is pipetted, and the phases are mixed for 3 min. Most of the organic phase, virtually free of activity, is poured into a centrifuge tube and transferred to a conventional laboratory. After centrifugation the organic phase is transferred to a 1-cm Corex cuvette, and the spectrum is scanned over the region of 400 to 500 mμ. Base-line corrections are made on the 452-mμ peak absorbance, and the results are computed based on standards processed concurrently with samples. This procedure takes about 30 min.

(b) *Iron in Dissolver.* A diluted aliquot is analyzed by the well-known *o*-phenanthroline spectrophotometric method.

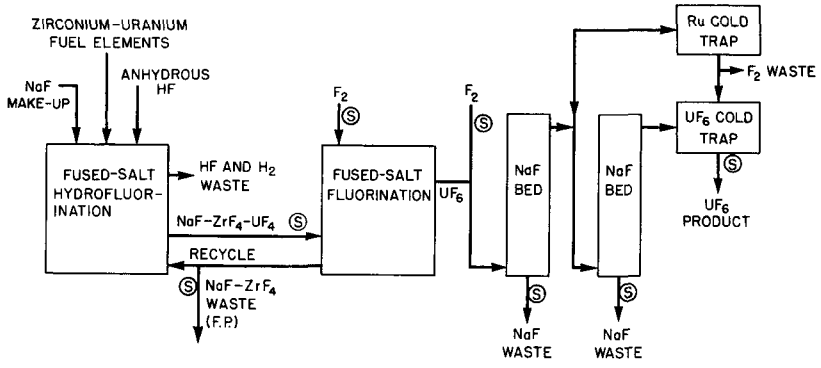
(c) *Nitrate in Various Samples.* The dissolver wash samples are analyzed for total acid by titration with standard base to a phenolphthalein end point. If the result is less than $0.01M$, the dissolver is considered to be sufficiently flushed for the next fuel batch.

The other samples are analyzed for nitrate by a spectrophotometric method [71, 72] based on the purple complex of ferrous nitrosyl sulfate. A test tube containing ferrous sulfate reagent and sulfuric acid is transferred to the remote facility and placed in an ice bath, and a sample aliquot containing from 0.007 to 0.16 millimole of nitrate is remotely pipetted into it. After a color development period of 40 min, the absorbance is measured at 530 mμ in a remotely operated colorimeter. The ice bath is necessary to prevent loss of volatile oxides of nitrogen.

(d) *Sulfate.* A remote amperometric titration with lead nitrate at -1.2 volts vs. the saturated calomel electrode with a dropping-mercury electrode is used for the determination of sulfate.[71] The remote-titration apparatus is the same as that used for the zirconium titration (Sec. 6–4). An aliquot of the sample, containing from 0.05 to 0.45 millimole of sulfate in a 40 vol. % methanol medium, is adjusted in pH to the incipient iron(III) hydroxide formation, deaerated with nitrogen, and titrated with standard $0.088M$ lead nitrate.

6–6 FLUORIDE-VOLATILITY RECOVERY PROCESS

The fluoride-volatility reprocessing scheme is especially applicable to fuel alloys containing a small percentage of fissionable material and to molten-salt fuels. So that the corrosion rates of containment vessels will be sufficiently low, ternary salt mixtures with eutectic points in the 500 to 700°C range are used. The most promising systems include: UF_4, ZrF_4, NaF, LiF, and BeF_2. A typical flow sheet used at ORNL [73] is shown in Fig. 6.7. For fused-salt reactors the



Ⓢ ROUTINELY SAMPLED FOR ANALYSIS.
(F.P.) FISSION PRODUCTS.

Fig. 6.7—ORNL fused-salt volatility process flow sheet.

initial hydrofluorination–dissolution step would not be required. The uranium hexafluoride product can be directly used in the gaseous diffusion plants for increasing the enrichment to reactor specifications. Processes developed at ANL using interhalogen compounds for dissolution and fluorination are similar, using fractional distillation in place of sodium fluoride bed chromatography.

Table 6.6—FLUORIDE-VOLATILITY-FUSED-SALT RECOVERY PROCESS ANALYTICAL PROGRAM

Sample	Constituent	Concentration, mg/g	Usual method
Fluorination feed	U(IV)	60	Thiocyanate colorimetric or iron potentiometric.
	Zr(IV)	387	Thoron colorimetric.
	Na^+	117	Flame photometric.
	F^-	440	Pyrohydrolytic, U_3O_8 accelerator, back-titration with acid.
	Fission products		Gamma scintillation.
			Conventional radiochemistry.
Adsorption beds	NaF	~1000	
	U(VI)	Trace	Fluorimetric.
			Dissolution in aqueous $Al(NO_3)_3$.
Fluorine feed	F_2	~1000	In-line absorption in KI, titration with $Na_2S_2O_3$

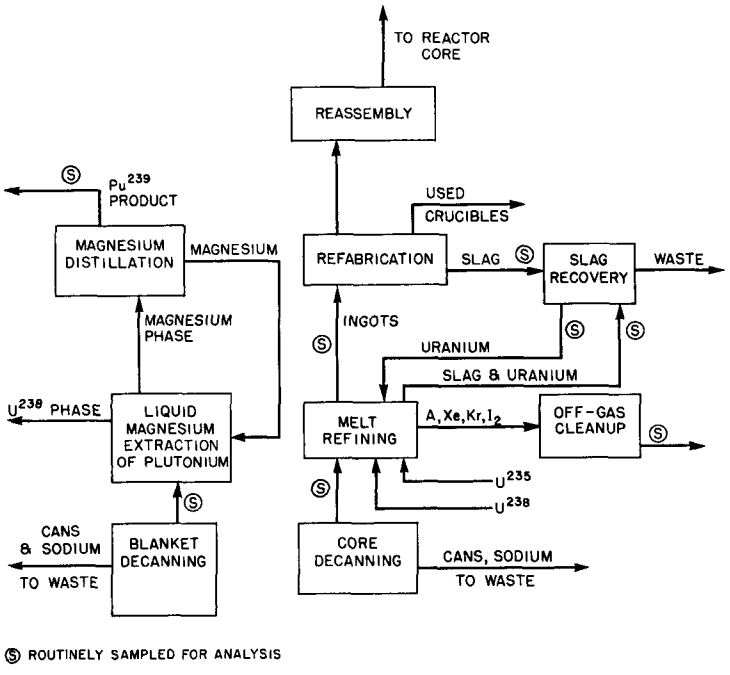


Fig. 6.8—A pyrometallurgical process flow sheet.

6–6.1 Types of Samples

Table 6.6 gives the composition of typical UF_4, ZrF_4, and NaF fused salt, and sodium flouride adsorption-bed matrices.

6–6.2 Discussion of Methods

Dissolution of samples requires special remote-handling treatment. Boiling with mixed nitric and perchloric acid is effective but was not used when the analysis of volatile fission-product constituents was required. Aqueous dissolution in an aluminum nitrate–nitric acid mixture is rapid. Subsequent boiling serves to oxidize the uranium to the hexavalent state.

6–7 PYROMETALLURGICAL RECOVERY PROCESS

Pyrometallurgical processing has inherent economic advantages as a fuel-reprocessing scheme. Figure 6.8 shows a suggested flow sheet for processing the (EBR–2) fuel.[74] The flow sheet and methods discussed are for an enriched-uranium core loading. The use of plutonium core loading would require little change in method require-

Table 6.7—PYROMETALLURGICAL RECOVERY PROCESS ANALYTICAL PROGRAM

Sample	Equilibrium composition, wt. %		Usual method
Unrefined uranium	U^{235}	48	Mass spectrometric.
	U^{236}	7.1	Mass spectrometric.
	U^{238}	35.9	Mass spectrometric.
	Pu^{239}	1.9	Not determined.
	Zr	0.1	Not determined.
	Mo	2.2	Not determined.
	Tc	1.0	Not determined.
	Ru	1.8	Not determined.
	Rh	0.3	Not determined.
	Pd	0.2	Not determined.
	Xe	0.2	Not determined.
	Cs	0.2	Radiochemical.
	Total rare earths	0.6	Radiochemical.
	Other fission products.	0.4	Radiochemical.
Refined uranium	U^{235}	50	Mass spectrometric.
	U^{236}	7.1	Mass spectrometric.
	U^{237}	curies/g—2.1	Mass spectrometric.
	U^{238}	37.7	Mass spectrometric.
	Total U	94.9	Lead reductor, ceric sulfate titration.
	Pu^{239}	1.9	Radiochemical.
	Np^{237}		Radiochemical.
	Zr	0.1	Alizarin red S colorimetric.
	Mo	2.0	Polarographic or thiocyanate colorimetric.
	Tc	1.0	Thiocyanate colorimetric.
	Ru	1.6	Perruthenate colorimetric.
	Rh	0.3	Hypochlorite colorimetric.
	Pd	0.2	Dimethylglyoxime or 2-nitroso-1-naphthol colorimetric or polarographic.
	Ba		Radiochemical.
U^{238} discharged from blanket.	U^{238}	>98	Amperometric titration.
	Pu^{239}	≤ 1	Radiochemical.
	Total fission products 0.02 to 0.6% (total atom burn-up).		Selected fission products by radiochemical means.
Pu^{239} product	Pu^{238}	*2×10^{-5}%	Mass spectrometric.
	Pu^{239}	*~100%	Radiochemical.
	Pu^{240}	*0.1%	Alpha pulse analysis.
	Mg	~1	Colorimetric.

Table 6.7—PYROMETALLURGICAL RECOVERY PROCESS ANALYTICAL PROGRAM—Continued

Sample	Equilibrium composition, wt. %	Usual method
Miscellaneous constituents at other sampling points.	Cs 0.5	Flame photometric.
	Kr^{85}	Radiochemical, total activity.
	Xe^{133}	Radiochemical, total activity.
	I^{129}, I^{131}, I^{133}	Radiochemical, total activity.
	Trace U 0.1	Dibenzoylmethane. colorimetric.
	Sr 0.8	Flame photometric.

* Isotope composition.

ments. Extraction with liquid metal, distillation of metals, and slagging operations are illustrated in the flow sheet.

6–7.1 Types of Samples

Table 6.7 gives typical concentrations and analysis methods for important sampling points.

6–7.2 Discussion of Methods

Many of the methods used are conventional and are discussed in Chaps. 1, 2, 11, and 14.

Some fission products are present in relatively large concentrations in the equilibrium reactor fuel; this fact necessitates the development of methods of analysis suitable for the complex matrices encountered in the fuel cycle. Another problem unique to the pyrometallurgical process is that of obtaining a representative 1-g sample for analysis from a large quantity of slag or accumulation of waste cans and trimmings. The subsequent quantitative dissolution of the alloy containing several per cent of the platinum-group metals is also a problem. Proper sampling may require special mechanical pretreatment.

Dissolution techniques applicable to these metal samples have been discussed by Larsen.[75] Aqua regia is recommended as the only satisfactory solvent for pyrometallurgical equilibrium fuel (uranium-fissium). The addition of hydrofluoric acid is necessary for solubilizing zirconium. Since the dissolution involves several critical steps, close adherence to the suggested scheme is recommended.

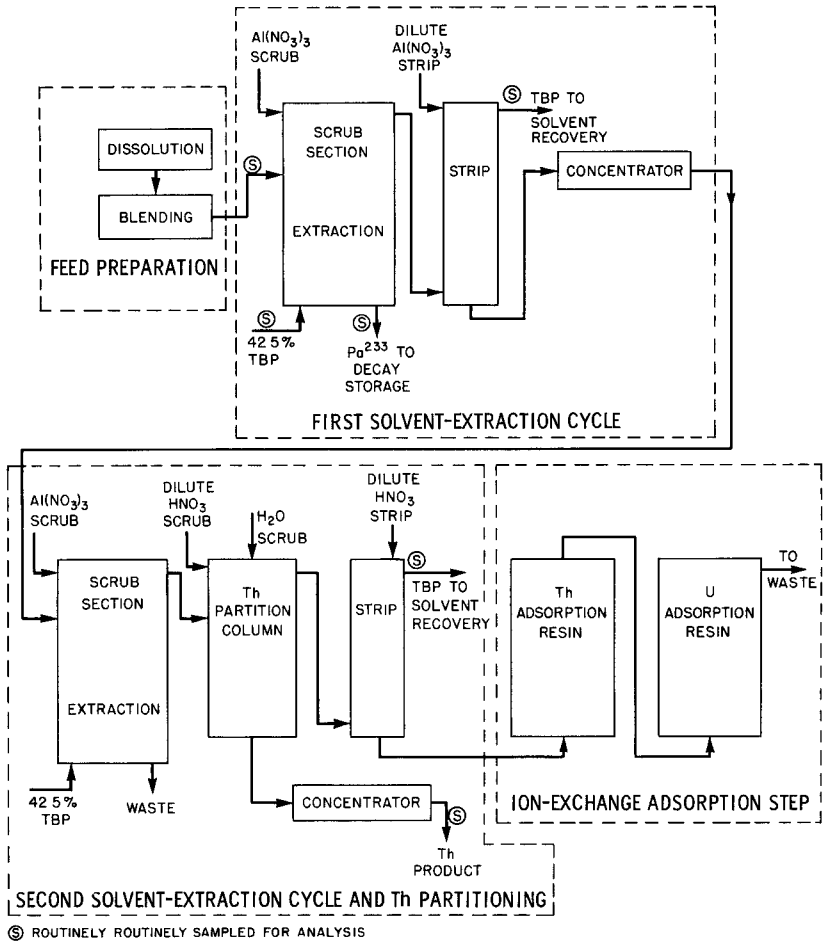


Fig. 6.9—Flow sheet for Thorex recovery process.

(a) *Ruthenium.* The use of alkaline media and the measuring of the perruthenate absorbance allow sufficient sensitivity and ease of sample preparation as compared to the use of organic complexing agents with ruthenium in acidic media. The method[76] involves bismuthate oxidation in an acid medium, ruthenium tetroxide being distilled into a 1*M* sodium hydroxide and 0.3 per cent sodium hypochlorite solution. The perruthenate absorbance is measured at 385 mμ. The molar absorbance index at this wave length is given as 2150±10.

(b) *Technetium.* A sensitive thiocyanate colorimetric method[77] has been used for technetium. The molar absorbance index of the Tc(V) thiocyanate complex is 47,500±500 at 510 mμ. The color is developed in a 4.0*M* sulfuric acid media by reduction of the Tc(VII)

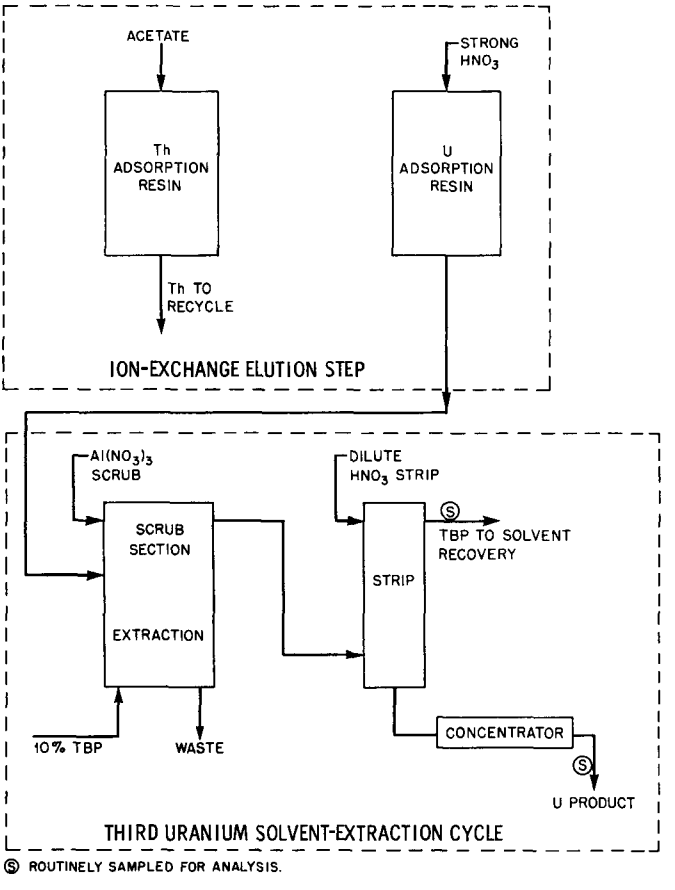


Fig. 6.9—(Continued).

with ammonium thiocyanate. Acetone is added to increase the specificity. Under the conditions used (outlined in Ref. 77), the rate of formation of interfering rhenium and molybdenum thiocyanate complexes is sufficiently slow to cause no significant interference.

6–8 NITRIC ACID RECOVERY PROCESS FOR IRRADIATED THORIUM

A simplified flow sheet of the revised Thorex process [13] is given in Fig. 6.9. This process has been used only for thorium metal, but it is applicable to other fuel or blanket materials containing thorium with appropriate head-end treatment.

6–8.1 Types of Samples

Table 6.8 gives typical concentrations and analysis methods for important sampling points.

Table 6.8—THOREX RECOVERY PROCESS ANALYTICAL PROGRAM

Sample	Composition	Usual method
First-cycle feed	320 mg/ml Th(IV)	Thoron colorimetric.
	5.0*N* acid	Oxalate potentiometric.
	3×10^6 counts/min/ml U^{233} (VI).	Alpha counting.
	Specific gravity, 1.6	Falling drop.
	10^{10} counts/min/ml Pa^{233} (V)	Diisobutyl carbinol extraction (not routine), gamma scintillation counting.
Organic waste	Variable acid	Oxalate potentiometric.
	Trace Th(IV)	Strip, thoron colorimetric.
Thorium product	450 mg/ml Th(IV)	Thoron colorimetric.
	1.8*N* acid	Oxalate potentiometric.
	0.03 mg/ml PO_4^{-3}	Colorimetric phosphate.
Organic extractant	TBP to 42.5%	Dielectric constant.
	Specific gravity, 0.84	Westphal balance.
Uranium product	200 mg/ml U(VI)	Thiocyanate colorimetric.
	0.5*N* acid	Oxalate potentiometric.
	5 mg/liter Fe(III)	*o*-Phenanthroline colorimetric.
	1 mg/liter Al(III)	Aluminum colorimetric.
	Trace Pu(IV)	TTA extraction, counting.

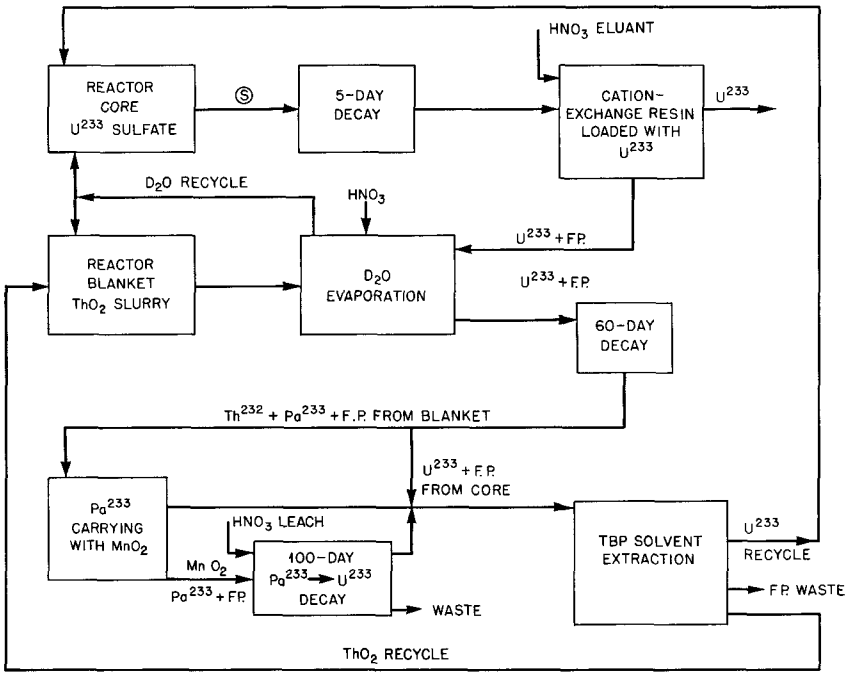
6–8.2 Discussion of Methods

The analytical methods are all given in detail in the *ORNL Master Analytical Manual.*[78] Because of the high specific activity of U^{233} and because high accuracy was not required, sensitive methods were used with large dilutions of the sampels. Solid $Th(NO_3)_4 \cdot 4H_2O$ served as the thorium standard.

(a) *Protactinium.* The diisobutyl carbinol extraction method for protactinium was not used extensively. Protactinium rapidly plates out on glass. A hydrochloric acid solution (1+1) keeps protactinium in solution; immediate dilution into this media is advisable. Plating occurs also on polyethylene, but vigorous shaking will redissolve the deposited material.

(b) *Acid in Organic Samples.* The acid was determined in organic samples by adding the sample aliquct directly to an oxalate solution at pH 7.0 (see Sec. 6–10.1) and titrating to a visual phenolphthalein end point instead of the usual potentiometric titration.

(c) *Tributyl Phosphate–Dielectric Constant Method.* The dielectric-constant method for tributyl phosphate gave as much as 1 per cent



Ⓢ ROUTINELY SAMPLED FOR ANALYSIS.
(F.P.) FISSION PRODUCTS.

Fig. 6.10—Flow sheet for homogeneous-reactor recovery process.

bias when a new batch of kerosene diluent was used. Use of the acid equilibration procedure eleminates this problem (see Sec. 6–10.3).

6–9 RECOVERY PROCESS FOR HOMOGENEOUS–REACTOR FUEL

The aqueous homogeneous-reactor program [73] is a study that includes continuous chemical processing of aqueous streams directly from the reactor. As shown in the flow sheet in Fig. 6.10, several unique chemical steps are involved in this process. The fuel and blanket streams are made up of highly enriched heavy water. Short decay times between process steps result in extremely high radiation levels from analytical samples. Special thick-walled concrete shielding is required (see Sec. 6–1). Large quantities of protactinium are present, giving rise to sample stability problems through severe hydrolysis and plating out on containers. Uranium-233, also present at high levels, necessitates isolation and shielding from the alpha activity.

Table 6.9—HOMOGENEOUS-REACTOR RECOVERY PROCESS ANALYTICAL PROGRAM

Component determined	Usual method employed
U	Controlled potential coulometric (sequentially).
Ni	Controlled potential coulometric (sequentially).
Cu	Controlled potential coulometric (sequentially).
Acid	pH, oxalate potentiometric or cation exchange, photometric titration.
SO_4^{-2}	Cation exchange, photometric titration with Ba(II).
Fe, Cl^-, Li, K, F^- — trace level	Fe^{59} by TTA extraction and gamma counting, others by conventional methods.
D_2O	Distillation, falling drop or distillation, pycnometric.

6–9.1 Types of Samples

Typical concentrations of ions present in the reactor-core solution and the analytical method are given in Table 6.9. The analytical samples encountered in blanket processing, including the final solvent-extraction separation, are similar to those encountered in the Thorex process (Sec. 6–8).

6–9.2 Discussion of Methods

Again, detailed information on procedures used for samples from the homogeneous-reactor program is given in the *ORNL Master Analytical Manual.*[79] Radiochemical analysis poses no special problems after the initial dilution. Spectrographic analysis requires the excitation source to be installed behind heavy shielding, which makes control of chemical contamination in the arcing region difficult. The influence of thorium dioxide particle size on stability and corrosion requires special measurements of settling rate and particle size. Obtaining aliquots of slurry samples was simplified by the use of a graduated centrifuge cone with a rubber diaphragm screw top to transfer samples from the process plant to the remote-control analytical facility.

(a) *Sulfate.* The remote adaptation of a cation-exchange separation method for the determination of sulfate [80] was successful with these high-activity samples. Decomposition of the resin was sufficient to necessitate periodic replacement with new resin.

(b) *Heavy Water.* Remote distillation of a few milliliters of sample, followed by density determinations with a pycnometer or by the falling-drop method, was used for heavy-water analysis. Measurement of the characteristic absorption bands in the near infrared region has been considered for routine use at the Savannah River Laboratories, being operationally superior to mass-spectrometric measurement. Careful density measurements using pycnometers are necessary for calibration standards (see Chap. 9).

(c) *Coulometric Analysis.* The use of controlled-potential coulometry for the sequential analysis of copper, uranium, and nickel in one sample aliquot proved to be an excellent analytical method for these ions.[81, 82] In this method, copper and uranium are reduced in 1*M* sulfuric acid, the copper is then stripped anodically, and the nickel is reduced after ammonium hydroxide has been added to give a suitable medium.

6–10 GENERAL DISCUSSION OF METHODS

Several analytical methods are of prime importance for process control almost independent of the fuel-reprocessing scheme. Acidity is important for dissolution and extraction control. Uranium and plutonium analyses are required for establishing separation efficiencies, for determining fissionable-material inventories, and for criticality control. Solvent properties must meet strict specifications to maintain adequate decontamination from fission products. Specific-gravity determinations are simple and reliable, serving as a quickly obtainable guide for checking process steps. Radiochemical measurements are essential in all fuel reprocessing plants for evaluating decontamination and for protection of personnel.

6–10.1 Acid

The presence of large concentrations of hydrolyzable ions, such as aluminum, uranium, plutonium, thorium, zirconium, and iron, greatly complicate the determination of acidity in process samples. Separation of acid and metal ions by ion exchange (Sec. 6–9), the formation of complex species showing smaller acidity effects, extrapolation to zero metal-ion concentration, and the use of two or more measurements such as pH and metal-ion concentration have been used.[59] Thermometric titration is feasible in some specific cases.[83] An accurate knowledge of the bias of the different methods has been hampered by lack of suitable metal salts or solutions of known acid content for use as standards. Conductometric standardization [59] or careful chemical analysis of the salt is recommended.

690–457 O—64——35

Methods involving the formation of complexes followed by a potentiometric titration are commonly used but are subject to considerable bias.[59] The constant-pH titration procedure [59] ensures an identical pH for complex formation independent of the sample composition.

After a method for the determination of acid has been chosen, the interaction of acidity and metal-ion levels should be measured if such data are not available.

6–10.2 Uranium

The literature on methods for the analysis of uranium is extensive (see Chap. 1). In quite pure solutions advantage can be taken of the high molecular weight enabling simple density measurement or X-ray absorption measurement. For high accuracy an ignition at a temperature between 900 and 1000°C and a weighing of the U_3O_8 is commonly used (see Sec. 6–3). A highly specific and rapid spectrophotometric method using extraction of the uranium tetrapropyl ammonium nitrate complex from acid-deficient aluminum nitrate into methyl isobutyl ketone followed by measurement of the very characteristic uranyl trinitrate absorption is applicable to samples in the semimicro range.[70]

Trace uranium is usually determined by measurement of the uranyl fluorescence in sodium fluoride–lithium fluoride or sodium carbonate melts.[84] Although possessing a high sensitivity, the method is limited in precision by a critical dependence on the melting and annealing conditions. Improvement of this method by refined control techniques is probably not warranted because of the concomitant complexity.

Dibenzoylmethane is the preferred colorimetric reagent for microgram amounts of uranium. Since the reagent is not specific, very high separation factors from major solution components are required. An adaptation of the extraction into methyl isobutyl ketone from acid-deficient aluminum nitrate [57, 70] appears to offer the best separation from all interfering species with ease of color development although other separation schemes may be advantageous for specific samples.[85, 86]

Since mass-spectrometric measurement of the isotopic composition of the uranium is required during the recovery process, uranium concentration can also be obtained by spiking the sample with a uranium isotope not present in the process material (see Sec. 6–3).

A separation step is required in nearly all uranium determinations. The classical ether extraction has been displaced by simpler, more specific separation schemes. Among the extraction methods the methyl isobutyl ketone method mentioned above, and variations in this method (Sec. 6–3), is quite specific; but, as with ether extractions,

destruction of the organic material is often required before a redox method can be used for the final determination.[2] Extraction methods with trioctylphosphine oxide–hexane or triisooctylamine–hexane [85, 87] offer advantages of fewer organic degradation products but are not as specific. The carbonate and hydroxide separation methods are seldom used. Separation on an anion resin can be accomplished with the nitrate or sulfate anionic complexes of uranium. Reproducibility and simplicity of experimental conditions and apparatus make a single extraction preferable to an ion-exchange separation, especially when the separation must be done behind shielding.

Titrimetric methods are required for high-precision analysis of samples having insufficient uranium for gravimetric determination. An excellent volumetric method uses a lead reductor for reducing U(VI) to U(IV) with a subsequent Ce(IV) titration.[88] Controlled-potential coulometry is being used extensively; it offers the advantages of specificity and simplicity over volumetric titrimetry. The method has been adequately described.[2, 50, 81, 87] Improvements in cell design to give more reproducible geometry and in design of the potential-control current-integrating circuitry to give optimum control have been described.[98] These should improve sensitivity and precision and should make coulometry an even more useful analytical tool. An example of the versatility of controlled-potential coulometry is given in Sec. 6–9.

6–10.3 Organic Solvents

Since liquid–liquid extraction is presently the only large-scale separation process used, the analysis of constituents in the organic phase is required for process control. Methyl isobutyl ketone can be determined [89] by the absorption of the carbonyl group at 280 mμ.

The quality of the high-purity kerosene diluent used in the Purex process, besides meeting density and flash-point requirements, is often checked by a chromyl chloride number test ("C" test) and by the "Z" test. Measurement of the amount of material oxidized by the disappearance of chromyl chloride and the rate at which oxidation occurs is a measure of branched aromatic and unsaturated compounds in the solvent.[90] If the excess reagent is measured as a function of reaction time over a period of 90 min and the difference between the Cr(VI) added and the back extrapolation at zero time is obtained, a measure of aromatic compounds having attached methyl groups is obtained. The Z-number test is a measure of degradation products in the solvent using the distribution of tracer zirconium.[91] This method involves equilibration of the tributyl phosphate-kerosene phase with zirconium tracer, three washes with nitric acid, and counting. The Z number is defined as the amount of zirconium retained in the solvent under the

specified conditions. Since zirconium activity is the limiting factor on decontamination in the Purex process, a quite direct solvent-quality measurement is obtained.

Purex process control also requires knowledge of the concentration of the extracting reagent, TBP. A plot of dielectric constant vs. TBP concentration [92] is a simple method that works well as long as the dielectric constant of the diluent remains constant. This method is unsuitable when many different batches of diluent are used or when the diluent is changed often since recalibration would be required. A method based on the extraction of nitric acid with TBP (see Sec. 6-4) to form a TBP–$2HNO_3$ stoichiometric compound allows a precise measurement of TBP concentration through the simultaneous stripping and titrating of the acid to a bromthymol blue end point.[67, 68] By relying on a specific property of the TBP, the effect of changes in physical properties of the diluent is eliminated.

6–10.4 Plutonium

Isotopic distribution is obtained by a combination of thermal-emission mass spectrometry and alpha counting. Plutonium-238, having a half life of 90 years and being present in very small quantities, is determined by alpha counting. Alpha pulse-height analysis with a solid-state detector and a pulse-energy analyzer is necessary for confirmation of purity and to show that the characteristic Pu^{238} decay energy is present. An isotopic-dilution mass-spectrometric method has been developed for the simultaneous determination of plutonium and uranium in dissolver samples of nuclear fuels with U^{233} and Pu^{242} as the added isotopes. The two elements are separated from cladding components, fission products, americium, and curium by a selective extraction system and then are stripped under conditions that provide a controllable ratio of uranium to plutonium for simultaneous measurement with a triple-filament mass spectrometer.

As with uranium, the simple measurement of the absorption of X-rays is a rapid method for highly concentrated and relatively pure solutions. Titrimetric methods (see Chap. 2), giving very good precision, have been developed using the reduction of Pu(VI) to Pu(IV) with excess standard ferrous iron followed by back-titration with dichromate. Controlled-potential coulometry, following reduction of Pu(IV) to Pu(III) has advantages of specificity and high precision with submilligram samples.[49]

The separation of plutonium from interferences can be accomplished by the use of multiple hydroxide and lanthanum fluoride carrier precipitations (see Chap. 2) but is a lengthy procedure requiring yield determination. The extraction of plutonium with thenoyltrifluoroacetone (TTA) is quite specific for quadrivalent ions in strongly acidic

media.[93] Oxidation-state adjustments and multiple extractions give a clean separation. A procedure more easily adaptable to shielded facilities involves oxidation of plutonium to the hexavalent state with permanganate, extraction from acid-deficient aluminum nitrate into methyl isobutyl ketone, scrubbing, stripping with nitric acid plus hydroxylamine, adjustment to the tetravalent state with Fe(II) and nitrate, and extraction into TTA-xylene.[94]

A specific spectrophotometric method [100] for plutonium involves silver (II) oxidation, quantitative extraction of plutonium (VI) as the tetrapropylammonium trinitrate complex into methyl isobutyl keton, and measurement of the characteristic absorption spectrum.

6–10.5 Specific Gravity

Specific gravity is a highly reliable measurement and is widely used to follow dissolution, to check composition, and to identify flowing-stream samples. The falling-drop method, using Stokes' law to calculate specific gravity from the velocity of a small drop falling in a reference liquid of slightly less specific gravity than the drop, is a standard method in shielded facilities.

A 5-μl drop falling into appropriate binary mixtures of mineral oil, *o*-nitrotoluene or bromonaphthalene, with sufficient mixtures available to give a 10- to 30-sec drop-time measurement with process samples is used at one installation.[96] Ternary mixtures for reference liquids with mineral oil, phenylcyclohexane, and 1,1,2,2-tetrabromoethane have also been used.[97] Recently, a single reference liquid consisting of a mixture of light and heavy mineral oils has been described [101] which covers the specific gravity range of 1.00 to 1.40.

6–10.6 Radiochemical Methods

For the analysis of complex fission and transuranic mixtures encountered in fuel-processing plants, multichannel gamma- and alpha-energy analyzers (see Chap. 14) are indispensable. Because analytical time is expensive and results are often needed quickly, the recent emphasis is on the development of fast methods.[95] These methods should require a minimum of manipulation, should have sufficient purity only to meet the requirements of separation by energy spectra, and should give close to 100 per cent yields to eliminate separate chemical yield determinations. Important radiochemical analyses for the reprocessing industry include Cs^{137} for reactor fuel burn-up calculation, Zr^{95}, Nb^{95}, and $Ru^{103, 106}$ for determining decontamination throughout the process, and the hazardous radioisotopes of iodine and strontium.

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CHAPTER 7

GRAPHITE

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7–1 INTRODUCTION AND HISTORY

Graphite is used extensively as a moderator or reflector in existing reactors because of its desirable nuclear, physical, and chemical properties.

Other materials that have been used for these purposes are considered in detail elsewhere in this book. However, a brief summary of the properties of some of these materials is presented for purposes of comparison. Under conditions of high temperature and oxidizing atmospheres, beryllium may display adverse metallurgical properties with respect to strength, brittleness, and machinability, as well as insufficient inertness to oxygen and water. Hydrogen and deuterium, gases under normal conditions of temperature and pressure, offer problems with regard to containment. The oxides of hydrogen and deuterium, water and heavy water, have been successfully utilized in reactors but have presented problems of instability under conditions of high temperatures and high concentrations of radiation. Severe operating and safety hazards have been encountered as a result of the corrosion of containers and the failure of a reactor component.

Graphite, however, is self-contained and strong, can be machined into intricate shapes, and is resistant to corrosion. It has good mechanical properties and thermal stability, in addition to being a good conductor of heat. Most important, artificial graphite is available in a high state of purity in multiton quantities at a reasonable cost. Disadvantages of graphite are oxidation in the presence of air at elevated temperatures, a relatively low impact strength, and its porous nature. Also, it forms carbides with some metals and metal oxides.

Although all three natural forms of carbon—amorphous carbon, graphite, and diamond—theoretically satisfy reactor requirements from a nuclear viewpoint, only artificially produced graphite fulfills the extreme purity requirements, can be fabricated into shapes capable of supporting considerable weight, can be machined to close tolerances, and is available in the large amounts needed for the nuclear reactor program. In early experiments during World War II at Chicago,

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Ill., Oak Ridge, Tenn., and Hanford, Wash., graphite was used as a neutron moderator. Following those successful applications the use of artificial graphite in atomic reactors has steadily increased.

Nuclear-grade graphite can be defined as graphitized carbon that is as free as possible of elements that absorb neutrons. Greater reactor efficiency and neutron economy are attained as the purity of the graphite is increased. The analytical chemist should know that a wide variety of graphite grades is utilized by industry and that specific impurities are added in production processes to yield a product giving maximum performance for a specialized use. Should such a graphite sample be encountered, the sample should be reviewed for specifications. Graphite has been produced of such a high degree of purity that the most sensitive emission-spectrographic techniques have failed to detect appreciable quantities of any inorganic contaminant. It has not been possible, however, to produce this quality of graphite consistently. The highest quality graphite has been produced in small quantities where strict control of raw materials, blending operations, and handling has been exercised. This graphite is used in emission spectroscopy as electrodes in research and production control when it is desired to control or study inorganic impurities in the general concentration range of 0.1 to 1000 ppm. The best quality of graphite produced on a large scale, however, has proved satisfactory for use in nuclear reactors. The range of total inorganic impurities found in this material is from 5 to less than 1000 ppm, expressed as ash.

The physical, electrical, mechanical, and nuclear properties of artificially produced graphite vary so greatly depending on the raw materials used, graphitization temperatures, and other variables, that no attempt is made to summarize them in this chapter. A thorough discussion of these properties of graphite for nuclear reactors has been presented in the literature.[1-7]

At the conclusion of World War II, interest (which had been forced to remain passive as nuclear reaction theories were proven practical in military applications) was directed to the construction of nuclear power plants. As more reactors were built throughout the world, the additional sites and levels of neutron activity made possible a more detailed study of radiation damage to graphite (along with other materials) under a wide variety of conditions of temperature, controlled atmospheres, and neutron fluxes. Radiation has been observed to have definite effects on stored energy, electrical resistivity, size of crystallites, lattice spacing, thermal conductivity, and the physical dimensions of graphite. Although the analytical chemist, as a rule, has not yet been asked to determine these properties, he should be aware that he might be requested to assist in the control of any one of these

physical properties. Any of the foregoing physical properties may be found essential to the successful performance of graphite in specific applications.

Much progress has been made in the last 10 to 15 years in correlating the physical properties of graphite with certain specific uses. Improved instrumentation and advances in the fields of physics and electronics have made possible the study of porosity, surface area, particle size, degree of graphitization, crystallite size, and other properties that can make graphite meet or fail specifications.

7–2 PRODUCTION PROBLEMS

The problems of prime concern in the production of nuclear-grade graphite have been resolved to the following:

1. Adequate quality-control analyses and utilization of purest available raw materials, particularly with respect to elements with high neutron-absorption cross sections.
2. Shipping, storing, and blending raw materials without appreciable contamination.
3. Purification of material in special atmospheres at high temperatures.
4. Representative sampling and analyses, and minimum contamination in machining, wrapping, shipping, and loading operations.

The quantitative determination of boron and the determination of total ash have proved to be essential to the achievement of adequate production control of nuclear-grade graphite.

7–3 SAMPLING OF NUCLEAR-GRADE GRAPHITE

An analysis can be no better than the sample taken to represent a given lot of material; this is particularly true with nuclear-grade graphite. The low concentration of contained impurities plus the very real danger of contamination during handling and sampling operations both contribute to the analytical problem. The established heterogeneity or nonuniformity of impurities in artificially produced graphite constitutes a major problem in the procurement of an analytical sample that is truly representative of a production lot. The following special precautions are recommended for the handling of nuclear-grade graphite:

Stock bars and samples should be handled with cotton gloves that have been laundered with boron-free soap and thoroughly rinsed. Hands and equipment should be similarly washed with boron-free soap or detergent. The samples should be cut from the stock with saws, drills, or machine tools of known composition so that, in the event that subsequent analyses reveal some evidence of contamination, it

will be possible to more readily trace this contamination to its source. An approximate evaluation of the amount of contamination from sampling equipment can be obtained by weighing saw blades, machine tools, etc., before and after sample cuts are made. More accurate evaluations of the contamination can be made by analyzing portions of the material sampled by approved procedures and comparing the results with those obtained by analyzing chunk samples broken from the same piece of graphite with sharp blows from a hammer. If the stock is wrapped in clean, dry, heavy wrapping paper before breaking with the hammer, the sample is not scattered as it is broken nor does the hammer contact the sample. (This wrapping paper should be analyzed to assure its freedom from impurities.)

Although no single sampling procedure is applicable to all situations, these generalizations are deemed important in the preparation of analytical samples that are representative of nuclear-grade graphite production lots.[8]

1. The ends of bars of graphite are less pure than the stock as a whole; a slice at least 1 in. thick, cut from the end of the bar, should be discarded before taking the sample.

2. Boron tends to concentrate in the outer layers of the bars; if possible ⅛ in. of the surface should be discarded.

A typical sampling procedure for obtaining an analytical sample that is representative of a production or shipping lot is presented. Five to twenty per cent of the pieces in a production lot or shipment are statistically selected for sampling. Two adjacent slabs are sawed from each piece at a distance from the end equivalent to one-third of the length of the stock. One slab, equal in cross section to that of the stock piece, is ¼ in. thick; the adjacent slab is cut to a thickness of ⅛ in. The saw used for this operation must be clean; it should be kept covered with a plastic sheet when not in use to protect it from dust and it should be used exclusively for the same type material.

The ¼-in.-thick slabs used for the determination of contaminating elements and the ⅛-in.-thick slabs cut for ash determinations have $\frac{3}{16}$ in. trimmed off the original surface from each of the four sides of the cross section. Test slabs are trimmed in this manner to remove impurities and contamination that might have accumulated in the outer surfaces of the stock during graphitization processes and subsequent storage and handling. Handling and sampling operations should be performed in such a manner that the chemist will measure impurities representative of the stock as finally used in the field.

The trimmed ¼-in.-thick slabs are reduced in size by passing them through a jaw crusher. The small pieces of each slab are now reduced to a homogeneous powder by passing them through a laboratory-size

pulverizer. Precautions should be exercised to maintain the crusher and pulverizer in the same clean condition as described previously for the saw. Each pulverized graphite-powder sample is stored for subsequent analyses in a clean boron-free glass or plastic bottle, properly identified as to lot number, date, etc.

Each ⅛-in.-thick test slab is hand-broken into a clean tared platinum dish in such a manner that portions representing the outside and inside sections of each slab constitute the final 50-g sample for the determination of ash content (see Sec. 7–4.1).

Triplicate 1-g portions of the homogenized material from the ¼-in.-thick slabs are weighed for the determination of boron content. Blanks are run in parallel with the samples [see Sec. 7–4.2(a)].

7–4 ANALYTICAL METHODS FOR DETERMINATION OF IMPURITIES IN NUCLEAR-GRADE GRAPHITE

The most accurate methods for the determination of inorganic impurities in nuclear-grade graphite have proved to be specific colorimetric methods after removal of the carbon by an oxidation method. Several proposed methods that are more rapid than the colorimetric procedures are discussed in Sec. 7.6.

7–4.1 Ash Determination

The determination of the total weight of nonvolatile constituents in nuclear-grade graphite has proved to be the most valuable analysis from the viewpoint of production control as well as for research and development. The physical appearance of the ash and the quantity found are extremely meaningful to an experienced analytical chemist. A light-colored ash has been found to be highest in calcium, magnesium, aluminum, silicon, or titanium. An ash of red or brown coloration is composed of iron, vanadium, or manganese as major constituents. The quantity of ash found has been verified by addition of the quantitatively determined metals, expressed as oxides. If these oxides do not equal the quantity of ash found, within experimental error, an emission spectographic analysis or X-ray fluorescence analysis of the ash has disclosed the presence of a completely unsuspected element. Large samples are required for maximum accuracy, and, when possible, no homogenization of the sample is undertaken because of the danger of introducing contaminants from equipment. In the study of homogeneity of bar stock from end to end, outside to inside, or in other special studies, the samples must be sawed from the stock as described in Sec. 7–3.

Between 400 and 650°C, the oxidation of graphite has been found to be penetrative as demonstrated by greater weight losses than

volume losses. At higher temperatures the oxidation is diffusion-controlled and very sensitive to air velocity over the surface; the oxidation losses are principally at the outer surface. Oxidation experiments in air have been performed on purified and general-purpose grades of graphite; the results of some of these experiments are cited in Table 7.1.

Table 7.1—OXIDATION RATES OF GRAPHITE IN AIR [9]

Graphite type	No. of varieties (av.)	Oxidation temperature, °C	Time for 1% weight loss, hr	Time for 6% weight loss, hr
Purified	13	500	200	----------
Purified	13	600	7	25
Purified	13	700	0. 6	1. 8
General purpose	1	500	6	----------
General purpose	6	600	0. 75	2. 5
General purpose	6	700	0. 2	0. 7

The more highly purified graphite requires a longer period of time for complete oxidation as compared with equal weights of less pure graphite under identical conditions of atmosphere and temperature. It is proposed that the kinetics of graphite oxidation are affected by the quantity and kind of contained impurities in the graphite, as well as its density, porosity, and other properties.[10]

Oxidation times are decreased by ashing at higher temperatures; however, if much vanadium is present the temperature should not exceed 720°C because above this temperature any vanadium pentoxide formed will fuse around the graphite crystals and thus prolong the ashing procedure. All nuclear-grade graphite does not contain enough vanadium for this to be a serious factor. It is recognized that the temperature in a furnace cannot be uniform from front to back, nor can it be precisely controlled.

In order that the greatest accuracy be attained for samples of very high purity, special precautions on the part of the analytical chemist might be necessary:

1. Balance calibration at the time of weighing platinum dishes, sample, and ash.

2. Evaluation of weight change of platinum dishes during the ashing procedure by running blanks of empty platinum dishes (from the same lot of platinum fabrication) along with the samples.

A typical procedure for ashing nuclear-grade graphite is as follows:

Procedure. Approximately 50 g of ⅛-in.-thick sample slab (obtained as described in Sec. 7–3) is hand broken into clean tared 100-ml platinum dishes in such a manner as to be representative of the cross section of the stock. Clean cotton gloves are worn while breaking the sample. After the gross weights have been obtained, the samples are ashed to constant weight in an electric muffle furnace at 680°C in an oxidizing atmosphere. Clean dry air (or oxygen) is passed into the furnace to flow over the samples (50 to 200 ml/min depending on furnace size) to hasten the oxidation reaction. The time required for complete oxidation varies from two days to five days, depending on the atmosphere over the samples, the quantity of impurities in the graphite, and the specific elements that constitute the total impurity. Duplicate samples are analyzed.

For graphites of greater or lesser purity, sample weights taken for analysis are increased or decreased as necessary. The samples of ash are retained for subsequent analyses.

7–4.2 Boron Determination

Boron has been recognized as the most important contaminant that can easily be incorporated into nuclear-grade graphite in detrimental quantities. Because of the high neutron-absorption cross section of this element, it is essential that the concentration of boron be maintained at the lowest possible level. Early production experience proved that graphite could be produced in multiton quantities with boron concentrations of less than 1 ppm. Owing to technological advances, graphite can now be produced rather consistently with a boron concentration of only 20 ppb. The major problems encountered in the determination of boron in concentration ranges of 10 ppb to 1.0 ppm can be summarized as follows:

1. Boron is prevalent in air-borne dust. It is frequently an additive of salves and medications, baby powder, cosmetics, or soaps which the analytical chemist might occasionally or regularly use. It is a common ingredient in some grades of glass used for the manufacture of laboratory glassware. Analytical reagents, unless they are specially purified prior to use, usually contain sufficient boron to invalidate results obtained on nuclear-grade graphite samples. Consequently, extreme precautions are exercised and rather expensive equipment is used to eliminate significant contamination from such a wide variety of possible sources.

2. Prior to its determination, boron must be quantitatively converted to a soluble form. Dry-ashing techniques result in losses of boron as a result of volatilization unless special methods are employed. Wet-ashing techniques are cumbersome and subject to contamination from glassware. They also allow for appreciable volatilization of boric acid when the sample is heated much above room temperature in the presence of oxidizing acids.

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These facts indicate that the accurate and precise determination of trace quantities of boron in nuclear-grade graphite is both difficult and expensive to achieve. It approaches the challenge that faces the analytical chemist in the analysis of semiconductor- and transistor-grade materials, which has not yet been satisfactory and generally accomplished in an economical manner. By exact reproduction of analytical conditions and techniques, precise analytical values for boron can be attained in any one laboratory. However, samples having an apparent boron content of approximately 1 ppm have yielded a wide range of results when three or more laboratories report on the same sample. This lack of agreement in interlaboratory control programs is considered to be the result of one or more of the contamination sources previously listed.

(a) *Spectrophotometric Determination.* The colorimetric determination of boron, employing curcumin to develop the colored complex, has been found to display more than adequate sensitivity. When utilized with sufficient precaution in regard to contamination, this method has demonstrated improved accuracy of analytical results. Emission-spectrographic techniques are considered because they have been demonstrated to be reasonably accurate and precise and have the added advantage of much greater speed. Unfortunately, boron cannot be determined directly by present-day radiochemical techniques following radioactivation because of the extremely short half life of the radioactive products.

Much work has been done in an effort to determine the most accurate, precise, and economical method for the determination of trace quantities of boron.[11, 12] In the early phases of the Manhattan Project, Rodden and coworkers [13] found the visual colorimetric procedure utilized by Smith [14] for the determination of boron in aluminum-silicon alloys by reaction with quinalizarin to be lacking in sensitivity. The procedure of Cassal and Gerrans [15] using curcumin as the color-developing reagent, following distillation of the boron as methylborate, was modified and used in early work.[13] Although certain impurities,[16, 17] e.g., iron, molybdenum, titanium, vanadium, and oxidizing agents, interfere with the curcumin procedure, it is important to bear in mind that graphite production technology has progressed to such an extent that the impurities in a 1-g sample are so small as to allow distillation techniques to be omitted.[18] Should it be necessary to very accurately and precisely determine boron in carbon or graphite containing total inorganic impurities well in excess of 1000 ppm, the distillation procedure of either Richmond and Telford [19] or Metz [20] may be followed. The first of these two distillation procedures is broader in scope; microquantities of boron by colorimetric

procedures are covered, as well as macroquantities of boron determined by the rather universal mannitol volumetric method. The excellent, detailed distillation method of Metz [20] has been applied to quantities of boron ranging from 0.05 to 0.5 μg. Although this method was developed to determine boron in calcium, uranium, etc., it can be applied to graphite by simply ashing the graphite sample in the presence of purified calcium oxide prior to distillation.

A thorough study of the determination of microgram quantities of boron in reactor materials has been reported by Spicer and Strickland.[21, 22] Included are studies of interferences, recovery of boron by distillation techniques, contamination problems, equipment, and lower limits of sensitivity for the detection of boron.

Spectrophotometric Determination of Boron with Curcumin. The spectrophotometric method for the determination of boron in graphite, coke, and pitch, as it is used for production control, is presented in detail: [23]

Special Apparatus Used:

Quartz crucibles, 30 ml capacity, tall form.
Quartz distillation flask and condenser.
Quartz-lined Hoskins electric muffle furnace, size No. FH–204.
Quartz containers for boron-free reagents.
Labconco laboratory mill.
Fisher electric steam bath, No. 15–496.
Ace water bath (100°C), Electri-Magni-Whirl, model No. 2642.

NOTE:—Quartz should be specified as boron-free.

Special Solutions Necessary:

Boron-free methyl and ethyl alcohols (redistilled in quartz in the presence of NaOH pellets).

Oxalic acid–hydrochloric acid mixture (8.0 g of oxalic acid, 6.0 ml of concentrated HCl, and 40 ml of redistilled water); prepared daily as needed.

Curcumin solution (0.01 g per 50 ml of 95 per cent redistilled ethyl alcohol); prepared daily as needed.

Calcium hydroxide suspension (2.8 g of boron-free CaO per liter of distilled water). Selected lots of J. T. Baker CaO, C.P. reagent grade, have proved sufficiently boron-free for use in this procedure.

Standard boron solutions. Stock solution: dissolve 0.1428 g of H_3BO_3 crystals in distilled water and dilute to a liter. Standard solution: 10 ml of stock solution diluted to 250 ml yields a standard solution containing 1 μg of boron per milliliter.

Procedure. One gram of finely pulverized graphite, coke, or pitch is weighed into a quartz crucible. The sample is covered with 5 ml of methyl alcohol and 10 ml of calcium hydroxide suspension. Methyl alcohol achieves better wetting of the sample, and promotes more intimate mixing of the sample with the calcium hydroxide. The crucible containing the sample and mixture is transferred to the steam bath and the sample and mixture are evaporated to dryness.

The crucible is placed in a cool quartz-lined muffle furnace, the oxygen flow rate into the furnace is adjusted to 100 to 125 ml/min, and the

temperature controller is set to 700°C. The sample is ashed for 12 to 16 hr.

NOTE.—If the sample is a pitch sample, the more volatile fraction is burned off at 200°C prior to adjustment of the temperature controller to 700°C. Complete ashing of the sample must be assured, as indicated by a nearly white ash. Oxygen flow over the sample is essential for complete oxidation. Samples high in iron or vanadium will show characteristic oxide colorings.

The crucible is cooled, and 2 ml each of warm oxalic–hydrochloric acid mixture and curcumin solution are added.

The solution is evaporated in the water bath at 55°C until just dry; this is ascertained by the discontinuation of evolved hydrogen chloride fumes. Evaporation time is critical; evaporation should be completed in less than 2 hr and 20 min.

The residue in the crucible is leached with distilled 95 per cent ethyl alcohol and filtered through a double boron free 11-cm filter paper into a 25-ml glass-stoppered volumetric flask. The sample is diluted to volume with distilled ethyl alcohol.

Blanks are run in triplicate, just as each sample must be run, owing to the possibility of contamination. Blanks are carefully spaced among the samples throughout the analytical operations. Optical density of samples and blanks is measured against distilled water at 540 mμ in matched 1-cm cells in a Beckman DU spectrophotometer.

Aliquots of the standard boric acid solution (1 ml=1 μg of boron) are taken for preparation of the standard working curve. A minimum of five points covering the range of 0.1 to 1.5 μg of boron is necessary to establish the curve. The desired quantity of standard boric acid solution essential to obtain each point on the curve is pipetted into a clean quartz crucible. From this stage each standard is treated in an identical manner as a sample and is carried throughout the entire procedure as outlined above. Blanks are run along with the standards. Extreme care must be observed to prevent contamination from boron in reagents, glassware, water, and atmospheric dust.

(b) *Alternate Methods.* The above colorimetric procedure has been widely accepted as probably the most accurate method for the trace determination of boron in graphite as well as in other materials.

Possibly less opportunity for contamination and greater economy furnish the basis for several emission spectrographic methods that have been reported. Paterson et al.[24] reported a spectrographic production-control method for the determination of boron and vanadium with lower limits of detection of 0.1 and 4 ppm, respectively. A 1-g sample of pitch, coke, or graphite was mixed with 1 g of calcium oxide and dry ashed at 800°C in a boron-free oxygen atmosphere. The volatile constituents from the pitch samples were allowed to escape through the open door of the muffle furnace, which was set at 350°C. After the sample had been completely oxidized, the calcium oxide residue was ground to achieve homogeneity in a mullite mortar. Dupli-

cate 50-mg samples were weighed into pedestal type spectrographic electrodes with craters 5 mm in diameter and 6 mm deep. The sample charges were tamped and center vented, and the electrode wall was vented near the base of the crater. The loaded electrodes were placed in a stainless-steel block and heated to 800°C for 15 min; each electrode immediately arced at 20 amp direct current for 45 sec. Eastman Spectrum Analysis No. 1 plates were positioned to photograph the region from 2400 to 3200 A on a large Littrow type spectrograph. Analyses were made by comparison of the boron lines at 2496.8 and 2497.7 A and the vanadium lines at 2924.0 and 2924.6 A against standard samples photographed on the same plate as the samples. Boric acid and vanadium pentoxide were ground into boron- and vanadium-free calcium oxide, and the mixtures were heated at 800°C for 20 to 30 min to make satisfactory standards. An identical compound was found by X-ray diffraction techniques if either crystalline boric acid or boron carbide were reacted with calcium oxide.

In a very thorough study of the chemistry of boron and carbon in the arc, Feldman and Ellenburg [25] reported a lower limit of detection of 0.5 ppm of boron in a d-c arc in an argon–oxygen atmosphere; the internal standard utilized was iridium. They achieved a lower sensitivity of 0.25 ppm of boron by a "sifter" type electrode with a high-voltage spark-excitation source. These authors expressed doubt that appreciable molecular distillation of boron carbide occurs in the arc, assuming that boron probably exists in purified graphite as the carbide. Because iridium displayed properties similar to boron carbide in its high boiling point (4800°C) and low volatility at high temperatures and appeared to enter the arc stream by a process of entrainment, they theorized that there was insufficient dissociation of the boron carbide in the anode to yield uniform volatilization of the boron produced.

Garton [26] used the d-c arc for the direct determination of boron in graphite, coke, and pitch. The powdered sample was pelletized with a phenol formaldehyde resin binder and arced in graphite holders. A boron concentration range of 0.2 to 1.5 ppm was covered. The possibility of extending the lower limit of detection down to 0.01 ppm by utilization of cathode-ray microphotometry was discussed.

Morrison and Rupp [27] recently proposed a method for the determination of boron in silicon to include a lower concentration of 0.001 ppm up to 1 ppm. They avoided contamination by using all polyethylene equipment and by concentrating the boron from the sample by electrodialysis through a cation semipermeable membrane. This technique possibly can be extended to include the determination of traces of boron in graphite and related raw materials.

7–5 METHODS FOR DETERMINATION OF INORGANIC IMPURITIES MOST COMMONLY FOUND IN ARTIFICIAL GRAPHITE

7–5.1 Ashing Techniques

The dry-ashing technique has been presented in detail in Sec. 7–4.1. Since the determination of boron and the dry oxidation technique have been presented in detail in Secs. 7–4.2 and 7–4.1, respectively, they will not be discussed here. The residue obtained from the dry oxidation of nuclear-grade graphite is reserved for chemical analysis by conventional colorimetric methods because of the accuracy of these methods compared to other more rapid techniques.

The primary disadvantage of dry oxidation of graphite has been the long period of time for completion. The wet-ashing technique can be faster but has been in disrepute in the past for application to trace-element determinations because of the impurities in the oxidizing reagents per se as well as the possibility of extraction of impurities from laboratory equipment in which the oxidation was performed. With the advent of atomic energy programs, transistor and semiconductor development and studies of properties of ultrapure metals and compounds, interest in wet-ashing techniques has been revived. Factors that make wet-oxidation methods more practical are: the production and improved technology of fused-silica laboratory equipment; inert polymers and nonwettable plastics, some of them capable of withstanding relatively high temperatures; and gradually the production of truly high-purity reagents. Graphite has no appreciable solubility in cold or hot or dilute or concentrated acids such as acetic, hydrochloric, nitric, and sulfuric. However, since Willard [28] reported an economical method for the manufacture of perchloric acid on a commercial scale, a tremendous amount of work has been done employing this acid as an oxidant. Smith [29, 30] and coworkers have published reports of a large number of applications of perchloric acid to the oxidation of metals and inorganic and organic compounds, previously considered time-consuming and difficult. Use of the fused-silica apparatus designed by Bethge [31] enabled Smith [32] to obtain a series of graded oxidation potentials which could be established and rigidly controlled. He took advantage of these graded potentials to quickly and completely oxidize easily decomposed materials as well as such complex and difficult materials as cocoanut charcoal, decolorizing carbon, coal, wool, quinoline, Oxine, nylon, Dacron, Orlon, and rubber using controlled concentrations of sulfuric and perchloric acids. Diamond is one form of carbon that is unaffected by hot concentrated perchloric acid. Beck [33] employed similar equipment and techniques to completely oxidize more than 20 g of powdered nuclear-

grade graphite in less than 4 hr. Smaller samples are completely oxidized in correspondingly less time. Since trace quantities of vanadium are usually found in nuclear-grade graphite, the addition of that element to act as a catalyst has been found unnecessary. The solutions from the wet-oxidation of the samples are diluted to volume and used for subsequent determinations.

7–5.2 Determination of Al, Cr, Fe, Mo, Mn, Ni, Ti, and V

Because the quantity of ash obtained from 50-g samples of nuclear-grade graphite may vary from less than a milligram to more than 50 mg, judgment must be exercised as to the amount of sample ashed and the volume to which both the sodium carbonate soluble and insoluble elements are finally diluted. Observation of the ash (Sec. 7–4.1) frequently aids the chemist in determining the size of the aliquot to be taken for any element to be determined by the following colorimetric procedures. Only typical aliquots are recommended below.

(a) *Sodium Carbonate Soluble Elements.* (1) *Preparation of Sample Solution.* The residual ash from 50-g samples (Sec. 7–4.1) is ground and intimately mixed in a smooth agate mortar with 3 g of anhydrous sodium carbonate; the mixture is then transferred to a clean platinum crucible. The platinum dish used for the ashing and the mortar are rinsed with an additional 2 g of sodium carbonate. The rinsings are added to the crucible; it is covered and cautiously heated until the contents are molten. The crucible containing the molten mass is swirled occasionally for assurance of complete mixing and cooled after 20 min in the fused state. Two or three small crystals of potassium nitrate (the size of a grain of rice) are added, and the mixture is again fused for 5 min. The melt is cooled, and the crucible is placed in a clean 250-ml beaker containing sufficient water to cover the crucible and lid. The beaker is heated on a hot plate or steam bath until the melt is completely dissolved, except for a slight residue which may be present.

The crucible and lid are removed from the beaker, are policed, and are rinsed thoroughly with water, the washings being collected in the beaker. Six drops of ethyl alcohol are added to the contents of the beaker; the contents are then heated nearly to boiling and digested on a steam bath for 15 min. The hot solution is filtered through double No. 42 Whatman filter papers; the residue on the paper is washed five times with hot 1 per cent sodium carbonate solution and finally three times with hot distilled water. The filtrate from the sodium carbonate fusion is neutralized with 6*N* sulfuric acid, evaporated to a volume of 60 to 80 ml, cooled, quantitatively transferred

to a clean 100-ml volumetric flask, and diluted to volume. Aliquots of this solution are pipetted for the determination of aluminum, chromium, molybdenum, and vanadium, as described in the following paragraphs.

(2) *Determination of Aluminum.* A yellow chloroform-soluble complex of aluminum hydroxyquinolate is formed when aluminum in an aqueous solution is allowed to react with 8-hydroxyquinoline.[84] Although 8-hydroxyquinoline is not specific for aluminum, good sensitivity can be attained by the addition of a masking agent and adequate pH control. For graphite of very low ash content (<50 ppm) it is recommended that a separate sample of 25 to 50 g be ashed and the total filtrate from the sodium carbonate fusion be used for the determination of aluminum. A typical procedure is described using a 25-ml aliquot of the solution of the sodium carbonate fusion of the ash [Sec. 7–5.2(a)].

Reagents:

8-Hydroxyquinoline solution 1 per cent solution in chloroform. Dissolve 5 g of 8-hydroxyquinoline in 500 ml of chloroform.

Ammonium acetate. Dissolve 15 g of C.P. reagent-grade ammonium acetate in 100 ml of deionized water.

Potassium cyanide. Dissolve 20 g of C.P. reagent-grade potassium cyanide in 100 ml of deionized water.

Standard aluminum solution: 1 ml=0.01 mg aluminum. Stock solution: weigh 0.1000 g of pure aluminum metal into a platinum crucible or dish. Add 1.0 ml concentrated hydrochloric acid and a few drops of 30 per cent hydrogen peroxide.[85] When the aluminum is dissolved, transfer the solution into a 1000 ml volumetric flask and dilute to volume with deionized water. One milliliter=0.1 mg of aluminum. Standard solution: dilute 100 ml of stock solution to 1000 ml (1 ml=0.01 mg of aluminum).

Procedure. Pipet a 25-ml aliquot of the solution containing the carbonate soluble elements [Sec. 7–5.2(a)] into a 150-ml beaker. Add 2 ml of ammonium acetate solution and 5 ml of the potassium cyanide solution (caution, work in a hood). Adjust the pH to 9.0 with dilute sulfuric acid. Transfer the solution, plus the rinsings from the beaker, into a 125-ml separatory funnel. Add 10 ml of the 1 per cent 8-hydroxyquinoline solution to the solution, place the stopper in the funnel and shake the funnel vigorously for 1 min. Allow the chloroform phase to separate from the aqueous layer. Place a small wad of filter paper in the end of the separatory funnel stem to absorb any water droplets that might be in the chloroform layer. Drain the chloroform layer containing the 8-hydroxyquinolate complex into a 25-ml volumetric flask. Rinse the funnel with 2 ml of chloroform. Repeat the extraction with a 5-ml portion of chloroform; followed by a final rinse of the funnel with 2 ml of chloroform. Dilute the combined chloroform extracts and rinsings to exactly 25 ml. Measure the absorbancy at 395 mμ in a 1-cm cell in the spectrophotometer against a blank of the reagents which have been carried through the identical treatment as the sample

aliquot. Calculate the aluminum concentration by referring to an absorbance vs. concentration curve prepared by treating 1.0-, 3.0-, 6.0-, and 9.0-ml aliquots of the standard aluminum solution as above described.

$$\text{Ppm of Al} = \frac{\mu\text{g Al from curve x aliq. factor}}{\text{sample weight}}$$

Reagents used for this procedure should be checked to assure their purity with respect to aluminum. Distilled water should be passed through a mixed-bed ion-exchange column prior to use for the determination of aluminum.

(3) *Determination of Chromium.* Chromium is determined as the red-violet complex formed with (1,5-diphenylcarbohydrazide) diphenylcarbazide.[36]

Reagents:

Diphenylcarbazide reagent (0.5 per cent solution in a 1+1 acetone–water mixture).

Standard chromium solution: 1 ml=0.01 mg of chromium. Stock solution: 0.2828 g of U.S. Bureau of Standards $K_2Cr_2O_7$/100 ml of water: 10 ml of stock solution diluted to 1000 ml to make a standard chromium solution such that 1 ml=0.01 mg of chromium.

Procedure. The chromium calibration curve (absorbancy vs. chromium concentration) is obtained as follows:

Volumes of 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 ml of standard chromium solution are placed in a series of 250-ml beakers. Five to ten milliliters of water and 1.25 g of sodium carbonate are added to each beaker. The carbonate in each solution is carefully neutralized with a total of 7.4 ml of 6*N* sulfuric acid; the solutions are cooled and transferred to 100-ml volumetric flasks. The contents of each flask are adjusted to a volume of approximately 80 ml with distilled water, and 10 ml of diphenylcarbazide reagent is added. The solution is diluted to volume, mixed, and allowed to stand for 20 min prior to the absorbancy determination at 540 mμ in the spectrophotometer. The absorbancy of each solution is obtained in a 1 cm cell against the reagent blank solution in the comparison cell of the spectrophotometer. The absorbancy values are plotted as a function of the chromium concentration in the usual manner to obtain the standard curve.

The chromium content of the sample is determined by pipetting a 25.0-ml aliquot from the treated filtrate [Sec. 7–5.2(a)] from the sodium carbonate fusion into a clean 250-ml beaker. The procedure given for the standards is followed, except no chromium or sodium carbonate is added to the sample and only 3.3 ml of 6*N* sulfuric acid is added. A solution of the reagents is used as a blank in the comparison cell against the sample in the spectrophotometer.

(4) *Determination of Molybdenum.* Molybdenum is determined as the orange-red complex of thiocyanate after reduction with stannous chloride. The colored complex is extracted into an organic phase prior to measurement of the absorbancy.[37]

Reagents:

Stannous chloride solution (87.5 g of $SnCl_2 \cdot 2H_2O$+50 ml of 1+1 HCl). Place on steam bath until the salt is almost all in solution; filter and dilute with water up to 250 ml.

Standard molybdenum solution: weigh into a small beaker 0.0750 g of MoO_3; add 0.20 g of solid sodium hydroxide, followed by some water; then add 1 ml of concentrated sulfuric acid. Cool the solution and dilute to 500 ml to make the stock solution. For the standard solution dilute 50 ml of stock solution to 1000 ml volume and mix thoroughly. One milliliter of standard molybdenum solution=0.005 mg of molybdenum.

Procedure. The standard curve (absorbancy vs. molybdenum concentration) is obtained as follows:

Two and one-half grams of solid sodium carbonate is placed into each of six 250-ml beakers and dissolved in 50 ml of water. The carbonate is neutralized with 8.0 ml of 6*N* sulfuric acid. The following volume of standard molybdenum solution is added to the successive beakers: 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 ml. The solutions are quantitatively transferred to separatory funnels, and 20 ml of sulfuric acid (1+1) is added. The solutions are then cooled to 15 to 20°C. (All reagents should be cooled to 15 to 20°C.) Following the addition of 2 ml of 20 per cent ammonium thiocyanate, the funnels are stoppered and shaken. Five milliliters of stannous chloride solution is added to each funnel, and the solutions are mixed; then 25 ml of butyl acetate is added. The funnels are shaken vigorously for 2 min. The liquids are allowed to separate, and the lower aqueous layer is discarded. Fifty milliliters of sulfuric acid (1+9), 2 ml of 20 per cent ammonium thiocyanate solution, and 2 ml of stannous chloride solution are added to the butyl acetate layer. After being shaken for 1 min, the layers are allowed to separate, and the aqueous layer is discarded. The organic layer is filtered through a clean dry filter paper or cotton plug directly into the 1-cm absorption cells of the spectrophotometer. The absorbancy of the solutions containing added molybdenum is measured at a wave length of 470 mμ against that of the solution to which no molybdenum was added. The calibration curve is plotted in the usual manner.

For the determination of molybdenum in the sample, a 25-ml aliquot from the treated sodium carbonate fusion filtrate [Sec. 7–5.2(a)] is treated in a manner identical to the standards above except, of course, for the addition of molybdenum, sodium carbonate, and 8.0 ml of 6*N* sulfuric acid. A reagent blank is carried through the procedure with the sample and extracted. The acetate layer of the reagent blank is used in the comparison cell of the spectrophotometer against the acetate layer from the sample in the sample cell.

(5) *Determination of Vanadium.* Vanadium is determined as the phosphotungstovanadate complex by a slightly modified procedure of Sandell.[38]

Reagents:

Na_2WO_4 (41.25 g of $Na_2WO_4 \cdot 2H_2O$ per liter).

Standard vanadium solution, 1 ml=0.01 mg of vanadium per milliliter. Stock solution: carefully ignite 2 g of V_2O_5 at 500°C. Cool, weigh

1.7853 g into a clean 250-ml beaker, and dissolve in a small excess of sodium hydroxide. As soon as solution is complete, acidify with sulfuric acid, quantitatively transfer to a 1000-ml volumetric flask, and dilute to volume with distilled water. One milliliter =1 mg of vanadium. Standard solution: dilute 10 ml of the stock solution to volume in a 1000-ml volumetric flask. One milliliter=0.01 mg of vanadium.

NOTE.—Unless the vanadium content of the oxide is certified, or of known composition, it is recommended that a chemical analysis for vanadium content be run.

Procedure. The vanadium standard curve (absorbancy vs. vanadium concentration) is obtained as follows:

Volumes of the standard vanadium solution are pipetted into each of a series of clean 150-ml beakers so that the range of vanadium concentration covered is from 0.1 to 5.0 mg, including one beaker to which no vanadium is added. Five milliliters of concentrated sulfuric acid is added, the solutions are heated nearly to boiling, and dilute potassium permanganate (0.02 to 0.1*N*) solution is added dropwise until the solution maintains a pink color for 1 to 2 min. A few drops of hydrochloric acid (1+1) are added, and the solutions are warmed to destroy the excess of potassium permanganate. Five milliliters of phosphoric acid (1+1) is added, followed by the addition of 10.0 ml of sodium tungstate solution. The solutions are heated to boiling and maintained hot for 30 min. The standards are cooled to room temperature, quantitatively transferred to a 100-ml volumetric flask, and diluted to volume. The absorbancy of each vanadium standard is determined in the sample cell of the spectrophotometer compared to the reagent blank in the comparison cell at a wave length of 400 mμ using a 1-cm sample cell.

Vanadium is determined in a 25-ml aliquot (or less, if vanadium is extremely high) of the filtrate obtained from the sodium carbonate fusion [Sec. 7–5.2(a)]. To the aliquot, in a 150-ml beaker, 5 ml of concentrated sulfuric acid is added, and the solution is heated to near boiling. Sufficient potassium permanganate (0.02 to 0.1*N*) solution is added, dropwise, until a pink color is maintained by the solution for 1 to 2 min. A few drops of hydrochloric acid (1+1) are added, and the solution is warmed to destroy the excess potassium permanganate. Five milliliters of phosphoric acid (1+1) is added, followed by the addition of 10.0 ml of sodium tungstate solution. The solution is then heated to boiling and maintained hot for 15 to 30 min to assure complete color development of the vanadium complex. The solution is cooled, transferred to a 100-ml volumetric flask, diluted to volume and thoroughly mixed. The optical density is determined in the 1-cm sample cell of the spectrophotometer compared to a blank of reagents in the comparison cell at a wave length of 400 mμ.

(b) *Sodium Carbonate Insoluble Elements.* (1) *Preparation of Sample Solution.* The filter papers containing the precipitates from the dissolved carbonate melt [Sec. 7–5.2(a)] are placed in the platinum crucible that was used for the original carbonate fusion. The

paper is carefully charred, ashed, and cooled, and 2 ml of distilled water, 4 drops of sulfuric acid, and about 5 ml of 48 per cent hydrofluoric acid are added. The crucible is placed on a steam bath and evaporated to dryness; then it is carefully heated over a burner at red heat for 5 min. The crucible is cooled, and sufficient potassium pyrosulfate is added to result in a complete fusion. The contents of the crucible are fused over a burner and cooled, and the melt is dissolved in 50 ml of distilled water and 2 ml of sulfuric acid. The solution is quantitatively transferred to a 100-ml volumetric flask and diluted to volume. Aliquots are removed for the determination of iron, manganese, nickel, or titanium as described in the following paragraphs.

(2) *Determination of Iron.* The orthophenanthroline complex of iron has proved to be the most suitable for the quantitative determination of this element.[39] A 25-ml aliquot of the solution from the pyrosulfate fusion of the carbonate-insoluble elements [Sec. 7–5.2(b)(1)] is taken if the original ash content was small and displayed an off-white color. If the ash weight was large and possessed the characteristic rust color, a smaller aliquot is used.

Reagents:

Sodium acetate buffer solutions: (a) 2.0*M* or 16.4 g of anhydrous salt per 100 ml or (b) 0.2*M* or 1.64 g of anhydrous salt per 100 ml.

Standard iron solution: 1 ml=0.01 mg of iron. Stock solution: dissolve 0.7021 g of Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water containing a few drops of concentrated sulfuric acid. Dilute to 100 ml, 1 ml=1 mg. Standard iron solution: dilute 10 ml of stock solution to 1000 ml, 1 ml=0.01 mg of iron.

Procedure. Into a series of clean 50-ml beakers are placed 0.0, 2.5, 5.0, 7.5, 10, 15, and 20 ml of standard iron solution. The total volume of each solution is adjusted to about 20 ml by the addition of distilled water. One milliliter of 10 per cent hydroxylamine hydrochloride is added, and the pH of each solution is adjusted to 3 to 6 with sodium acetate solution. One milliliter of *o*-phenanthroline (0.3 per cent) is added, and each solution is transferred to a 50-ml volumetric flask. Each solution is diluted to volume and mixed. The absorbancy is determined in a 1 cm-cell in the spectrophotometer at 508 mμ against the standard solution to which no iron was added in the comparison cell. The absorbancy values are plotted against the iron concentration to obtain a working curve.

An aliquot of the sample estimated to contain 0.05 to 0.15 mg of iron is taken from the pyrosulfate solution of the carbonate-insoluble elements [Sec. 7–5.2(b)(1)] contained in the original ash. This aliquot is placed in a 50-ml volumetric flask and treated as the standard solutions, above, beginning with the addition of 1 ml of 10 per cent hydroxylamine solution. The iron concentration is obtained from the working curve using the absorbancy of the sample. The iron is then calculated as per cent or parts per million of the original sample.

(3) *Determination of Manganese.* Manganese is oxidized to the permanganate form with potassium periodate. A 10- to 25-ml aliquot [Sec. 7–5.2(b)(1)] is used for this colorimetric determination.[40]

Reagents: Standard manganese solution (1 ml=0.1 mg of manganese). Dissolve 0.2877 g of $KMnO_4$ in distilled water containing a few drops of sulfuric acid and dilute to volume in a 1000-ml volumetric flask.

Procedure. Known amounts of the standard manganese solution (0 to 1.0 mg) are accurately pipetted into a series of clean 250-ml beakers. To each beaker, 50 ml of water, 10 ml of sulfuric acid, and 10 ml of 85 per cent phosphoric acid are added. Add about 0.3 g of potassium periodate to each beaker and heat to boiling with constant stirring. The solutions are maintained near the boiling point for 10 min. The solutions are cooled to room temperature, transferred to 100-ml volumetric flasks, and diluted to volume with distilled water. The absorbancy of each solution is measured at 525 mμ in a 1-cm cell against the solution to which no manganese had been added. The calibration curve is plotted in the usual manner.

A 25-ml aliquot is pipetted from the solution of the Na_2CO_3 insoluble elements reserved for iron, manganese, nickel, and titanium [Sec. 7–5.2(b)(1)]. The same procedure outlined above for the standards is followed except that no manganese standard solution is added. The absorbancy of the sample is determined against a reagent blank in the spectrophotometer. From the observed absorbancy of the sample, the amount of manganese present in the sample is determined from the curve and calculated to parts per million.

(4) *Determination of Nickel.* Nickel is determined by the dimethylglyoxime colorimetric procedure of Sandell [41] using an aliquot to contain 5 to 30 μg of nickel pipetted from the above-mentioned 100-ml flask [Sec. 7–5.2(b)(1)].

Reagents: Standard nickel solution (1 ml ≈ 5 μg of nickel) Stock solution: dissolve 0.2476 g of $Ni(NO_3)_2 \cdot 6H_2O$ in water and dilute to 1000 ml. Standard solution: pipe 100 ml of stock solution into a 1000-ml volumetric flask and dilute to volume. One milliliter of standard solution ≈ 0.000005 g of nickel (5 μg).

Procedure. For the determination of nickel in the sample, a 25-ml aliquot of the ash solution is pipetted into a 125-ml separatory funnel. Five milliliters of sodium citrate solution (10%) is added, and the sample is made slightly ammoniacal with ammonium hydroxide, with a few drops added in excess. Two milliliters of dimethylglyoxime reagent is added, and the solution is extracted with three 3-ml portions of chloroform, each extraction being shaken for one-half minute. The chloroform extracts are combined and shaken with 5 ml of ammonium hydroxide (1 + 50). The chloroform layer is passed into another separatory funnel. The aqueous layers are shaken with 2 ml of chloroform, and this chloroform is added to that which was washed with ammonium hydroxide (1 + 50). The aqueous phase is discarded.

The nickel is extracted from the chloroform by shaking with two separate 25-ml portions of 0.5*N* hydrochloric acid (shake each extraction for 1 min). The hydrochloric acid solutions are transferred to a 100-ml volumetric flask, 10 drops of bromine water are added, followed by sufficient ammonium hydroxide, added dropwise, to dispel the bromine color, plus 6 drops of ammonium hydroxide in excess. One milliliter of 1 per cent dimethylglyoxime is added, and the solution is diluted to volume and mixed. The absorbancy is measured against a blank of the reagents at 525 mμ.

Known amounts of the standard nickel solution to cover the range of 0 to 35 μg are added to a series of eight 125-ml separatory funnels. Ten drops of bromine water are added to each, and the solutions are mixed. Next, sufficient ammonium hydroxide (1 + 1) is added drop by drop to destroy the bromine color plus 6 drops in excess. One milliliter of 1 per cent dimethylglyoxime solution is added. From this stage, the standards are treated as the samples above described, beginning with the three 3-ml chloroform extractions. The absorbancy is determined at 525 mμ in a 1 cm cell in the spectrophotometer. Use the solution to which no nickel was added in the comparison cell as a blank. The calibration curve is plotted in the usual manner.

Nickel in the sample is calculated from the nickel content obtained from the standard curve and the sample weight represented by the aliquot taken.

(5) *Determination of Titanium.* A 25-ml aliquot of the solution of the sodium carbonate fusion of the ash [Sec. 7–5.2 b(1)] has been found to be generally satisfactory for the colorimetric determination of titanium by the standard peroxide technique.[42]

Reagents: Standard titanium solution. Dissolve 0.1669 g of TiO_2 in a minimum amount of sulfuric acid and dilute to 100 ml. One milliliter $\approx$ 1 mg of titanium.

Procedure. Standards are prepared by adding necessary aliquots of the standard titanium to a series of clean 100-ml volumetric flasks. (Standards containing 0 to 8.0 mg of titanium have been found satisfactory.) To each flask are added 50 ml of sulfuric acid (1+10), 4 ml of 85 per cent phosphoric acid, and 3 ml of 3 per cent hydrogen peroxide. The solutions are cooled and diluted to volume. The absorbancy is determined at 400 mμ in the spectrophotometer against the reagent blank. The concentration of titanium is then plotted against the absorbancy in the usual manner.

The titanium concentration of the sample is determined as follows: A 25-ml aliquot of the solution [Sec. 7–5.2(b)(1)] resulting from the sodium carbonate fusion of the graphite ash is placed in a 250-ml beaker. Ammonium hydroxide is added in slight excess to precipitate titanium, manganese, iron, etc. The precipitates are coagulated by boiling the solution and are filtered through double filter papers. The precipitate is washed six times with hot distilled water and the filtrate is discarded. The precipitate is dissolved with 50 ml of hot sulfuric acid (1+10) into a 100-ml volumetric flask. The paper is washed three times with small portions of hot water to assure removal of all titanium from the paper into the volumetric flask. The sample is cooled, and 4 ml of

85 per cent phosphoric acid and 3 ml of 3 per cent hydrogen peroxide are added. The sample is then diluted to volume. The absorbancy of the sample is measured against a reagent blank prepared as outlined above for the preparation of the standard curve. The quantity of titanium in the sample is determined from the standard curve and calculated in per cent or parts per million, as desired.

7–5.3 Determination of Calcium

Calcium is usually determined volumetrically by titration with standard potassium permanganate solution.[43] Separate samples (usually 50 g) are ashed at 680°C (see Sec. 7–4.1) for the determination of calcium.

Procedure. Sufficient potassium pyrosulfate is added to the graphite ash in the platinum dish to permit a complete fusion. The contents of the dish are fused thoroughly over a burner and cooled; then the melt is dissolved in a few milliliters of water and 2 ml of concentrated hydrochloric acid. The solution is quantitatively rinsed into a 250-ml beaker with distilled water, and the volume is adjusted to 100 to 125 ml. A few drops of methyl red indicator (0.1%) solution are added, and the pH of the solution is adjusted by the dropwise addition of ammonium hydroxide until a reddish-yellow tint is maintained. (If iron was apparent in the original ash, add two to three small crystals of citric acid.) The slightly acid solution is now heated to boiling, and about 20 ml of saturated ammonium oxalate solution is slowly added. The solution is boiled for a few minutes, made just alkaline with ammonium hydroxide, and digested on the steam bath for 3 to 4 hr.

The hot solution is filtered through a No. 42 Whatman filter paper (some workers prefer to filter through an asbestos mat on a Gooch crucible), and the paper and precipitate are very thoroughly washed with hot water to remove excess oxalate. To test for adequacy of washing, 20 to 25 ml of wash water should not decolorize 1 drop of standard potassium permanganate solution (0.05 to 0.1*N* accurately standardized). The precipitate of calcium oxalate is dissolved from the paper with about 50 ml of hot 10 per cent sulfuric acid, followed by rinsing with about 50 ml of hot water. The solution is heated to boiling and titrated with standard potassium permanganate solution (0.05 to 0.1*N*) contained in a 5- or 10-ml buret to the first faint pink color. A reagent blank should be run with the sample and titrated to the same end point. Calculation (50-g samples ashed):

Milliliters of $KMnO_4$ (corrected for blank) $\times$ normality of $KMnO_4$ $\times$ 0.02004 $\times$ 20,000 = parts per million calcium.

7–5.4 Determination of Hydrogen

The accurate and precise determination of small quantities of hydrogen in nuclear-grade graphite has proved to be a difficult task. Hering[44] reported an apparent average hydrogen content of 10 to 20 ppm in nuclear graphite; a 50-g sample was thoroughly dried in

a dry-nitrogen atmosphere at 250°C in a tube furnace then burned to completion at 900°C in oxygen. The resultant water, trapped in a series of three tared weighing tubes, was determined gravimetrically. Guldner and Beach [45] found the hydrogen content in most purified carbon to be so small that a modified Pregl gravimetric method was inadequate with respect to precision. After being degassed, a 500-mg sample was burned in a purified oxygen atmosphere with an induction heating furnace. The water was frozen in two traps, in series, immersed in a mixture of Cellosolve and crushed dry ice to maintain a temperature of −78°C. The water vapor was transferred into an appropriate manometer and was allowed to come to equilibrium at 25°C. The pressure was measured in three different calibrated volumes. Blanks were run in parallel with the samples. A precision of 7 per cent was obtained in the range of 4 to 100 ppm of hydrogen.

7–5.5 Determination of Sulfur

The determination of sulfur in graphite has not been considered as important as the determination of other impurities for two reasons: (1) sulfur has a very low neutron-absorption cross section and (2) sulfur is almost completely removed during the graphitization procedure.

Hering [46] reported sulfur to be present in a concentration of less than 20 ppm, based on a turbidimetric method for $BaSO_4$, in nuclear-grade graphite.

The Eschka method has been found satisfactory for the quantitative determination of sulfur in graphite, coke, and coal samples. The maximum accuracy has been obtained by carrying reagent blanks through the procedure along with the samples.[47] The Eschka method, along with modifications, has been most successfully applied to samples in which the sulfur concentration is in excess of 0.1 per cent. The recently developed techniques of burning the sulfur to SO_2 in a stream of oxygen in high-temperature induction furnaces are best applied to samples containing more than 0.05 per cent sulfur. High blank values, resulting from reagents and ceramic sample crucibles, tend to limit the sensitivity of these techniques and to confine their application to samples in which the sulfur concentration is in excess of several hundred parts per million. It has been reported that sulfur has been detected in concentrations as low as 1 ppm by neutron-activation analysis.[48]

7–6 PHYSICAL METHODS FOR ANALYSIS OF NUCLEAR GRAPHITE

Because of the speed and rapidity with which impurities can be determined in given matrices by physical methods, a brief discussion

of methods for such measurements as well as a résumé of common analytical methods for determining physical properties of interest in nuclear reactor application is presented.

7–6.1 Emission Spectrographic Method

Smith [49] reported the application of a spectrographic method to the determination of 30 trace elements in fuel ash. Twenty milligrams of pulverized ash were mixed with 80 mg of buffer mixture consisting of 20 per cent lithium carbonate and 80 per cent graphite. Internal standards of mixed tin and cobalt oxides or beryllium oxide were used (the latter was used for boron determination).

The procedure used by Feldman and Ellenburg [50] for the study of the behavior of boron in the spectrographic arc has been proposed for the determination of other contaminants in carbon and graphite. Emission spectrographic methods are, in general, satisfactory for control purposes and comparison studies. However, the heterogeneous distribution of impurities in graphite is a major factor which must be considered in spectrographic methods.

7–6.2 Radioactivation Methods

The extremely low limits of sensitivity or detection of those elements that react with nuclear particles to produce radioactive isotopes have led many analysts to express the opinion that activation analysis was the ultimate in analytical techniques. Few requests for the analysis of rare-earth elements in graphite have been made. Because these elements are present in very low concentration in nuclear-grade graphite, activation methods seem most appropriate for their determination. Leddicotte et al.[51, 52] claimed as little as 0.01 ppb of europium or dysprosium could be detected by this method. Meinke [53, 54] compared the activation method of analysis with other methods and reported the sensitivities were tremendously improved over conventional methods as a general rule. Smales and Mapper [55] determined the vanadium content of five graphite samples by this technique; the vanadium concentration found ranged from 12.0 to about 440 ppm. They concluded the method was sufficiently accurate and precise to be used on small samples of graphite in homogeneity studies.

7–6.3 Functional Testing of Nuclear Graphite

The behavior of graphite exposed to constant or carefully controlled neutron fluxes has been used to evaluate graphite manufactured for reactor use. Diffusion-length measurements and neutron-capture measurements have been applied to arrive at a value for the amount of

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total impurities in a sample, a bar, or a large production lot of nuclear-grade graphite. Such techniques overcome one major fallacy in analytical schemes, namely, the known and recognized nonhomogeneous distribution of impurities in artifically produced graphite.

The success of these neutron-physics methods has been found to be dependent upon several factors:

(1) The absolute cross-section value of completely pure graphite for thermal neutrons.

(2) The ability to correct for pile variables such as neutron streaming in voids; reflection of escaped neutrons back into the moderating medium; absorption of neutrons in hydrogen, nitrogen, etc., contained in the many small voids in the graphite as well as in machined openings in the pile; absorption of neutrons in metal process tubes; and other variables.

(3) The procurement, establishment, and successful maintenance (kept free from contamination) of satisfactory standard bars of graphite.

Maximum neutron economy can be achieved in nuclear reactors by utilizing the purest graphite available. Therefore, nuclear-measurement methods have received a great deal of effort.[56-62] They can be used to classify and separate, according to purity, artificially produced nuclear-grade graphite so that it can be most efficiently used in reactor programs. The neutron-measurement methods have the advantage of precisely evaluating the total impurities in a sample, a piece, or lot of graphite compared to a standard bar, if desired. From this viewpoint, neutron-measurement methods offer the ultimate in production-control methods. The chief disadvantage of such methods is the fact that the impurities contributing to the measured value are not qualitatively identified. The analytical chemist must be called upon to identify the element responsible for values that deviate from the standard or desired measurement, as well as to satisfactorily analyze the primary standard bar.

7–6.4 Determination of Real Density

The definition of density is the mass of unit volume and is usually determined and expressed as grams per cubic centimeter (g/cm^3). Investigation of the real density versus the apparent density of porous material was made by Kanagy and Wallace.[63] An excellent practical and theoretical discussion of methods for density determination of solids has been given by Reilly and Rae.[64] Apparent density defined as the mass per unit volume including the voids, has little value in nuclear applications. Voids contribute undesirable effects of moderating materials. Therefore, real density, which takes voids or free

spaces into consideration, has proved to be an important measurement. Typical, artificially produced nuclear-grade graphite must be considered as a porous material since the range of density has been experimentally found to be from 1.61 to 1.72 g/cm^3 as compared to a theoretical real density of 2.26 g/cm^3.

The method that has been most generally used to determine the real density of nuclear-grade graphite is essentially that described by Clarke.[65] The dried samples are placed in carefully calibrated pycnometers and degassed under kerosene in vacuum. The voids are assumed to be filled with kerosene. Density is calculated from the weight of kerosene displaced by the sample.

In certain instances density values obtained by the above method are in disagreement with results obtained by other methods. As a result of this disagreement, some workers prefer to use the helium-displacement method.[66–69]

This technique is worthy of consideration because of the negligible surface adsorption of helium at room temperature and above; helium is also considered capable of filling the smaller voids more satisfactorily than liquids. The basis of the method involves the careful measurement of the change in pressure required to decrease or increase a given volume of gas by a calibrated amount as compared with the same measurement when part of the gas volume is occupied by a weighed portion of the powdered solid.

7–6.5 Determination of Pore Spectra

Graphite for some nuclear applications, in addition to high chemical purity, should be of very high density and be nonporous. A great deal of effort is being made to produce an artificial nuclear grade of graphite with appreciably greater density. The size distribution of pores (pore spectrum) is important in the evaluation of the structures of graphite resulting from changes in raw materials or manufacturing processes.

The measurement of the sizes of voids or pores is still rather controversial. A wide variety of factors influence values obtained for pore size and volume. An excellent theoretical summary of the problems encountered in porosity measurements is presented by Everett [70] along with a bibliography of recent work on this subject. A method frequently employed in determining the mean pore diameter is that suggested by Washburn and Ruoss.[71, 72]

Measurements are made using one of a variety of viscous liquids such as glycerine, paraffin oil, water, or mercury. Ritter and Drake [73] describe a procedure whereby pore volume can be determined over a wide range of pore diameters by forcing mercury into the pores

under high pressures. The method is based on the fact that surface tension opposes the entrance of a nonwetting liquid (in this case, mercury) into a small opening. This opposition due to surface tension is overcome by the application of high external pressure. The pore-size distribution of a sample immersed in mercury is then calculated from observed volume changes of mercury resulting from the application of controlled increments of high pressure.

Porosimetry measurement equipment should be considered as reasonably complex equipment and of a type not normally utilized by an analytical chemist. For occasional measurements of this nature, samples might best be sent to a reliable commercial physical testing laboratory. In any event, the advice of an expert would be advantageous prior to setting up the equipment.

7–6.6 Determination of Gas Content

Beginning with the sodium-cooled reactor, followed by the helium-cooled reactor and the fused-salt reactor, the gas content of nuclear-grade graphite has been of increasing importance. Some of the gases evolved from graphite under conditions of high radiation and temperature have demonstrated deleterious effects on materials of reactor construction and operation. It was necessary to determine the quantity and composition of these absorbed gases in order to study methods to reduce or eliminate them from the graphite.

Norton and Marshall [74] designed and built equipment to study products of desorption from various metals and graphite used as electrodes in vacuum tubes. Winter [75] applied similar equipment and techniques to a thorough study of the degassing properties of graphite used in the electronic industry. Carter and Greening [76] analyzed the desorbed gases from various grades of nuclear graphite by mass spectrographic methods as part of the search for a satisfactory moderator in the sodium-cooled reactor experiment. Mitchell [77] used samples 1 ¼ in. in diameter by 1 in. in length, which were cored 2 to 6 in. from the end of graphite bars, in his study of gas evolution at two temperatures; 1000°C and 1800°C. No analysis of the evolved gas was obtained. Overholser et al. at Oak Ridge National Laboratory [78–81] have extended investigations to include: (1) gas evolved under resistance heating conditions; (2) gas evolved under induction heating conditions; (3) gas evolved under equilibrium conditions, with respect to pressure; (4) gas evolved under conditions of reduced pressure, i.e., constantly pumping off evolved gas; and (5) quantitative analysis of evolved gas by mass spectroscopy and gas chromatography.

Cylindrical samples, varying in size from 1 to 1½ in. in diameter and 1 to 2 in. in length, were degassed at various temperatures up to a maximum of 1800°C. Temperatures above 1000°C were de-

termined with an optical pyrometer. Pressures were measured with a McLeod gauge connected between the Toepler pump and the sample manifold. The gas sample was transferred into a 200- or a 1000-cm^3 sampling bulb with the Toepler pump.

The collected gas was analyzed in a mass spectrometer. This did not permit the resolution of nitrogen and carbon dioxide at mass 28. With the development of gas chromatographic techniques, more of the gas analysis is being done by this method. The precision attained for replicate analyses of synthetic samples composed of nitrogen, oxygen, carbon monoxide, and methane is about 2 per cent using sample volumes of 100 and 500 μl in the gas chromatograph.

Major gaseous components evolved from nuclear-grade graphite consist of hydrogen, carbon dioxide, water, nitrogen, and carbon monoxide. Minor constituents identified have included hydrogen sulfide, sulfur dioxide, methane, and some other hydrocarbons. Results have been reported as per cent gas by volume, or as cubic centimeters of gas per 100 cm^3 of graphite. Typical volumes of gas reported have ranged from 6 to almost 80 cc of gas per 100 cm^3 of graphite in studies of total gas evolved up to 1800°C from various grades of nuclear graphite.

7–7 DETERMINATION OF CARBON IN GRAPHITE

Occasionally the determination of carbon is desired. The general analytical methods for the determination of carbon are based on the oxidation of carbon to carbon dioxide. This reaction has proved to be the most outstanding chemical property of free carbon. Carbon is relatively insoluble in common reagents such as water, organic solvents, and most concentrations of acids and bases at temperatures below 100°C.

7–7.1 Wet-oxidation Methods

Wet-oxidation methods were rather universally used for the quantitative determination of free carbon until about 1920. Chromic acid, used with either sulfuric or phosphoric acid, was most commonly employed as the oxidant.[82-83] Permanganates, iodates, and persulfates have been successfully employed in oxidizing carbon, with silver or mercury compounds added as catalysts.[84, 85] Wet-oxidation methods still have wide application for the determination of carbon in organic compounds, in liquid or highly volatile samples, and in explosive materials or samples that would evolve large quantities of gases such as chlorine and oxides of sulfur or nitrogen. Common techniques and apparatus are applicable for either organic or inorganic samples.

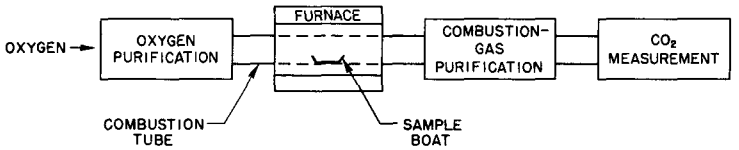


Fig. 7.1—Schematic diagram of dry-oxidation combustion apparatus.

7–7.2 Dry-oxidation Methods

The development of improved combustion tubes capable of withstanding severe oxidation conditions at high temperatures plus the rapidity and simplicity of direct combustion of the sample in an atmosphere of oxygen have allowed more work to be accomplished by the dry-combustion technique. A schematic diagram of the combustion apparatus is shown in Fig. 7–1. Simultaneous to the advent of improved refractory combustion tubes, better sample containers or boats of similar material were manufactured. Electric furnaces replaced gas burners and were extended to include resistance furnaces and the high-frequency furnace. Several manufacturers have developed the high-frequency furnace into a package unit for the very rapid determination of carbon and sulfur in metal samples. These high-frequency units are rapidly increasing in popularity because only the samples are heated and not the combustion tubes.[86-88] The short combustion tubes are made of transparent silica and are returned almost to room temperature between sample runs. Warm-up times are a few minutes with induction heating compared with as much as several hours with resistance-heated furnaces. Blanks are usually maintained at a minimum in the induction equipment. The chief disadvantage of the induction-heated apparatus is that sufficient conducting material must be present in the sample or container for the high-frequency current to "couple" and subsequently heat. This is readily done by heating the sample in a platinum- or quartz-enclosed graphite crucible. This kind of technique has been applied to the analysis of cokes.[114]

7–7.3 Measurement of Evolved Carbon Dioxide

After the carbon has been evolved from the sample by oxidation to carbon dioxide and freed of impurities, it must be measured quantitatively. The following are some of the more common and widely used methods of measurement.

(a) *Volumetric Method.* After removal of the oxides of sulfur by oxidation of sulfur dioxide to sulfur trioxide in a sulfuric acid solution of chromic acid in a scrubbing column (the sulfur trioxide thus formed

is simultaneously absorbed in the sulfuric acid solution), the combustion products are composed of carbon dioxide and the excess oxygen used as a sweep gas. The total volume of gas is measured and calculated to volume under standard temperature and pressure conditions. The carbon dioxide is then removed by absorption in sodium hydroxide solution in an Orsat-type gas analyzer, and the final volume of oxygen is measured. Smaller burets can be used by freezing out the carbon dioxide from the oxygen with liquid nitrogen traps,[89-91] resulting in improved precision in the measurement of the evolved carbon dioxide. This freeze-out technique has been incorporated into a commercially available automatic carbon analyzer. Volumetric measurements of gases require precise control of temperature.

(b) *Precipitation and Titration.* Carbon dioxide can be weighed as $BaCO_3$ after the gas has been reacted quantitatively with an excess of barium hydroxide solution. The precipitated barium carbonate is recovered by filtration, washed, dried, and weighed. This method has the inherent disadvantage of contamination from atmospheric carbon dioxide, particularly during filtration operations. Where small amounts of carbon are contained in the sample, this method has no value because of poor precision and questionable accuracy.

The titration of the excess hydroxide ion, after precipitation of the carbon dioxide as barium carbonate from a standard barium hydroxide, has been more widely accepted than the above-mentioned gravimetric determination as barium carbonate.[92-94] Contamination from atmospheric carbon dioxide can be more readily avoided in this procedure, but all acidic gases must be removed from the carbon dioxide-containing sweep-gas stream prior to the precipitation of the barium carbonate.

(c) *Gravimetric Method.* The gravimetric determination of carbon dioxide following absorption in a tared tube by a solid absorbent and subsequent weighing of the tube to obtain the net weight of absorbed carbon dioxide has been the most widely used and universally accepted technique for the determination of carbon following standard oxidation methods. The method devised by Pregl (for which he received the Nobel Prize in 1923) for the determination of carbon in organic compounds was proved practical in 1924 by Nicloux and Guillemet [95] for the determination of the carbon content of diamond. They used a 2- to 5-mg sample size and obtained an average carbon value that was 99.95 per cent of the theoretical carbon content.

Because of the simplicity of apparatus and ease of operation, this method has been widely accepted for routine work. Many papers have been published with regard to modification of the original Pregl procedure. The following general statements concern techniques necessary for the utmost precision and accuracy. Soda-asbestos [96] has generally

replaced the original soda-lime as a solid absorbent. Soda-asbestos presents a larger surface area for absorption and has demonstrated less channeling and packing. A desiccant, usually anhydrous magnesium perchlorate, is packed on top of the soda-asbestos on the sweep-gas exit side of the absorption tube to absorb the water produced in the reaction between soda and carbon dioxide. The gas stream entering the absorption bulb must be rendered free of water vapor and acid-gas constituents if accurate and precise results are to be achieved. Many sizes and designs of absorption bulbs are commercially available. For the larger oxygen flows used in high-temperature combustion and where greater quantities of carbon dioxide are weighed, larger absorption bulbs have been found necessary for complete absorption. If special precautions are applied to absorption bulb packing, if two counterbalanced absorption bulbs are used so that final weights of carbon dioxide are obtained by difference, if static charge on bulbs prior to weighing is eliminated, and if it is assured that temperature equilibrium has been reached in absorption bulbs before weighing, etc., carbon can be accurately and precisely determined in amounts of less than 1 mg (see Chap. 1).

(d) *Conductometric Method.* The measurement of small amounts of carbon dioxide based on the change in conductivity of a barium hydroxide solution when the barium ion is removed as barium carbonate has gained tremendously in application during the last few years. The method is more rapid and more simple than any other method for the determination of microquantities of carbon. Cain and Maxwell [97] originally proposed the method, but it was not until modern instrumentation was applied to proven theory that it became widely applied.[98-103] Temperature and electrical sensitivities in the system are overcome by balancing it against an identical blank cell in a Wheatstone bridge circuit. The simplicity, rapidity, and precision of this microdetermination of carbon, particularly in metals, have made these commercial instruments extremely popular for control analyses.

(e) *Manometric Method.* The measurement of very small quantities of carbon dioxide by manometric methods after elimination of oxygen by freezing out the carbon dioxide in a trap cooled by liquid nitrogen has been accomplished by several workers.[104, 105] After elimination of the oxygen, the solid carbon dioxide is allowed to come to an equilibrium temperature in a known volume, and the pressure is measured. Several authors have utilized this technique with low-pressure combustion equipment.[106-111] Better control of blanks was obtained than in standard combustion trains by heating the sample in vacuum prior to admission of the oxygen. Equipment and techniques required were more elaborate than for standard high-temperature combustion procedures.

(f) *Gas Chromatography.* Gas-chromatographic techniques have not been applied to the analysis of massive carbon. However, the field of column chromatography, both liquid and gas, has expanded tremendously in the last five years. With the development of ionization detectors for gas chromatographs, the lower limits of detection for carbon monoxide and carbon dioxide should be on the order of a few parts per million in a matrix of most of the stable gases, such as oxygen, nitrogen, argon, and helium. Activated-charcoal columns maintained at 170° C and silica gel columns have been used [112, 113] to determine carbon dioxide in a mixture of gases. In many absorption columns carbon dioxide is fixed irreversibly. Advantage can be taken of this property in some instances to purify sweep gases for use in combustion trains or chambers. In the future, utilization of gas-chromatographic techniques could assure low or very precise blanks, which would, in turn, assure greater precision and accuracy in the determination of carbon.

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CHAPTER 8

BORON

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8–1 INTRODUCTION

The element boron is important in nuclear technology because of the B^{10} isotope, which has a thermal-neutron cross section of 4020 barns and a natural abundance of about 20 per cent.

The natural abundance of B^{10} is not firmly established. The formerly used value [1] of 18.80 at.% was determined with a gas mass spectrometer and boron trifluoride as the charge material. It has been shown that this method of analysis suffers from uncertainty owing to mass discrimination effects [2] and instrument memory. Recent measurements made with surface ionization instruments and the charge material sodium tetraborate indicate this value is low. These measurements also tend to confirm the suspicion held for some years now that the natural abundance varies somewhat with the particular mineral studied. [3, 4] The values reported [3, 4] for various minerals from world-wide sources fall in the range 19.45 to 20.32 at.%. Fractionation of isotopes during the manufacture of boron compounds may also occur.[5] Isotopic ratios obtained by the analysis of certain "normal" boron compounds therefore may be different from those obtained from the corresponding raw materials.

The reactor physicist perhaps is more concerned with the natural abundance of boron than is the analytical chemist, who determines total boron and uses an atomic weight that suffices for most calculations. However, with the increasing use of B^{10}-enriched materials, it becomes increasingly important for the analytical chemist to know the B^{10} to B^{11} ratio in order to obtain the correct atomic weight. Although the determination of the B^{10} to B^{11} ratio is not within the scope of this chapter, the chemical separations needed to obtain the sodium tetraborate from various materials for the mass spectrometric analysis are discussed.

Boron-10 can be present in reactor materials in trace amounts as an undesirable impurity. It may be added in larger amounts to certain fuels as a burnable poison, which can be defined as a neutron absorber

*U.S. Atomic Energy Commission, New Brunswick Laboratory.
† General Electric Company, Knolls Atomic Power Laboratory.

Table 8.1—METHODS FOR DETERMINATION OF BORON

Range	Method
0.1 to 100 ppm	Colorimetric. Fluorometric. Flame photometric. Polarographic.
0.01 to 5%	Titrimetric. Colorimetric. Gravimetric. Polarographic. Flame photometric. Neutron absorptiometric.
Greater than 5%	Titrimetric. Gravimetric. Neutron absorptiometric.

that is removed by neutron capture at such a rate that it compensates approximately for the reactivity effects of fuel depletion and fission-product build-up. (After fuel burn-up the boron content may have decreased to the trace impurity range.) In still higher concentrations B^{10} is used in reactor control rods and neutron shielding materials. Also in this concentration range are various boron materials such as boron carbide and nitride, borides, and master alloys. Thus, the analytical chemistry of boron used in nuclear technology requires the determination of boron in three general ranges of concentration: 0.1 to 100 ppm; 0.01 to about 5 per cent; and greater than 5 per cent. These somewhat arbitrary ranges are used in Table 8.1, which lists the representative methods most useful in each range.

The colorimetric determination of traces of impurity boron in various materials is described in Chap. 11 and in other chapters. This chapter is devoted chiefly to discussions of the separation of boron from interfering substances, to general descriptions of the methods of determination, and to some detailed procedures not treated in the other chapters covering the three ranges of concentration.

8–2 STANDARDS

There is a need for a primary standard for boron. The lack of an established and accepted compound of definite stoichiometry and stability is a particularly serious obstacle to the preparation of isotopic standards. Another disturbing factor is the rather wide range of values reported for the normal isotopic abundance which, as discussed in Sec. 8–1, may vary with the mineral source and the method of processing.

For colorimetric, titrimetric, and related work, standard solutions are generally prepared from boric acid, fused boric oxide, or sodium tetraborate. Each of these compounds possesses an uncertainty regarding water content. Sodium tetraborate is the least satisfactory in this respect. The most convenient reagent is boric acid. Two recommended preparations of "standard" boric acid can be mentioned. In one the reagent-grade material is recrystallized three times, dried for 2 days in a loosely covered porcelain dish, and finally dried in a desiccator over concentrated sulfuric acid for four weeks.[6] The other procedure consists simply of drying the reagent-grade acid for two weeks over fresh calcium sulfate.[7]

The most commonly used "standard" is fused boric oxide prepared by fusing dried boric acid in platinum over a Meker burner for 20 to 30 min. Despite its frequent use, however, fused boric oxide is probably no more satisfactory than carefully dried boric acid because of the difficulty in removing the last traces of interstitial water in the oxide. Apparently the water is still incompletely removed even at temperatures at which the oxide appears to be slightly volatile.[7]

Because of the uncertainty in the stoichiometry of these boron "standards," it is recommended that the boron content of the standards be checked by the titrimetric mannitol method. Ultimately the primary standard for boron becomes National Bureau of Standards potassium acid phthalate, which is used to standardize the sodium hydroxide titrant. Table 8.2 shows the results obtained on titrating macroamounts of each of the three boron standard materials. The reason for the high results of the borax was found in a thermolysis curve in which the anhydrous salt was formed at >565°C and only 9.89 molecules of water were found for the decaborate salt.[8]

Isotopic standards are made by combining highly enriched B^{10} and B^{11} materials. Because of the lack of compounds possessing definite stoichiometry, the standards preparation must include analysis of the available materials. These chemical analyses contribute a major portion of the uncertainty in the final isotopic ratio of the prepared standards.

Table 8.2—MANNITOL TITRATION OF BORON "STANDARDS"[8]

No. of determinations	"Standard"	Boron added, mg	Boron found, % theoretical
5	$Na_2B_4O_7 \cdot 10H_2O$	51–81	101. 1
3	B_2O_3(H_3BO_3 fused at 550°C for 2 hr)	19–38	100. 7
5	H_3BO_3	5–25	99. 7

690–457 O—64——38

One preparation of isotopic standards by Haas and coworkers [7] can be described briefly. Starting materials were B^{10} prepared in a calutron at Oak Ridge National Laboratory (ORNL) and amorphous B^{11} obtained from Hooker Chemical Corp. Boric acid was made from these materials. Both acids were dried over calcium sulfate for two weeks. Stock solutions of the boric acids were then prepared by adding weighed amounts of boric acid or boric oxide made from the boric acid to weighed amounts of water. Polyethylene containers were used to avoid exchange of boron with the natural boron in glass. Isotopic analyses were made of sodium tetraborate prepared from these stock solutions by treatment with sodium hydroxide. Weighed aliquots of the B^{10} and B^{11} boric acid stock solutions were then analyzed titrimetrically for boron by the mannitol procedure. Standards having nominal B^{11} to B^{10} ratios of 1:1 and 4:1 were made by combining weighed amounts of the enriched stock solutions.

Boron isotopic standards have also been made by Bentley and Hamer [9] from boron trifluoride.

8–3 SEPARATIONS

Most analyses of boron-containing materials require a separation of boron from interfering elements. For example, in the titration procedure with mannitol, all elements reacting with sodium hydroxide or forming strong boric acid complexes may interfere. Fortunately the separation of boron for a particular analytical procedure can be accomplished easily by one of the methods discussed below.

8–3.1 Distillation

The classic distillation of methyl borate is perhaps the most common separation procedure for boron. The literature involving this technique is voluminous, and only a few observations will be given here. A good summary of much of the early work is reported by Russell [10] and by Richmond and Telford.[11] Current techniques are reviewed by Spicer and Strickland.[12] Borrowdale and coworkers [13] have also studied the variables involved.

In general, the procedure consists simply in adding methanol to a slightly acid solution of the sample and distilling off the ester and excess methanol into an absorbing solution. Calcium chloride or sulfuric or phosphoric acid is frequently added to the methanol solution to obtain the more nearly anhydrous conditions that favor the formation of the ester. Borrowdale and coworkers [13] recommend the use of a small volume, 1 to 2 ml, of sample solution for the same purpose. Spicer and Strickland [12] similarly advocate distilling off most of the

water before the methanol addition. Higher alcohols are less effective than methanol for ester formation.

The apparatus may be a simple distillation flask and condenser,[10] or it may consist of a methanol distillation flask and a sample flask arranged so that a constant stream of methanol vapor is passed through the sample solution from which the ester is distilled. Special units involving small distillation flasks and condensers have been designed [13, 14] which increase the efficiency of the distillation and minimize the amount of boron remaining behind.

The distillate is caught in either a lime suspension or a dilute sodium hydroxide solution, which hydrolyzes the ester. Other absorbants have been used.[10] For a discussion of the subsequent evaporation of the distillates, see Sec. 8–4.1.

The distillation separation is simple but frequently erratic. Low recoveries are frequently experienced in the presence of many elements, e.g., tungsten, aluminum, chromium, iron, and silicon. Multiple distillations are often used, but incomplete recovery under these conditions may still be obtained. Although the technique is distinctly characterized as being tedious, time consuming, and plagued by the appearance of erratic blanks, it is still applied to many analyses because of its simplicity and because it gives satisfactory results when the "art" is learned. The basic procedure as evolved from many sources is described fully in Chap. 4, Sec. 4–4.12(a).

Some modifications of the technique can be mentioned briefly. When the bromine–methanol dissolution procedure [15] for metal samples can be used, ester formation and distillation under the nearly anhydrous conditions is very efficient; complete recovery of even traces of boron is obtained on distilling only a portion of the solution. This procedure is described in Chap. 4, Sec. 4–4.12(b). A high-vacuum apparatus for the distillation has been developed to avoid the large volumes of distillate.[16] Trentleman and Van Velthuijsen [17] continuously distill the methanol and ester directly onto an anion-exchange resin column of Dowex-2 (OH^-). The ester is hydrolyzed, and the boric acid is retained on the column; the methanol returns to the distillation flask. After a 2-hr period, the boric acid is eluted with dilute hydrochloric acid for the titrimetric determination. Fluoride in the sample is suppressed with sodium aluminate. This continuous circulation of the methanol is also suggested by Ehrlich and Keil.[18] With this method the ester is absorbed in sodium methylate in methanol; the methanol is distilled and returned to the sample. The addition of concentrated zinc chloride solution is said to be helpful in distilling solutions containing halides, including fluoride, and nitrate.[19] Fluorides are also suppressed by the addition of aluminum chloride.[20]

8–3.2 Pyrohydrolysis

Boron in metals, alloys, and compounds, such as zirconium, Zircaloys, Zircaloy–uranium, stainless steel, and boron carbide, can generally be separated completely and easily by pyrohydrolysis.[21] With a nickel tube holding a nickel or platinum boat and a steam flow of 1 to 3 ml per minute, boron is removed in 90 min at 1100°C. Temperatures to 1300°C accelerate the removal but considerably shorten the life of the nickel tube. The technique is readily adaptable to remote operation. (With certain materials, e.g., uranium–zirconium alloys, Rynasiewicz [22] has found that total boron in the parts per million range may be incompletely separated. Depending on the pyrohydrolysis temperature, from 1 to 8 per cent of the initial quantity of boron may be found in the pyrohydrolysis residue by spectrographic analysis.)

Boric oxide in various glasses is similarly separated.[23] A mixed catalyst of U_3O_8 and sodium metasilicate nonahydrate and a temperature of 1300 to 1350°C in a platinum tube are recommended. This procedure is described in detail in Sec. 8–7.

The pyrohydrolysis technique is particularly useful for separating boron from minerals, alloys, and other materials in pure form for isotopic analysis by the mass spectrometer.[24] The necessary 100 per cent recovery is usually obtained, lengthy dissolution steps with accompanying high reagent blanks are avoided, and few elements distill with the boron.

8–3.3 Ion Exchange

A good separation of the cations interfering with the conventional titrimetric or colorimetric determinations of boron can be made with a column of a strongly acid cation-exchange resin.[25–27] Boron passes through. Iron, aluminum, beryllium, magnesium, zinc, cadmium, cobalt, copper, mercury, nickel, thorium, tin, titanium, and uranium are among the potentially interfering cations removed completely. The complete removal of zirconium is questionable. Martin and Hayes [27] separated 3 mg of boron from 31 mg of zirconium. However, Jones [28] was unsuccessful in quantitatively separating parts per million quantities of boron from zirconium either because of the high acid concentration required to prevent hydrolysis or because of the formation of colloidal zirconium hydrous oxide when the acid concentration was reduced. Anions such as chromate, vanadate, and permanganate are removed after reduction with hydrogen peroxide.

Anions such as arsenite, arsenate, phosphate, permanganate, formate, acetate, oxalate, and molybdate, which can interfere in the titrimetric procedure by their buffering or complexing action, and cations in the form of anionic complexes must be removed by anion

exchange. Three general techniques are available. Strongly basic resins are used to remove all anions including borate from the solution. A chromatographic elution with water then separates them in the order of their increasing affinity for the resin.[29] With Amberlite IRA–400 in the hydroxide form, the order of elution is borate, chloride, nitrate, arsenite, phosphate, and arsenate. When chloride, which can be added to the sample solution as an indicator ion, first appears in the effluent, all the borate and none of the more strongly held anions have been eluted. In another technique [30] the strongly basic resin is used in an anionic form such that the interfering anions are retained but the borate is not. Thus Amberlite IRA–400 in the formate form retains phosphate but not borate.

Weakly basic anion resins do not retain weak acids such as boric, silicic, or carbonic acids. If such a resin is mixed with a strongly acid cation resin to give a mixed-resin bed, all cations and most anions are separated from the boron without the necessity of an elution procedure. If the resins are in the free base and acid forms, the effluent is also deionized. This technique was applied by Wolszon, Hayes, and Hill [29] to separate boron prior to a titrimetric determination. Difficulty was experienced in the application to the colorimetric determination of boron because of the high blanks obtained. The high blanks were subsequently traced to the slow release of impurity boron in the resin.[31] Fluoride cannot be separated by these methods.

Similar techniques have been reported. After removing the cations and anions of strong acids with the mixed-resin bed, Cerrai and Testa [32] pass the effluent through a column of strongly basic Dowex 1–X10 saturated with gluconic acid. The boron is complexed by the resin gluconate and is eluted with 0.1*N* sodium chloride for colorimetric or titrimetric determination.

Muto [33] uses successive columns of strongly acid cation resin, Amberlite IR–120 (H^+), and the strongly basic resin Amberlite IRA–400 (Cl^-). Boron is not retained strongly by the latter resin in the chloride form.[29, 33] This separation is recommended prior to a titrimetric or colorimetric determination.

8–3.4 Precipitation or Complexation of Interferences

In the past iron, aluminum, and other interfering elements forming weak bases were separated prior to the titrimetric determination as the hydrous oxides with alkali- or alkaline-earth hydroxides, carbonates, or oxides.[34, 35] These hydrous oxides can occlude much boron, and either dilute solutions or reprecipitation is required for precise work. Although precipitation is generally unattractive, in some cases it is still recommended.

Hollander and Rieman [36] precipitate iron, aluminum, silica, and other elements in glasses with sodium hydroxide at pH 5.0 to 5.5. Reprecipitation is only necessary when the quantity of precipitate is rather large. In the analysis of metal borides, Blumenthal [37] precipitates the metals with barium carbonate with little loss. Tests with barium hydroxide, sodium hydroxide, and calcium carbonate gave low boron results. The separation has been applied successfully to borides of iron, chromium, tungsten, titanium, zirconium, thorium, vanadium, niobium, tantalum, calcium, and aluminum, to boron nitride and carbide, and to elemental boron. For dissolution all the borides are fused with sodium carbonate except aluminum and chromium borides, which are fused with sodium carbonate–sodium nitrate mixture, and tantalum and niobium borides, which require a potassium carbonate–potassium nitrate mixture. The melts are decomposed with hydrochloric acid before the precipitation. Vanadium solutions require an Fe(III) carrier for complete precipitation; chromium solutions require a second precipitation with barium chloride.

In magnesium materials magnesium, calcium, iron, and titanium can be removed without significant loss of boron with sodium hydroxide plus sodium carbonate.[38] In the analysis of ferroboron, barium hydroxide precipitation of the iron and other metals is recommended.[39]

Norwitz and Codell [40] separate the bulk of the titanium and the other cations in titanium alloys with cation-exchange resins and precipitate the residual titanium plus tungsten, silicon, and phosphorus with calcium carbonate. The carbonate precipitation without the prior ion-exchange separation was deemed worthless. The carbonate also serves to adjust the acidity prior to the titrimetric determination.

Solutions containing chromium are treated with sodium peroxide to oxidize the chromium to chromate. The chromate is then precipitated with barium ions from weakly acid solution.[41] Schäfer and Sieverts [42] separate zinc, nickel, iron(III), and aluminum with 8-quinolinol(oxine). The excess oxine is removed with magnesium chloride prior to the titrimetric determination. Bush and Higgs [43] precipitate molybdenum as sulfide in the titrimetric analysis of boronized molybdenum. If hydrogen sulfide is passed into a sodium hydroxide solution of the sample to form the thiomolybdate and if the warm solution is acidified, molybdenum trisulfide precipitates quantitatively without loss of boron.

Complexation to eliminate interferences has been applied. Thus, the iodide complex of copper,[44] the thiosulfate complex of silver,[45] and the cyanide complex of cobalt [41] can be formed to prevent the interference of these metals in titrating boron. (Large quantities

of cobalticyanide interfere with the indicator end point by its intense yellow color and must be precipitated as the silver salt before the titration.)

Pribil and Wünsch [46] titrate boron in the presence of lead, manganese, iron, zinc, and aluminum by complexing these metals with ethylenediaminetetraacetic acid (EDTA). The heavy-metals content must be known before one can use the calculated minimum amount of EDTA. A similar procedure has been applied to the analysis of thorium–boron alloys.[47] Edgerton and Henley [48] determine 0.5-mg quantities of boron in the presence of twenty times as much aluminum and uranium by titrating in the presence of 0.3*M* potassium oxalate.

8–3.5 Precipitation of Boron

In the presence of barium and tartrate ions in dilute ammonium hydroxide solution, borate gives a precipitate of barium borotartrate.[49-51] Microgram amounts of boron can be separated. [Although it is stated that the precipitate can be weighed to determine boron,[49] a discrepancy regarding the formula exists.[49, 52] The precipitate can be dissolved in concentrated sulfuric acid, and the boron can be determined by measuring the color given by tartaric acid with bromine and resorcinol.[53] Other indirect procedures for the determination involve: dissolution in hydrochloric acid, precipitation of barium chromate, and iodometric determination of chromate; [49, 50] determination of barium flame photometrically at 873 mμ; [54, 55] determination of excess barium ion used in the precipitation by ethylenediaminetetraacetic acid (EDTA).[56]]

Arabotrihydroxyglutaric and mannosaccharic acids have been used similarly with barium ions at pH 8.8 to 9.0 to form three component insoluble complexes.[57] Carbonate, sulfate, chromate, oxalate, calcium, and magnesium interfere. The precipitates can be weighed after drying at 120°C for 3 hr.

Nitron, 1,4-diphenyl-3,5-endanilohydrotriazole, precipitates fluoboric acid.[58-61] Weak acids or bases do not interfere. (The precipitate can be weighed as $C_{20}H_{16}N_4 \cdot HBF_4$ after drying at 110°C for 2 hr.) Nitrate, perchlorate, iodide, bromide, thiocyanate, chromate, nitrite, and chlorate interfere by forming insoluble salts with nitron, but many of these ions can be removed easily by oxidation or reduction.[58]

The water-soluble salt hexadecyltrimethylammonium chloride (cetyltrimethylammonium chloride) gives a precipitate with fluoboric acid which is one-tenth as soluble as that with nitron.[62] (The precipitate does not dry at 105°C to a definite composition. To determine boron indirectly, one must precipitate the excess precipitant with

ferrocyanide and titrate the excess ferrocyanide with permanganate.) Mercuric, ceric, and stannous ions interfere as do metavanadate, tungstate, ferrocyanide, ferricyanide, silicate, metaphosphate, persulfate, chlorate, perchlorate, iodide, iodate, dichromate, permanganate, nitrate, and bromide.

8–3.6 Leaching and Extraction

Boron in glass can be separated after a sodium potassium carbonate fusion by leaching the melt with methyl alcohol.[63] Some carbonate accompanies the borate. Similarly, boron can be leached from sodium chloride with ethyl alcohol;[64] some sodium chloride also follows the boron. Recovery is generally not quantitative in these procedures.

Extraction of ethyl alcohol solutions, obtained by fusing glass samples with sodium carbonate, dissolving the melt in sulfuric acid, and adding ethyl alcohol, with diethyl ether separates boron.[65] A similar extraction has been used to remove boron from fluoride salts after dissolution in hydrochloric acid–aluminum chloride.[66] Pohl [67] has studied this type of separation with various alcohol and ether systems: methyl alcohol–isopropyl ether was recommended. Generally, in these ether extractions, as with alcohol leaches, the recovery of boron is not quantitative, but the fraction extracting is so constant the separation is useful. Russell [10] has reviewed the early use of chloroform, acetone, and diethyl ether for boron extraction.

The tetraphenylarsonium salt of fluoborate is extractable with chloroform.[68] The separation is lengthy, however, because of the 18-hr standing period required for the fluoborate formation. Separation of microgram amounts is possible. The procedure has been applied to the determination of boron in silicon.[69]

Similarly, the fluoborates of methylene blue [70, 71] and the related monomethylthionine, Azure C,[72] have been extracted with 1,2-dichloroethane. The colored extracts can be used for the spectrophotometric determination. For the analysis of steel, the Azure C procedure is superior to methylene blue; the reagent blank is smaller and the effective range is larger. Other thionine derivatives have been studied.[72, 73] These thionine extraction procedures offer the advantages of freedom from interference, good sensitivity, and simplicity.

At pH 3.4 the fluoborate–methyl violet complex is extracted with benzene for its spectrophotometric determination.[74, 75] A colored product with methyl violet and salicylate is also produced with borate at pH 2.0;[76] the complex is extracted with 25 vol.% tributyl phosphate in carbon tetrachloride.

8–3.7 Mercury-cathode Electrolysis

Many metals interfering in the titrimetric mannitol determination of boron, e.g., iron, nickel, copper, and cobalt, can be removed by electrolyzing a dilute sulfuric acid solution with a mercury cathode.[43, 77, 78] Aluminum, beryllium, vanadium, titanium, zirconium, thorium, and uranium are among the elements not removed. No loss of boron occurs during the electrolysis even if the solution temperature reaches 60 to 70°C. Chirnside, Cluley, and Proffitt[79] dissolve nickel samples by making the sample the anode in a mercury electrolysis cell. Dissolution and deposition of the nickel thus proceed in one step.

8–3.8 Electromigration

Movement of the borate ion to the anode of a paper strip impressed with an electric field has been used by Hill, Merrill, and Palm[80] to separate and concentrate boron. The curcumin–boron complex is developed on the paper after ionophoresis.

To separate borate from large quantities of sodium ion, Logie[81] electrolyzes the solution placed in the anode compartment of an electromigration cell fitted with a cation-exchange membrane between the anode and cathode. Metal ions pass irreversibly into the cathode compartment; the borate remains in the anode compartment.

Morrison and Rupp[82] utilize a similar scheme with the cation-permeable membrane Amberplex C–1 to separate boron from sodium silicate. The boron is separated by water extraction from the silicic acid obtained.

8–3.9 Paper Chromatography

The distribution of borate with various solvents has been studied,[83, 84] and the effect of acids, bases, and salts on the R_f values has been determined.[83] The separation of borate from molybdenum,[84] as well as the isolation of borate from mineral waters, has been reported.[85] The separation of boron from iron, molybdenum, vanadium, and titanium by this technique is also possible.[86]

8–4 BORON LOSSES AND CONTAMINATION

8–4.1 Evaporation of Methyl Alcohol Distillates

In the evaporation of aqueous methyl alcohol solutions obtained from the distillation separation, it is necessary to have the solution sufficiently alkaline both to hydrolyze the methyl borate ester and

to prevent hydrolysis of the salt to the volatile free acid, otherwise losses of boron occur. The quantity of base added, however, often must be held to a minimum, especially in colorimetric work, because the water of neutralization may affect the color-producing step in the presence of concentrated acid or the large concentration of salt may decrease the color. Conflicting reports appear in the literature regarding the best boron-retaining conditions for the evaporation step. These different recommendations presumably result from the different volumes and alcohol-to-aqueous ratios obtained with the various distillation techniques.

Cogbill and Yoe [87] report that the addition of up to 0.5 milliequivalent of sodium hydroxide or calcium hydroxide or of a 0.4-milliequivalent sodium hydroxide and 15-milliequivalent ammonium hydroxide mixture is not satisfactory. A mixture of 0.4 milliequivalent of calcium hydroxide and 15 milliequivalents of ammonium hydroxide is recommended. Codell and Norwitz [88] suggest adding a pellet of sodium hydroxide and 10 ml of concentrated ammonium hydroxide. Russell [10] and Spicer and Strickland [12] recommend the addition of about 0.1 g of glycerol and 0.02 g of sodium hydroxide plus water equal to about half the distillate volume; even under these conditions 4 per cent of the boron is lost.[12] On the other hand, Borrowdale and coworkers [13] report that the addition of 5 ml of 0.1*N* sodium hydroxide alone is sufficient if the volume of distillate is 40 ml or less. Eberle and Lerner [15] add 15 ml of 0.37 per cent (w/v) lime suspension and about 50 ml of water to distillates that are chiefly methyl alcohol and obtain complete boron recovery.

8–4.2 Evaporation of Aqueous and Concentrated Acid Solutions

It is now well established that neutral or dilute sulfuric or perchloric acid solutions of boric acid can be evaporated to rather low volumes, e.g., 100 ml of 1 vol.% acid solution evaporated to about 5 ml, without significant losses of boron. [12, 89, 90] Evaporation of concentrated nitric acid solutions likewise gives little loss. Substantial losses do occur from hydrochloric acid solutions.[90]

Evaporation of aqueous solutions to dryness results in severe losses unless sufficient base or mannitol [90] is present. Callicoat and Wolszon [91] add 25 ml of lime suspension (8 g of calcium oxide per liter) to retain boron; sodium hydroxide, as used by Calkins and Stenger,[92] was not as effective as the lime. Eberle, Lerner, and Kramer [93] recommend the addition of 5 ml of pyridine to slightly acid effluents of ion-exchange resin columns prior to evaporation to dryness. Feldman [90] has shown that a 12-fold molar excess of mannitol will prevent

significant loss from acidic solutions (including hydrochloric acid solutions) in which mannitol is not destroyed by the hot solution.

Boron is volatilized from concentrated sulfuric acid at 228°C but may be retained in the system by refluxing action.[90] Wakamatsu[94] has reported that boron in fuming sulfuric acid is not lost but is converted to a form (possibly pyroborate) unreactive to the carminic acid colorimetric reagent used. Golubtsova[95] also states that boron is not lost from fuming sulfuric acid. Feldman,[90] however, has shown that such losses do occur and suggests that Golubtsova's conclusions may have been based on reproducible losses. From fuming perchloric acid, boron losses are serious; 95 per cent is lost in 5 min.[90]

8–4.3 Heating Acidic Residues

Although Wakamatsu[94] claims that boric acid in acid residues is not lost on heating at 250°C but is simply converted to a form unreactive to carminic acid, Feldman[90] has shown that boron is lost even at steam-bath temperatures. Anderson[96] also states that boron is not lost on baking residues containing a copper compound at 400°C, but here again the results can be explained by reproducible losses in both standards and samples.[90]

8–4.4 Dissolution and Oxidation of Organic Matter

The volatility of boric acid and other compounds such as hydrides and fluoride must be borne in mind during sample dissolution and subsequent manipulation steps. Acid dissolution of samples is generally carried out under reflux even if an oxidizing acid is present. Frequently the alkaline condition of a carbonate or peroxide fusion is preferred to avoid the possibility of loss. An interesting and useful dissolution for many metal samples for which a distillation separation is used is the bromine–methanol procedure.[15]

Oxidation of organic matter such as plant material can be carried out by dry ignition, after the addition of lime solution and drying, or by wet digestion, e.g., with sulfuric acid and hydrogen peroxide. Both general procedures have their advocates.[12, 87, 97, 98] With graphite samples the former oxidation technique is recommended. Borines and other organoboron compounds are easily oxidized by trifluoroperoxyacetic acid without boron loss.[99]

8–4.5 Contamination

Apparently borosilicate glass can be used when large amounts of boron in neutral or slightly acid solution are manipulated. However, for the greatest safety regardless of the quantity of boron involved,

low-boron glass, Corning No. 7280, or preferably quartzware should be used. Porcelain can be used often without danger. Polyethylene is useful for solution storage. Serious sources of contamination when traces of boron are determined are stopcock grease and filter paper.[100] Laboratory dust can contribute to contamination. Contamination from firebrick in muffle furnaces has been noted during ashing of blood samples [101] and plant material [100a] for colorimetric boron analyses [101] and during ignition of Zircaloy chips for spectrographic boron analyses.[102] On the other hand, ashing blood samples over an open flame and oxidizing Zircaloy chips in a quartz tube inserted into the muffle furnace gave low boron blanks. Ignition in covered tall-form crucibles also lessens furnace contamination.[101a]

Reagents such as water, methyl alcohol, and nitric and hydrochloric acid may contain small amounts of boron and should be redistilled from quartz. The boron content of sulfuric and perchloric acid can be reduced somewhat by adding hydrofluoric acid and evaporating the solution to strong fumes. Ammonium hydroxide is best prepared from tank ammonia; calcium hydroxide, from high-purity metal.

8–5 DETERMINATIONS

8–5.1 Titration

Innumerable variations of the classic polyhydroxy alcohol titrimetric determination of boron exist. Accordingly, only a brief discussion of the basic principles involved will be given here.

The conversion of borate to boric acid by excess mineral acid results in a mixture of a strong and a weak acid in the solution. The pK of boric acid is about 9.2. Since the two acids have a difference in their pK values of at least 4 units, the strong acid can be titrated satisfactorily with standard base before appreciable amounts of the boric acid are neutralized. The weakly ionizing boric acid, however, will give no detectable end point if the titration is continued. If a polyhydroxy alcohol such as mannitol is added to the solution after the strong acid equivalence point, the boric acid is converted to the complex mannitoboric acid with a pK of about 4. This stronger acid can now be titrated satisfactorily with visual, potentiometric, or other end-point detection.

It is possible therefore to titrate the strong acid and the boric acid successively, and this type of procedure is used often. Common indicators for the first end point are *p*-nitrophenol, methyl orange, methyl red, bromphenol blue [103] or a methyl red–methylene blue mixture.[25, 104] For the second end point, phenolphthalein, bromthymol blue, a bromphenol blue–phenolphthalein–*p*-nitrophenol mixture [103] or a methyl red–methylene blue–phenolphthalein mix-

ture [104] can be used. A mixed indicator suitable for both end points is a mixture of methyl red, bromcresol green, phenolphthalein, and thymolphthalein.[37] The titration is often performed potentiometrically.[104, 105]

Frequently, however, titrations to these different first and second end points may result in rather large errors, particularly in the determination of small amounts of boric acid. Weak acids and bases as impurities in the sample solutions, the ionic strength, the amount of mannitol used,[106] and other variables may have a pronounced effect on the pH or slope at the two end points. Some of this error can be eliminated in the titration of small amounts of boric acid by titrating the mannitoboric acid to the same pH as is used for the strong-acid end point.[27, 36, 107] Since generally only boric acid reacts with mannitol, the effects of interfering impurity weak acids and bases are eliminated. (Tellurium and germanium acids can also be "activated" by polyhydric alcohols.) This procedure, known as the fixed or identical pH method, is commonly used at the present time. The pH selected is rather arbitrary. Since small amounts of boric acid may be neutralized at the strong-acid end point and since the second end point may occur before all the boric acid is neutralized, that pH is chosen which gives the smallest errors under the conditions of the titration. The most accurate procedure is probably that recommended by Hollander and Rieman,[36] who advocate determining the actual corrections to be applied by titrating known amounts of boric acid under the same conditions to be used for the sample. These authors use pH 6.3. Other values, e.g., 7.2 to 7.6,[108] 7.6,[107] 7.0,[109] and 6.9,[110] have been recommended, depending on the amount of mannitol used, etc. With the use of invert sugar to complex the boric acid, Martin and Hayes [27] recommend a pH of 6.9; again, other values have been reported. By standardizing the sodium hydroxide titrant against the same weight of boric acid as found in the sample, Martin and Hayes [27] and Highfill [111] obtained fairly accurate results with the identical pH method without the necessity of applying corrections. The boron content of the boric acid used for standardization must be accurately known. The use of this technique, however, is limited to nearly identical samples.

Many cations and anions interfere in the titrimetric procedure by reacting with sodium hydroxide or boric acid in one way or another, the reaction resulting in hydrolysis, buffering, or complexing. The removal of many of these interferences is discussed in Sec. 8–3. Carbon dioxide interferes. [In the identical pH method, large amounts of carbonic acid (and silica) interfere by decreasing the slope of the titration curve near the end point.] Carbon dioxide is removed by boiling

the acid solution gently in a covered beaker or at reduced pressure, by aerating for 30 min at 60°C with air purified by passage through concentrated sulfuric acid and Ascarite,[36] by sweeping out gently with nitrogen, or by sweeping out at pH 3 in a covered beaker with filtered but unpurified air for 15 min.[112] During the titration a layer of pentane excludes carbon dioxide efficiently;[19] a nitrogen atmosphere is often used.

Other polyhydroxy alchols have been used to convert the boric acid to a stronger complex acid: sorbitol, fructose, glycerol, invert sugar, propylene glycol, etc.[113] Mannitol is generally preferred.

Some interesting variations in the basic procedure have appeared. Kubota[105] obtains satisfactory end points for both the free strong acid and boric acid by adding mannitol at the start and by titrating potentiometrically. An optimum amount of mannitol was found to be necessary to obtain good breaks. Kubota also has extended the range to 10 to 100 μg of boron. Hahn[114] prefers to add the complexing alcohol sorbitol to the titrant. Schuele, Hazel, and McNabb[104] determine the free acid and the boric acid end points spectrophotometrically. Methyl red or a mixture of methyl red and methylene blue is used for the first end point; phenolphthalein is added for the second. A wave length of 532 mμ is used for both end points. The method is rapid, and the results seem to be as good as the values obtained potentiometrically. The titration can be performed conductometrically.[104, 115] The method appears to be useful for large amounts of boric acid, and it requires no mannitol addition. The reproducibility is only fair. The mannitol titration can be carried out amperometrically with a rotating platinum electrode.[116]

A few indirect titrimetric procedures of lesser importance, based upon the precipitation of the fairly insoluble barium borotartrate, are available. These procedures are described briefly in Sec. 8–3.5.

(a) *Titrimetric Determination of Boron in Boron Carbide: Precipitation, Visual.*

Procedure.[117] About 1 g of sodium carbonate is fused in a 30-ml platinum crucible and cooled while the crucible is rotated so that the sodium carbonate forms a lining. A mixture of 0.1 g of sample and 1 g of sodium carbonate is then fused in the covered crucible at 900°C for 4 hr. The cooled melt is dissolved in water in low-boron (Corning No. 7280) glass, the solution is neutralized to methyl red with concentrated hydrochloric acid, and 1 ml of acid in excess is added. The solution is heated for 30 min and is neutralized with dilute sodium hydroxide solution. The solution is filtered and made up to 250 ml.

To an aliquot containing about 25 mg of boron in low-boron glass are added 2 drops of 0.1 per cent methyl red solution (1.0 g dissolved in

100 ml of 95% ethyl alcohol) and hydrochloric acid to the red end point plus 2 drops in excess. The solution is simmered for 10 min and cooled. After the addition of 2 drops of methyl red solution, the solution is titrated with 0.1*N* sodium hydroxide (standardized against potassium acid phthalate) to the color change. Mannitol, 20 g, is added, and the solution is titrated to the lemon color; 1 ml of 0.5 per cent phenolphthalein indicator solution (2.5 g dissolved in 500 ml of 95% ethyl alcohol) is added, and the solution is titrated to the pink end point. The volume of titrant used after the addition of the mannitol is noted.

(b) *Titrimetric Determination of Boron in Boron Steel Alloys: Ion Exchange, Potentiometric, Identical pH.*

Procedure.[110] A 1-g sample of chips is dissolved in 10 ml of concentrated hydrochloric acid plus 5 ml of water by heating under reflux. When the reaction stops, 2 ml of concentrated nitric acid is added, and the solution is again heated under reflux for 15 min. To the cooled solution is added 1 ml of 30 wt.% hydrogen peroxide, and heating is continued for another 15 min. The cooled solution is filtered and diluted to 100 ml.

An aliquot containing about 250 mg of sample is diluted to 90 ml and is passed through a column of cation resin (Amberlite XE–77, H^+ form, in a 1- by 15-cm glass column). The column is washed with 200 ml of water. The sample and washing are collected in a low-boron (Corning No. 7280) glass beaker. The solution is adjusted to pH 3.3 on a meter with 20 wt.% sodium hydroxide solution and simmered for 20 min. (The solution is kept on the hot plate until it is to be titrated.) The solution is cooled to room temperature.

The solution is titrated with 0.02*N* sodium hydroxide (standardized against potassium acid phthalate) to pH 6.9. Mannitol, 20 g, is added, and the solution is again titrated to pH 6.9. An empirical blank of 0.0145 per cent is subtracted from the per cent boron value obtained. This blank is caused by the buffering action of the large quantities of sodium chloride in the solution.

(c) *Titrimetric Determination of Boric Acid: General Potentiometric, Identical pH with Corrections.*

Procedure.[36] A solution of the sample containing from 5 to 100 mg of boric acid is freed of interferences by one of the separation procedures described in Sec. 8–3. The reaction is adjusted to pH 5 on a pH meter and carbon dioxide is removed by bubbling air (purified by passage through concentrated sulfuric acid and Ascarite) through the solution at 60±5°C for 30 min. The volume is adjusted to 250 ml with warm water, and the solution is cooled. The pH is adjusted to 6.30 with carbonate-free 0.05*N* sodium hydroxide (standardized against potassium acid phthalate); 40 g of mannitol is then added. The solution is titrated back to pH 6.30 with the 0.05*N* sodium hydroxide.

The corrections that must be added to the boric acid found are as follows:

H_3BO_3 found, milliequivalents	Correction, milliequivalents	H_3BO_3 found, milliequivalents	Correction, milliequivalents
0.1	0. 005	1.4	0. 026
0.2	0. 008	1.6	0. 029
0.4	0. 013	1.8	0. 031
0.6	0. 016	2.0	0. 033
0.8	0. 019	2.4	0. 036
1.0	0. 022	2.8	0. 040
1.2	0. 024		

[If it is desired to avoid the corrections, the 0.05*N* carbonate-free sodium hydroxide is standardized against the same weight (±10 per cent) of boric oxide as the sample contains.[27, 111]]

(d) *Titrimetric Determination of Boron in Elemental Boron: Precipitation, Potentiometric.*

Procedure. About 5 g of anhydrous sodium carbonate powder is tamped into a 30-ml platinum crucible. An intimate mixture of 200 mg of sample and 1 g of sodium carbonate is added, and finally 4 g of sodium carbonate is spread over the mixture. The crucible is heated gradually over a period of 60 min in a furnace to 1000°C and held for 15 min at this temperature.

The cooled melt is dissolved in 200 ml of water, the solution is digested for 30 min and then filtered through Whatman No. 42 paper, and the filter paper is washed thoroughly with 200 ml of 0.1 per cent sodium carbonate solution. The pH is adjusted to 3.5 on a meter with dilute sulfuric acid, and the solution is covered and boiled gently for 3 min. The rapidly cooled solution is titrated with 0.4*N* sodium hydroxide (standardized against potassium acid phthalate) to the strong acid inflection point near pH 5.5. Then 50 g of mannitol is added, and the titration is continued to the inflection point of the mannitoboric acid near pH 8.1.

8–5.2 Colorimetry

Colorimetric procedures for the determination of boron are conveniently divided into two groups. In one group boron and the chromogenic reagent react only in concentrated acid, generally sulfuric acid. The reagents in this group are chiefly substituted anthraquinones such as quinalizarin, carminic acid, and 1,1′-dianthrimide. Chromotrope-2B, a *p*-nitrobenzeneazo derivative of chromotropic acid, also requires the presence of concentrated sulfuric acid. The second group involves reagents that do not require color development in concentrated acid. Curcumin is the best known example of this group.

Table 8.3—USEFUL RANGES OF COMMONLY USED REAGENTS

Range, μg	Reagent
0–5	Curcumin, methylene blue, Azure C.
1–10	Carminic acid, 1,1′-dianthrimide, diaminochrysazin, quinalizarin, chromotrope 2B.
5–100	Chromotropic acid.
20–600	Victoria Violet.

Procedures based upon the complexes of borate with chromotropic acid and certain derivatives, morin and related compounds, the complexes of fluoborate with dyes such as methylene blue and similar compounds, and various miscellaneous procedures all are classed arbitrarily in this group.

Table 8.3 lists the approximate useful ranges of some of the more commonly used reagents of both types. When a particular reagent is being selected for a specific analysis, the discussions of color development, spectral characteristics, and interferences given under each reagent should be consulted.

(a) *Reagents Requiring Concentrated Acid.* Certain hydroxyanthraquinones, their derivatives, and other compounds react with boric acid in concentrated sulfuric acid to give colored products. The reagents themselves are often highly colored in the sulfuric acid. With simple hydroxyanthraquinones such as quinalizarin, the reaction with boric acid occurs without much color change: the absorption spectra of the reagent and complex overlap markedly. This overlap may have a detrimental effect on sensitivity and adherence to Beer's law. With certain other reagents such as 1,1′-dianthrimide (1,1′-dianthraquinoylamine), marked color changes occur and consequently the sensitivity may be higher and Beer's law followed more closely.

A wide variety of final sulfuric acid concentrations, reagent concentrations, temperatures, and standing periods for color development have been described for the commonly used reagents in this group, e.g., quinalizarin and carminic acid. No attempt will be made to list all these different conditions. Instead, brief statements regarding recently determined optimum conditions will be given. Also included will be references to recent reports involving basic studies of variables in the color reaction. Applications of the reagents to the determination of boron in specific materials are given in Tables 8.6 and 8.7.

A comparison of the sensitivities of many of the reagents in this group as listed by Goward and coworkers [118] is shown in Table 8.4.

690–457 O—64——39

Table 8.4—COMPARISON OF SENSITIVITIES OF SOME CONCENTRATED-ACID REAGENTS FOR THE DETERMINATION OF BORON [118]

Reagent	Reagent conc., mg/50 ml	H_2O added, ml/50 ml	Wave length, mμ	Absorbance in 1-cm cells, 10μg/50 ml
Quinalizarin	2. 25	4. 5	615	0. 013
	2. 02	4. 1	620	0. 011
	0. 5	5. 0	615	0. 008
	0. 28	2. 8	615	0. 006
Carminic acid	4. 65	2. 0	610	0. 008
	18. 6	5. 0	585	0. 008
	10. 0	2. 0	610	0. 012
	18. 4	4. 0	585	0. 012
Diaminochrysazin	1. 5	0	525	0. 011
Diaminoanthrarufin	1. 5	0	605	0. 010
Tribromoanthrarufin	1. 5	0	625	0. 024
Dinitroanthrarufin	0. 5	0	505	0. 009
Dinitrochrysazin	0. 5	0	490	0. 003
Dicyanoquinizarin	0. 5	0	560	0. 018
Tetrabromochrysazin	1. 5	0	540	0. 016
1,1′-Dianthrimide	10	1. 0	625	0. 030
	2	0	620	0. 032
5-Benzamido-6′-chloro-1,1′-bis(anthraquinoyl) amine	14. 5	0	635	0. 033
5-*p*-Toluidino-1,1′-bis(anthraquinoyl) amine	2. 7	0	720	0. 040

(1) *Quinalizarin.* This reagent possesses several disadvantages. The spectra of the reagent and its boron complex overlap badly.[119] Beer's law is not followed closely, and under most conditions the sensitivity is relatively low. The quality of the reagent is variable. The complex is unstable to ultraviolet light in the presence of ions such as uranyl. Chloride, however, inhibits the photodecomposition. The color is markedly temperature dependent; during color measurement the temperature must be controlled.

The optimum sulfuric acid concentration appears to be between 91 and 93 wt.%; that of the reagent 2.25 mg per 50 ml of solution when 1-cm cells are used, 0.5 to 0.8 mg per 50 ml when 5-cm cells are used.[118] The color is apparently developed fully after the reagent has been added and the solution has been cooled to 25°C.

Despite the disadvantages, the reagent is commonly used in direct (no separation) procedures because of their simplicity and relative

freedom from interferences. It is particularly useful for zirconium-base alloys, which represent a large segment of the nuclear fuel materials. Interferences include oxidizing agents, nitrates, fluorides, titanium, germanium, and colored ions. Detailed studies of the color reaction have been made.[98, 118, 120-123] The use of acetylquinalizarin offers little advantage.[124, 125] Most of the sulfuric acid can be replaced by a mixture of acetic acid and acetic anhydride.[126] The color can be titrated with water to a "blank" color as an alternate procedure.[127, 128] This technique eliminates the use of the spectrophotometer or color standards.

Spectrophotometric Determination of Boron in Aluminum Metal, Al–B_4C, UO_2–B, Zr–U–B, Zr–B, and UO_2–Al_2O_3–B (Metal, Carbide, Oxide, or Nitride) : Direct Quinalizarin.

Procedure.[118] With UO_2–B and UO_2–Al_2O_3–B, a 0.5- to 2-g sample is fused with sodium peroxide in an iron crucible. The cooled melt is leached with water, and the solution is diluted to volume in a volumetric flask. A portion is centrifuged in a plastic tube. Peroxide is destroyed by permanganate, and excess permanganate is reduced with hydroxylamine hydrochloride. An aliquot of 4.5 ml containing up to 40 μg of boron is pipetted into a 50-ml volumetric flask; 45 ml of quinalizarin reagent (2.25 mg per 50 ml of concentrated sulfuric acid) is added. The solution is cooled to 25°C, made to volume with reagent, and the color is measured at 615 mμ in 1-cm cells against a reagent blank. If 5-cm cells must be used, a 5.0-ml aliquot is made up to 50.0 ml with a less concentrated reagent, 0.5 mg/50 ml of sulfuric acid.

With Zr–U–B fuel alloy or Zr–B master alloy, a 1.5-g sample is dissolved in 10 ml of concentrated sulfuric acid plus 1 to 3 ml of water under reflux. The solution is filtered and diluted to volume, and a suitable aliquot is treated as above.

With aluminum metal and Al–B_4C, a 0.5- to 2.0-g sample is dissolved in dilute hydrochloric acid under reflux. The solution is filtered, and any residue is fused with sodium carbonate. The melt is dissolved in water, and the solution is neutralized with dilute sulfuric acid and added to the main solution. After the solution has been diluted to volume, a suitable aliquot is treated as above.

Standard curves are prepared in the same manner as above with 4.5 or 5.0 ml of standard boron solution containing from 0 to 40 μg (1-cm cells) or 0 to 20 μg (5-cm cells) of boron, respectively.

(2) *Carminic Acid (Carmine, Carmine No. 40 N.F., Carmine Red Ia).* Carminic acid, or the closely related carmine, is in some respects a better reagent than quinalizarin. The spectra of the reagent and the complex do not overlap to a great extent.[129] Reproducibility is better: in general, the effects of reagent and sulfuric acid concentrations are less pronounced than in the case of quinalizarin. Another advantage is the fact that concentrations of sulfuric acid as low as 88 wt.% can be used.[129a] In this medium, salts of stainless-steel com-

ponents are fairly soluble; they are relatively insoluble in more concentrated acid. A standing period of 60 min at 30°C is recommended for full color development, but shorter periods have been used. As with quinalizarin, the color is sensitive to ultraviolet light in the presence of uranyl ions; chloride ions stabilize the color.[118]

Strong oxidizing agents, highly charged ions such as Fe(III) and Al(III), nitrate, and fluoride interfere. In sufficient quantity uranium, vanadium, nitrite, and arsenate can interfere. The usual highly colored ions interfere. Chloride prevents the interference of nitrate.

Basic studies of the reaction variables have been made.[91, 92, 129–136] Modifications of the basic procedure have been described. Acetic acid plus acetic anhydride can replace much of the sulfuric acid.[126] Concentrated hydrochloric acid has been used with carmine, but a loss of sensitivity occurs.[137]

Spectrophotometric Determination of Boron in U–Al–B and U–Al–B_4C Fuel Elements, and Polyethylene Tape Impregnated with Boron: Direct Carminic Acid.

Procedure.[132] From 0.5- to 2-g samples of U–Al–B fuel are dissolved under reflux in 10 ml of concentrated hydrochloric acid and 15 ml of water per gram of sample. After dissolution, 2 ml of 30 wt. % hydrogen peroxide per gram of sample is added. The solution is boiled under reflux to destroy peroxides, diluted to a volume equal to 40 times the weight of sample, and stored in polyethylene.

For the analysis of boron carbide-containing fuel alloys, a sample containing 1 to 5 mg of boron is dissolved in the same quantity of acid used above containing 1 g of ashless cellulose paper. Boron carbide remains as an insoluble residue adsorbed on the paper. The solution is filtered on Whatman No. 42 paper. The paper is ashed, and the residue is fused with 4 g of sodium carbonate at 900°C for 15 min. The cooled melt is dissolved in water, and the solution is acidified with 20 ml of concentrated hydrochloric acid and diluted to 100 ml. (For the most accurate work, the filtrate from the initial acid dissolution should be checked for any small amount of acid-soluble boron.)

For the analysis of polyethylene tape, a sample containing 1 to 5 mg of boron is slowly burned in a platinum crucible. The ash is fused and treated as for boron carbide samples with 0.5 g of sodium carbonate.

An aliquot containing from 0.01 to 0.07 mg of boron is pipetted into a 25-ml volumetric flask. The maximum aliquot is 2 ml. If the aliquot is less than 2 ml, the volume is brought up to 2 ml. Two drops of concentrated hydrochloric acid are added. The solution is cooled in an ice bath, and 10 ml of concentrated cold sulfuric acid is added. The solution is shaken until gas evolution ceases. Then 10 ml of carminic acid reagent [0.05 wt.% in concentrated (96 wt.%) sulfuric acid] is added, and the solution is allowed to stand at room temperature for 60 min. The absorbance is measured at 585 mμ against a blank carried through the procedure.

The blank for the U–Al–B fuel is an aliquot of a U–Al matrix solution equal to the sample solution. The matrix solution is prepared by

dissolving 22.1 g of 81.5 wt.% 28 aluminum–18.5 wt.% uranium alloy (the individual metals can be used) and 2.9 g of 2S aluminum metal in 600 ml of 5*N* hydrochloric acid. After dissolution, 50 ml of 30 wt.% hydrogen peroxide is added. The excess peroxide is removed by boiling, and the solution is diluted to 1 liter. The blank for the carbonate fusion samples is water.

Calibration curves are prepared by carrying standard boron solutions through the identical procedure. Water serves as the blank solution.

(3) *Chromotrope 2B* (*Chromotrope B*). The effective range is somewhat better than that of quinalizarin; the sensitivity is nearly the same. When 10 ml of 0.005 wt.% reagent in concentrated sulfuric acid is added to a 1-ml aliquot of sample solution containing 70 vol.% acetic acid, the color is developed in 30 min and is measured at 620 mμ.[138] Acetic acid–acetic anhydride can replace the sulfuric acid.[126, 139] After heating the solution for 30 min at 100° C, Hegedus [140] adds sodium cobaltinitrite and holds the mixture in the dark for 8 hr before reading.

Oxidizing agents, nitrate, nitrite, fluoride, selenate, and germanate interfere. Hydroxylamine is used to eliminate germanate interference; hydrazine eliminates the oxidizing agents.

(4) *1,1′-Dianthrimide.* This reagent [141] ranks among the best available.[142] It is about three times as sensitive as carminic acid, and the reproducibility is good. There is little spectral overlapping.[141] Beer's law is followed up to 30 μg per 50 ml of solution. One disadvantage is the slowness of color development. Although the original procedure [141] specified heating at 90°C for 3 hr, this period can be reduced: conditions of 2 hr at 90°C,[93] 1.5 hr at 100°C,[142] or 1 hr at 110°C [142] have been recommended.

Strong oxidizing agents and appreciable amounts of highly charged ions interfere. Platinum probably interferes.[93, 141] Anions such as bromide, iodide, fluoride, nitrate, nitrite, phosphate, and arsenite can interfere. In a detailed study of the effect of foreign ions, Langmyhr [143] found that in the presence of hydrazine sulfate only germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate, and high concentrations of orthophosphate interfere. Hydroxylamine hydrochloride removes the interference of Ge(IV) and Te(IV). Basic studies of the application of the reagent to boron determination have been made.[118, 141-145]

Spectrophotometric Determination of Boron in U_3O_8: Ion-Exchange Separation, 1,1′-Dianthrimide.

Procedure.[93] A 2-g sample is dissolved under reflux in 40 ml of water, 1.0 ml of concentrated seulfuric acid, and 1.0 ml of 30 wt.% hydrogen peroxide. The solution is boiled for 1 hr, the condenser is washed with

25 ml of water, the solution is boiled again for 30 min, and the condenser is again washed with 25 ml of water.

The residual peroxide is destroyed with potassium permanganate crystals, and excess permanganate is destroyed by dilute ferrous chloride solution. The solution is added to a 3-in. column of Dowex 50–X8(H^+) in a 6- by 1.5-in. Lusteroid tube. The column is washed with four 25-ml portions of water. To the effluent in a quartz flask is added 5.0 ml of pyridine, and the solution is evaporated on a steam bath.

To the residue is added 5.0 ml of 1,1′-dianthrimide solution [400 mg dissolved in 100 ml of concentrated sulfuric acid in quartz (solution is stable for months); 5.0 ml of this stock diluted to 100 ml with concentrated sulfuric acid (diluted solution prepared fresh daily).] The flask is heated in an oven for 2 hr at 90±1°C. The solution is cooled, and 15.0 ml of concentrated sulfuric acid is added. The absorbance is measured as described below.

For the preparation of the standard curve, 1.0 ml of concentrated sulfuric acid, 50 ml of water, 5.0 ml of pyridine, and 0 to 2 μg of boron are added to identical quartz flasks. The solutions are evaporated to dryness and treated as described for the sample. The absorbance of each solution is measured against the 0-μg standard at 620 mμ in 5-cm cells. It is recommended that a standard curve be prepared with each set of samples.

For the blank correction 1- and 2-g samples of U_3O_8 containing less than 0.1 ppm of boron are carried through the procedure. The difference between twice the absorbance of the 1-g sample and the 2-g sample is the blank. The blank does not exceed 0.05 ppm when Merck sulfuric acid is used and can often be ignored.

(5) *Other Reagents.* The anthrarufin, chrysazin, quinizarin,[87, 146, 147] and 1,1′-dianthrimide derivatives[148] are shown in Table 8.4. Many are apparently superior to quinalizarin since they show little spectral overlap and have equal or better sensitivity. Arsenazo II has also been used.[95, 149] Apparently it is comparable to carminic acid or chromatrope 2B.

Diaminochrysazin[87, 146] is considered to be one of the most useful of the newer reagents. Beer's law is followed up to 5 μg. Color development is nearly instantaneous, but a standing period of 15 min is recommended. Oxidizing agents, such as nitrate and dichromate, and fluoride interfere. The color is somewhat temperature dependent, and it is destroyed by ultraviolet light in the presence of uranyl ions. Chloride ion stabilizes the color.

Alizarin Red S is very similar to quinalizarin in spectral overlap, sensitivity, and interferences.[150–152] At the working wave length of 620 mμ, Beer's law is not followed well. Alizarin Blue S and the unsulfonated dye base of Solvay Purple have also been used.[153] These reagents apparently offer no advantages. Among the unsubstituted hydroxyanthraquinones, chrysazin is apparently rather useful.[154] The boric acid complex of this reagent also fluoresces.[154]

(b) *Reagents Not Requiring Concentrated Acid.* (1) *Curcumin (Turmeric).* The classic curcumin procedure,[10, 155] involving the evaporation to dryness at a controlled temperature of an ethanolic solution of boric acid containing curcumin and oxalic acid and the extraction of the red color in the residue with ethyl alcohol, is one of the most sensitive procedures for boron. It is about 10 times as sensitive as that with carminic acid, and about 4 times that with 1,1′-dianthrimide. Although widely used, the procedure is tedious and may suffer from a lack of reproducibility: the color, produced during the evaporation step, is dependent upon the rate of heating and evaporation, on the quantity of salts, and the ratio of alcohol to water present. A typical procedure is given in Chap. 4, Sec. 4.12(a).

Appreciable amounts of iron(III), molybdenum, titanium, niobium, tantalum, and zirconium can interfere. Oxidizing agents such as nitrate, nitrite, chlorate, peroxide, etc. can interfere seriously. Germanium forms a complex with curcumin that interferes, but the reaction is relatively insensitive. Fluoride and phosphate interfere. The presence of alkali- or alkaline-earth salts is said to depress the color, although Rynasiewicz and coworkers[64] found that 0.58 g of sodium chloride could be tolerated in the 1- to 10-ppm range of boron.

The reaction variables have been studied.[79, 156–165] Substitutes for oxalic acid in the conventional reaction have been applied.[79, 158, 166, 167] Of the many compounds tested, only trichloroacetic acid [166] has gained any acceptance. The use of salicylic acid is suggested.[167] When salicylic acid is used, an intense blue color with a maximum absorbance at 520 mμ is produced by adding sodium carbonate to the alcohol extract. Solvents other than ethyl alcohol have been studied: acetone,[158, 161] 2-propanol,[158] butanone, [158] and acetic acid.[158, 168] These solvents offer no particular advantages.

The red color formed between boron and curcumin is due to rosocyanin and rubrocurcumin.[156, 157] The latter, a 1:1 complex, usually predominates when the conventional procedure with oxalic acid is used. Rosocyanin is a 2:1 (reagent–boron) complex. Both compounds have extremely high molar absorptivities, about 180,000, and absorb at the same wave lengths. Rosocyanin, however, in terms of gram atoms of boron, has twice the sensitivity of rubrocurcumin. Therefore, when rosocyanin is formed almost exclusively, one of the most sensitive colorimetric procedures known results. Spicer and Strickland [156] have shown that near quantitative production of rosocyanin can be obtained by the reaction of boric acid and curcumin in the presence of *o*-chlorophenol. The procedure, however, suffers the disadvantage of variable blanks arising from a decomposition product of curcumin, and absorbance measurements at two wave lengths must be made to reduce the error.

Hayes and Metcalfe,[168a] however, have described a procedure, leading to the near quantitative formation of rosocyanin, that is simple and rapid, and gives excellent results without the necessity of a correction factor. This procedure may prove to be the best curcumin method for the determination of boron in solutions obtained by a separation such as distillation. It has been applied to the analysis of reagent ammonium hydroxide[168b] and to the analysis of Zircaloys.[168c] The latter procedure is described below.

Spectrophotometric Determination of Boron in Zircaloy: Bromine-Methanol Dissolution, Distillation, Curcumin.

Apparatus. A 250-ml quartz flask connected by a standard-taper joint to a quartz air condenser 4 ft in length is used for the sample dissolution. The same flask is used for the distillation by attaching a quartz distillation head and condenser.

Procedure.[168c] A weighed 1-g sample of Zircaloy is placed in the flask, 30 ml of methanol (maximum water content 0.01 vol.%) and 2 ml of bromine are added, and the air condenser is attached immediately. The reaction is controlled by cooling the flask in an ice bath. When dissolution is complete, the condenser is washed down with 30 ml of methanol. Then 2 g of stannous chloride (recrystallized from methanolic hydrogen chloride) is added, and the flask is attached to the distillation head and condenser. The flask is heated gently by means of a mantle. The distillate is collected in a polyethylene beaker initially containing 2 ml of 10 wt.% sodium hydroxide solution and 5 ml of methanol, which is sufficient to cover the end of the condenser. When the first 35 ml of distillate is collected, the beaker is transferred to a water bath at 85 to 95°C, and the solution is evaporated to dryness.

To the residue is added 3 ml of curcumin solution (0.625 g of curcumin in 500 ml of glacial acetic acid), and the mixture is warmed to dissolve most of the salts. To the cooled beaker is now added 3.0 ml of acetic acid–sulfuric acid reagent (equal volumes of glacial acetic acid and concentrated sulfuric acid), and the mixture is mixed and allowed to stand for 15 min at room temperature. Then 30 ml of methanol is added, and solution is mixed well and diluted to 100 ml with methanol. A portion is filtered through Whatman No. 41 filter paper, and the absorbance is measured at 552 mμ against a reagent blank.

The standard curve is prepared by carrying 0 to 1.5 ml of standard boron solution containing 1 μg/ml added to 2 ml of 10 wt.% sodium hydroxide solution through the procedure.

(2) *Chromotropic Acid and Victoria Violet.* In aqueous solution at pH 7, boric acid reacts with chromotropic acid to form a colorless complex with a resulting decrease in absorbance at 361.5 mμ.[169, 170] In the optimum range of 5 to 120 μg, Beer's law is not followed. The procedure is of limited importance because of the relative insensitivity, the need for accurate wave-length setting, the requirement of photomultiplier detection in measuring the difference in absorbance

of the sample solution and the strongly absorbing reagent reference solution, and the tendency of the solutions to develop colors when exposed to light. Potential interferences include titanium, magnesium, aluminum, chromium, zirconium, uranium, vanadium, iron, silicon, and oxidizing agents.

The closely related Victoria Violet is used in the same way,[171] but the decrease in absorbance is measured in the visible range at 540 mμ with the solution adjusted to pH 8.75. Beer's law is followed from 25 to 500 μg per 25 ml of solution. In contrast to chromotropic acid, the solution is not affected by light. Essentially the same elements interfere. A sodium hydroxide precipitation at pH 8.5 has been found convenient to remove interferences such as iron, aluminum, chromium, and rare earths.

A significant advantage in the use of a reagent such as Victoria Violet is the freedom of interferences from fluoride, nitrate, nitrite, iodide, perchlorate, phosphate, oxalate, and chloride, many of which interfere with the conventional reagents.

(3) *Methylene Blue and Related Compounds, Methyl Violet, and Brilliant Green.* In the methylene blue procedure, boric acid is converted to BF_4^- by hydrofluoric acid and is extracted as the colored complex with methylene blue by 1,2-dichloroethane or 1,2-dichloropropane.[70,71] The color, measured at 660 mμ, is stable. From 0.1 to 6 μg, Beer's law is followed; the useful range is 0.2 to 25 μg. Nitric, hydrochloric, and perchloric acids and high concentrations of hydrofluoric acid interfere. The elements commonly found in iron- and steel-alloy samples do not interfere. One disadvantage is the high blanks obtained.

Other thionine derivatives have been studied by Pasztor and Bode,[72] who found monomethylthionine, Azure C, to be superior to methylene blue in regard to sensitivity and blanks. The effective range is greater, 0.1 to 200 μg, at 658 mμ. These authors have also studied the use of still other thionine derivatives commerically obtainable and other solvents.[73]

At pH 3.4 methyl violet forms a complex with fluoborate extractable with benzene.[74, 75] Crystal violet is apparently a better reagent for this reaction.[172] A colored product with methyl violet and salicylate at pH 2.0 is also produced with borate. The complex is extracted with 25 vol.% tributyl phosphate in carbon tetrachloride for the spectrophotometric determination.[76] The closely related dye Brilliant Green [173] also forms a complex with BF_4^-. The complex is extracted into benzene. In the analysis of titanium or zirconium for boron, the interference of these metals is prevented by the ammonium fluoride added to form the fluoborate ion.

Spectrophotometric Determination of Boron in Steel: Azure C.

Procedure.[72] A 0.1-g sample is dissolved in 10.0 ml of 2.5*N* sulfuric acid in boron-free glass under reflux. Any residue is filtered off, ignited, and fused with 1 g of sodium carbonate, and the melt is dissolved in the filtrate plus 4.0 ml of 2.5*N* sulfuric acid. The solution is transferred to polyethylene, and 5.0 ml of 5 wt.% hydrofluoric acid is added. After 2 hr, 0.1*M* potassium permanganate is added dropwise until the solution is pink; then 2 to 3 ml of 4 wt.% ferrous ammonium sulfate solution is added. The volume is brought to 50.0 ml; 10.0 ml of 0.002*M* or 0.005*M* Azure C (National Aniline) is added, and the complex is extracted with 25.0 ml of 1,2-dichloroethane. The absorbance is measured at 658 mμ against the solvent. Correction for a reagent blank must be made. The calibration curves are obtained similarly with standard boron solutions.

(4) *Other Reagents Not Requiring Concentrated Acid.* Rutin has been used in a procedure similar to that with curcumin.[174] The acetone extract of the residue obtained by evaporating the sample solution with hydrochloric acid, oxalic acid, and rutin solution is measured at 440 mμ. Beer's law is obeyed from 0 to 0.30 ppm of boron in the final solution. The procedure has been applied to the analysis of graphite.

The precipitation of boric acid with tartrate ions (sec. 8–3.5) and barium chloranilate at pH 8 liberates the highly colored chloranilate ion, which is measured spectrophotometrically[175] at 530 mμ. The useful range is 0.3 to 10 μg in an aliquot of 4 ml or less. Sulfate interferes. The method appears to be simple and rather sensitive.

The interference of fluoride in the reduction by chlorostannous acid of molybdate to molybdenum blue can be prevented by boric acid.[176] An indirect method based on this reaction can determine 0.1 to 2.5 mg of boron. The blue color is measured at 750 mμ. Elements forming strong fluoride complexes and heteropoly acids interfere.

In another molybdenum blue procedure, boron hydrides reduce the heteropoly phosphomolybdic acid to a blue color measured[177] at 660 to 670 mμ. Color development must be timed; insoluble hydrides must be solubilized by acetic acid, ethyl alcohol, glycols, sodium hydroxide, pyridine, or similar agents.

Morin gives a colored complex with boric acid in acetone containing citric,[178] tartaric,[179] or oxalic acid.[180] A distillation separation is necessary because of the insolubility of most inorganic salts in acetone. The residue obtained by evaporating a mixture of the neutral borate solution, hydrochloric acid, oxalic acid, and ethanolic morin solution is extracted with acetone. The color (452 mμ), developed by heating the acetone extract for 1 hr at 55°C and again extracting the residue

with acetone,[180] is unstable. The procedure is useful for 0.5 to 10 μg. A similar procedure has been reported for pentamethylquercitin–acetone–citric acid.[178, 181] Quercitin has also been used;[182] a distillation separation is recommended before color development.

The formation of the yellow pertitanic acid color by the addition of boric acid to a solution containing fluotitanate and hydrogen peroxide is useful for the determination of 2 to 18 mg of boron per 25 ml.[183]

Catechol Violet gives a colored complex[184] with boron at pH 6 to 7. Germanium, niobium, and tantalum also give colored products. The interference of other ions can be prevented by the use of oxalate and ethylenediaminetetraacetate. Hiiro[185] recommends a pH of 8.3 to 8.6.

The reaction of salicylaldehyde with H-acid to form an azomethine compound with an absorption maximum at 420 mμ is accelerated by boric acid and can be used for its determination.[186] Fluoride does not interfere. Similar reactions are used by Capelle.[187] K-acid can replace H-acid.

The blue color given by borate, iodine, and ferric sulfate in the presence of polyvinyl alcohol has been used to determine 0.75 to 2.0 mg of boron.[188] A prior separation by distillation or ion exchange is recommended although oxidation or sulfide precipitation is sometimes applicable for preventing interferences.

The reaction of potassium iodide with potassium iodate in the presence of hydrogen ions to give free iodine can be utilized to determine boron.[115, 189] Because of the weak ionization of boric acid, iodine liberation with boric acid as the source of hydrogen ions is only slight. The addition of a polyalcohol such as mannitol or sorbitol allows the reaction to proceed to a greater extent. Up to 100 μg of boron per milliliter can be determined. For 1 to 5 μg per milliliter, starch is added to obtain the sensitive blue starch–iodine color. A sodium hydroxide precipitation prior to color production is recommended.[189]

An indirect colorimetric procedure that may prove useful is based upon the precipitation of barium borotartrate,[51] Sec. 8–3.5, and the determination of the tartaric acid liberated on dissolving the precipitate in concentrated sulfuric acid by means of resorcinol–potassium bromide–sulfuric acid reagent.[53] This reagent gives a characteristic blue color (630 mμ) which can be used to determine down to 10 μg of boron.

Several rapid procedures have been described that utilize the reaction of boric acid with either fluoride or polyhydroxyl alcohols to give pH changes. Sawaya and Onuma[190] measure the color change of bromcresol purple occurring when the reaction with fluoride releases hydroxyl ions. Fizzotti and Selmi[191] measure the color change

of bromthymol blue upon the addition of mannitol. This procedure is reportedly useful in the range of 0.1 to 0.6 μg of boron per milliliter when spectrophotometric measurement of the color is made. Boron in heavy water is determined after a prior distillation of the water made alkaline with sodium hydroxide. Csapo and coworkers [192] report a similar pH method.

Spot tests often are useful for both qualitative and quantitative estimation. Burkhalter and Peacock [193] have studied the application of various polyhydric compounds to spot tests based on pH changes; sorbital gave the most sensitive response: 0.003 μg in 1 ml of solution can be detected. Other spot tests developed involve reaction of boric acid with hematoxylin and pyrocatechol derivatives.[194]

8–5.3 Fluorometry

The early work on the fluorometric determination of boron is summarized by Russell [10] and White and coworkers.[195] These procedures, involving the use of certain flavanols, *o*-hydroxycarbonyl compounds such as resacetophenone, and 1-amino-4-hyroxyanthraquinone, have had little acceptance. However, the latter reagent has been recommended by Ellis and coworkers [141] in their study of the fluorescence of various boron complexes. The use of benzoin is advocated by White and coworkers [195, 196] and Sommer.[197] Morin has also been recommended.[198] Chrysazin has been shown [154] to give a fluorescent product with boric acid.

The 1:1 benzoin–boron complex is excited with radiation of wave length 310 to 400 mμ; it fluoresces at 450 to 520 mμ.[196] Over the range 0.5 to 10 μg of boron in 50 ml, the response is proportional to concentration. The fluorescence is sensitive to molecular oxygen and ultraviolet light, but it is somewhat stabilized by the use of a glycine or isopropylamine buffer. Elliott and Radley [199] recommend formamide as a solvent and isopropyl- or isobutylamine as a buffer for 0.05 to 0.5 μg of boron. Instrumental factors and stability of the fluorescence have been studied by Parker and Barnes.[200] Few anions interfere.[197] Fluoride may increase or decrease the fluorescence and should be added to the reference solution.[201] The interference of chromate, periodate, persulfate, and ferricyanide can be eliminated by reduction with sulfite. Beryllium, germanium, and antimony give fluorescent products. In the presence of magnesium and silicon, zinc increases the fluorescence.[201] Those cations which precipitate in alkaline solution or form salts insoluble in the alcohol (or formamide) medium must also be removed.[195] The mercury-cathode separation is not recommended because of the large salt content obtained when the acid electrolyte is neutralized. Distillation of the ester is a satisfactory separation.[195] Other separations suggested involve ion exchange and

precipitation with zinc oxide.[197] Masking of some cations by cyanide is effective; carbonate prevents the interference of uranium and beryllium.[197]

8–5.4 Gravimetry

The early work on the gravimetric determination of boron is summarized by Russell.[10] Methods based upon the relative insolubility of calcium borate and potassium fluoborate and the absorption of methyl borate by lime or sodium tungstate solutions[34] are among the procedures that have little application at the present time.

In the search for a procedure in which fluoride would not interfere, Lucchesi and DeFord[58] investigated the precipitation of fluoboric acid with 1,4-diphenyl-3,5-endanilohydrotriazol (nitron).[59-61] In the analysis of samples containing 125 to 250 mg of boron in the absence of nitrate, nitrite, perchlorate, iodide, bromide, thiocyanate, chlorate, and chromate, satisfactory results were obtained. Various oxidation or reduction steps can eliminate many of the interferences listed above.[58]

The nitron procedure is applicable to hydrofluoric acid solutions of zirconium and uranium alloys.

Other possible gravimetric techniques are mentioned in Sec. 8–3.5, e.g., precipitation in alkaline solution by barium and tartrate, arabotrihydroxyglutarate, or mannosaccharate ions and by cetyltrimethylammonium chloride. Further work is required to make these techniques satisfactory. The latter reagent is promising because it gives a precipitate that is one-tenth as soluble as the nitron salt. However, it does not dry to a definite composition. Wakamatsu[202] ignites the barium borotartrate precipitate at 700 to 800°C and weighs the residue as Ba_2BO_6.

Gravimetric Determination of Boric Acid.

Procedure.[58] A solution of less than 60 ml containing 125 to 250 mg of boric acid is placed in a polyethylene beaker. The solution is diluted to about 60 ml, and 15.0 ml of nitron solution (37.50 g dissolved in 250 ml of 5 vol.% acetic acid, solution stored in dark bottle) and 1.0 to 1.3 g of 48 wt.% hydrofluoric acid are added. After 10 to 20 hr at room temperature and 2 hr in a ice bath, the solution is filtered through a Selas or Coors porous porcelain crucible. The crucible and precipitate are washed with five 10-ml portions of saturated nitron fluoborate solution (excess reagent added to water; mixture agitated at least 2 hr); the precipitate is drained dry after each washing. The crucible is dried at 105 to 110°C for 2 hr; the precipitate is weighed as $C_{20}H_{16}N_4 \cdot HBF_4$.

8–5.5 Flame Photometry

When boric acid is aspirated into a flame possessing the necessary excitation potential, band (molecular) spectra of B_xO_y molecules

rather than lines are emitted.[203] These bands overlap each other; the most intense emissions occur at the band heads at 492, 518, and 546 mμ. The development of the photomultiplier tube has provided a rapid, sensitive method of determining boron with the flame photometer. The increased amplification of the photomultiplier tube over the conventional phototube permits the use of very narrow slit widths. The increased resolution thus available is particularly useful for the examination of oxide band spectra such as is given by boric acid.

Dean and Thompson [203] have made a study of the flame-photometric determination of boron and have described the method as being more rapid than chemical methods and comparable in accuracy and precision in the range of 50 to 200 ppm of boron. The oxyacetylene flame is recommended. The intensity of emission is influenced strongly by the nature of the solvent. A 50 vol.% methanol medium gives a marked increase in sensitivity and is recommended. Ethanol and 2-propanol are less effective. Correction for background is made by measuring the minimum intensity of the trough between the band heads. Ammonium, cadmium, copper, lead, silver, and zinc ions ordinarily offer no interference. Most cations present in high concentration exhibit general background radiation. Chromium, manganese, iron, cobalt, and nickel interfere at all the band heads and their troughs. Magnesium and calcium enhance the 518-mμ band; potassium, the 505-mμ reference trough. These latter interferences can be mitigated by the use of narrow slits. Acid concentrations greater than 0.5*M* suppress the emission. Serious interference can often be eliminated by working at sufficiently high dilution or by adding the sample constituents to the standards. Frequently the concentration of an interfering element can be determined by another method, and its luminosity then can be measured at the boron wave length. Another procedure that may be useful is that of Gilbert and coworkers [204] in which twice the reading obtained with a sample solution diluted 1+1 minus one-half the reading on the undiluted sample solution is a first approximation of the correct reading of the diluted sample.

Bricker, Dippel, and Furman [205] have shown that 50 vol.% acetone or dioxane gives a greater luminosity to the emission than 50 vol.% methanol. Acetic acid and sulfuric acid also enhance the flame sensitivity.

Colichman [206] recommends the oxyhydrogen flame. Of particular interest in his report is the pronounced difference in the spectra of B^{10} and normal boron. Band peaks in the B^{10} spectrum are shifted 10 to 15A to shorter wave lengths, and the bands are broader with a different contour.

The oxyhydrogen flame and a 50 vol.% methanol medium are used by Fornwalt [207] to determine boron in the presence of large amounts of nickel.

Two indirect flame photometric procedures are of interest. Bovalini and coworkers [54, 55] precipitate barium borotartrate and determine the boron by dissolving the precipitate in hydrochloric acid and measuring the barium flame photometrically at 873 mμ. From 4 to 20 μg of boron can be determined. Dutina [208] measures the B^{10} burn-up by determining flame photometrically the lithium produced in the B^{10} (n,α) Li^7 reaction.

8–5.6 Thermal-neutron Absorptiometry

Boron-10 has a relatively high cross section for thermal-neutron capture and a rather high normal abundance (Sec. 8–1). The reaction occurring when a neutron is captured is $B^{10}(n,\alpha)Li^7$. The definite fraction of Li^7 that is produced in an excited state decays with the emission of a 480-kev gamma ray. These facts suggest that at least three methods can be used to determine boron irradiated with thermal neutrons: detection of either the alpha or the gamma particles or measurement of the neutron-flux attenuation.[209] Other methods based on the use of neutrons are possible.[210] An indirect neutron-absorption method involves the decrease in activation of an element such as indium due to the reduction of neutron flux by the boron in the sample.[211]

In general, these methods are simple, rapid, and nondestructive and are not dependent upon the state of chemical combination of the boron. They are also relatively free of interferences since few elements possess cross sections comparable to B^{10}. The most serious disadvantage is the low sensitivity and the corresponding need for large samples.

Most procedures currently in use are based upon attenuation of the neutron flux.[209, 212-215] The procedure of DeFord and Braman,[212] who have made a thorough study of the factors affecting the sensitivity and precision, is typical. In brief, the method consists simply of placing a boron-containing sample between a neutron source and a neutron counter. The source is a 10-mc radium–beryllium fast-neutron source. The neutrons are moderated to thermal energies by paraffin wax. Annular cells constructed of either aluminum or polyethylene hold a solution of the boron material in the annular space. The sample cell surrounds a boron trifluoride counting tube. Because of the limited solubility of boric acid and borates, solutions of triethanolamine borate, which is very soluble in water, are used. For the optimum arrangement and dimensions, the original paper should be consulted. With solutions containing about 1 g of boron, the precision is near 0.5 per cent. Smaller quantities of boron can be determined with an error of about 1 mg.

A similar technique is the measurement of the change in reactivity of a reactor following the introduction of a boron-containing material. An example of this type measurement can be found in the report of Branson and coworkers [216] on the determination of boron in graphite.

8–5.7 Polarography

Boric acid, mannitoboric acid, peroxyborate, and various amine–boron trifluoride complexes have been shown to give no polarographic reduction wave due to boron.[115]

Indirect procedures have been useful. The decrease due to borate in the reduction wave of fructose in 0.1*M* lithium hydroxide at pH 12 has been used [217] to determine down to 50 μg of boron per 25 ml. An amperometric technique is used because the decrease in wave height is not strictly proportional to boron concentration. The diffusion current is measured at −2.05 volts vs. the silver–silver chloride electrode. Reducible cations that yield large diffusion currents must be removed on a cation-resin column. Bromate and iodate, which are reduced at more positive potentials, must be reduced with sulfur dioxide. A similar polarographic procedure with sorbose in the same medium is reported.[218]

The decrease due to borate in the reduction wave of 2,2′-dihydroxybenzoin at −0.80 volt vs. S.C.E. in ammonia buffer solutions at pH 9 has been used to determine down to about 10 ppm boron.[219]

Lewis [220] has shown that the double wave at −0.50 and −1.0 volt vs. the mercury-pool electrode observed when sodium sulfite is added to a solution of mannitoboric acid is due to the reduction of bisulfite. The height of the first wave can be used to determine boron. The height of the wave is dependent both upon the boron concentrate and the pH. The base solution is a 0.2*M* sodium sulfite, 0.3*M* mannitol mixture. Prior removal of interferences by ester distillation is recommended. Reynolds and Terry [221, 222] have used this technique in determining down to 0.2 μg of boron per milliliter. Shalgosky [223] reports that a more sensitive procedure results if nitrite is substituted for sulfite. A 0.48*M* mannitol, 0.2*M* sodium nitrite supporting electrolyte is used; the height of the first of two waves occurring at −0.64 and −1.21 volt vs. S.C.E. is measured. The relation between diffusion current and boron concentration is linear. One disadvantage is that the sample solution and the base electrolyte must be deoxygenated before they are mixed.

8–5.8 Coulometry

Coulometric techniques can be applied to the determination of boron. The classic mannitol titration has been performed by constant-current electrolysis in a 0.2*M* sodium bromide electrolyte

solution containing greater than 3.5 g of mannitol.[224] A fixed pH between 6.3 to 6.8 was used, and down to 10 μg of boron was determined. The prior distillation of boron and the use of methyl red as the indicator in the electrolysis are recommended in a similar procedure.[225] Another procedure with a fixed pH between 8.5 to 9.0 for the titration is described for the determination of boric acid in heavy water.[226]

To dissolve microgram amounts of boron deposited on platinum targets, constant-current oxidation at +0.30 volt vs. S.C.E. in 0.1*N* sodium hydroxide is reported.[227] The end point is the inflection point in the anodic potential–time curve. (Platinum is oxidized at about +0.6 volt.) Good correlation was found between the quantity of boron dissolved, if a 3-electron oxidation process is assumed, and the amount of boron in solution as determined by a coulometric mannitol titration.[228]

8–5.9 Other Methods

When borate ions form complexes with certain optically active polyhydroxy compounds, changes in specific rotation occur. Various workers [115, 229–231] have thus determined borate polarimetrically with tartaric acid. Pickard, Kenton, and Naptune [115] and Isbell and coworkers [232] have studied other reagents. DeFord, Blonder, and Braman [233] and Kodama and Shiio [234] prefer mannitol, which forms complexes with fewer ions than tartaric acid and has little effect on the optical rotation since it is uncharged, for the determination of borate in the presence of fluoride or phosphate. These polarimetric procedures are hardly satisfactory, but they may be useful when the use of the mannitol titration is precluded.

An X-ray diffraction procedure has been reported for the analysis of boron carbide.[235]

8–6 LIST OF PROCEDURES FOR DETERMINATION OF BORON

Procedures for the determination of boron in the various materials of interest are listed in Tables 8.5, 8.6, and 8.7. The general type of separation required and the method of determination are indicated for each procedure.

8–7 CHEMICAL PROCESSING PRIOR TO MASS SPECTROMETRIC ISOTOPIC ANALYSIS

The charge material for the mass spectrometric isotopic analysis by thermal ionization is sodium tetraborate, which supplies $Na_2BO_2^+$ ions as the most abundant ionic species. Several procedures are available to separate the boron completely from various materials and convert it to the appropriate form.

690–457 O—64——40

Table 8.5—PROCEDURES FOR ANALYSIS OF ELEMENTAL BORON AND BORON COMPOUNDS

Sample	General method	Reference
Elemental boron	Oxalate complexation, mannitol titration	248
	Barium carbonate precipitation, mannitol titration.	37
	Iodate oxidation, mannitol titration	249
	Ceric oxidation, ferrous titration	250
Boron carbide	Sodium hydroxide precipitation, mannitol titration.	117
	(Free B_2O_3 in) 0.1N hydrochloric acid solubles, sodium hydroxide precipitation, mannitol titration.	251
	(Free B in) 0.1N nitric acid solubles, sodium hydroxide precipitation, mannitol titration.	251a
	Barium carbonate precipitation, mannitol titration.	37, 252
	Combustion, mannitol titration	253
	Pyrohydrolysis, mannitol titration	21
	Oxalate complexation, mannitol titration	248
	(Free B in) nitric acid and peroxide oxidation, invert sugar titration.	254
	Neutron absorption	255
	X-ray diffraction	235
Borides:		
Fe, Cr, W, Ti, Zr, Th, V, Nb, Ta, Ce, Al.	Barium carbonate precipitation, mannitol titration.	37
Ti, Zr, Nb, Ta, Cr, W.	Barium carbonate precipitation, mannitol titration.	256
Ni	Sodium hydroxide precipitation, mannitol titration.	108
Mo, V, Ni	Diethyldithiocarbamate extraction, mannitol titration.	256
Fe, Ni, Cu, Co	Mercury cathode, mannitol titration	43
Mo	Sulfide precipitation, mannitol titration	43
Rare earths	Ethylenediaminetetraacetate complexation, mannitol titration.	257
Zr	(Free B in) nitric acid and peroxide oxidation, mannitol titration.	257
V	Precipitation of barium pyrovanadate, mannitol titration.	258
General	Iodate oxidation, mannitol titration	249
Boron nitride	Barium carbonate precipitation, mannitol titration.	37
	(Free B in) nitric acid and peroxide oxidation, invert sugar titration.	254
Organoboron	Combustion, mannitol titration	259–262
	Trifluoroperoxyacetic acid oxidation, mannitol titration.	99

Table 8.6—PROCEDURES FOR DETERMINATION OF BORON IN APPROXIMATE RANGE 0.01 TO 5 PER CENT

Sample	General method	Reference
B–U	Cation exchange, mannitol titration	47
B(B_4C, B_2O_3, BN)–UO_2.	Direct quinalizarin	118
B(B_4C)–UO_2	Pyrohydrolysis, quinalizarin	21
B–U–Zr	Direct quinalizarin	118, 263
	Ethyl alcohol extraction, curcumin	264
B–U–Zircaloy	Pyrohydrolysis, quinalizarin	21
	Direct quinalizarin	118
	Ethyl alcohol extraction, curcumin	264
B–U–Al	Direct carminic acid	132
	(Cation exchange), oxalate complexation, mannitol titration.	248
	Neutron absorption	265–267
B_4C–U–Al	Direct carminic acid	132
B(B_4C–B_2O_3–BN)–UO_2–Al_2O_3.	Direct quinalizarin	118
B–UO_2–stainless steel	Direct carminic acid	268
B_4C–UO_2–stainless steel.	Cation exchange, mannitol titration	269, 270
B–Al	(Cation exchange), oxalate complexation, mannitol titration.	248
	Direct 1,1′-dianthrimide	271
	Direct quinalizarin	118
B_4C–Al	Direct quinalizarin	118
B–Zr	Direct quinalizarin	118
	Direct tetraacetylquinalizarin	125
	Barium carbonate precipitation, mannitol titration.	272
	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
B–Zircaloy	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
B_4C–Zr–Zircaloy	(Acid soluble) barium carbonate precipitation, mannitol titration.	273, 274
	(Acid insoluble) mannitol titration	273, 274
B–Th	Cation exchange, mannitol titration	47
B–Pu	Anion exchange, flame photometer	275
B–Nb	Direct tetraacetylquinalizarin	125
B–stainless steel	Cation exchange, mannitol titration	269, 270
	(Cation exchange), oxalate complexation, mannitol titration.	248
	Pyrohydrolysis, mannitol titration	21
	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
B–steel	Cation exchange, mannitol titration	110

Table 8.6—PROCEDURES FOR DETERMINATION OF BORON IN APPROXIMATE RANGE 0.01 TO 5 PER CENT—Continued

Sample	General method	Reference
B–Cu	Cation exchange, oxalate complexation, mannitol titration.	248
B–Ni, Fe, Si	Cation exchange, oxalate complexation, mannitol titration.	248
B–Co, Cr, Ni, Mo	Direct quinalizarin	120
B–Ni, Co, or Fe	Mercury cathode, sodium hydroxide precipitation, carmine (chromotrope 2B, arsenazo II).	95
B–Mo	Sulfide precipitation, mannitol titration	276
B–Pb	Distillation, mannitol titration	277
B–Ti (alloys)	Cation exchange, carminic acid	92
	Cation exchange, barium carbonate precipitation, mannitol titration.	40
	Cation exchange, quinalizarin–water titration.	128
	Distillation, 1,1′-dianthrimide	88
	Barium carbonate precipitation, mannitol titration.	278
	Mercury cathode, sodium hydroxide precipitation, carmine (chromotrope 2B, arsenazo II).	95
B–polyethylene tape	Direct carminic acid	132
B_4C–Pb–polyethylene tape.	Barium carbonate precipitation, mannitol titration.	279
H_3BO_3–H_2O	Neutron absorption	280

Samples of boron carbide, boron carbide–Zircaloy, and boron carbide–aluminum oxide [236] are simply fused with sodium carbonate, the melt is dissolved, and the solution is neutralized with hydrochloric acid. The solution is filtered and diluted to volume, and an aliquot is evaporated to dryness after the addition of sufficient base to convert the boron to tetraborate.

Boron-stainless-steel samples [236, 237] are dissolved in 10 vol.% hydrochloric acid under reflux. The solution is filtered and diluted to volume. An aliquot is passed through a cation-exchange resin column as in the Martin and Hayes [27] procedure to remove the steel cations. Boric acid in the effluent is treated with sodium hydroxide.

A pyrohydrolysis technique (Sec. 8–3.2) is convenient and rapid. Wiederkehr and Goward [21] pyrohydrolyze the sample in a nickel or platinum boat held in a nickel tube. With a steam flow of 1 to 3 ml per minute at 1100°C, the boron is completely removed in 90 min. The distillate is collected in a Teflon beaker containing 20 ml of water and

Table 8.7—PROCEDURES FOR DETERMINATION OF BORON IN APPROXIMATE RANGE 0.1 TO 100 PPM

Sample	General method	Reference
U (compounds)	(Bromine-methanol), distillation, diamino-chrysazin.	15
	Direct carminic acid	118, 134, 135
	Distillation, curcumin	11, 159, 281, 282, 283, 287
	Cation exchange, curcumin	288
	Cation exchange, 1,1′-dianthrimide	93
	Direct curcumin	284, 285
	Precipitation of barium borotartrate, flame photometer (Ba).	54, 55
	Tetraphenylarsonium chloride extraction, curcumin.	68
	Distillation, carmine	286
	Tri-*n*-octylphosphine oxide extraction, carminic acid.	289
U–Zr	Direct carminic acid	290
U–Zr–Zircaloy 2	Direct carminic acid	290
U–Al	Distillation, curcumin	291
Th	(Bromine–methanol), distillation, diamino-chrysazin.	15
	Distillation, curcumin	293–295
Pu	Anion exchange, flame photometer	275
Zr (ZrO_2, ZrH_2)	Distillation, curcumin	296–298
	(Bromine–methanol), distillation, diamino-chrysazin.	15
	Brilliant green–BF_4^- extraction	173
	Direct quinalizarin	125, 263
	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
Zircaloy	Distillation, curcumin	299
	(Bromine–methanol), distillation, curcumin.	300
	(Bromine-methanol), distillation, diamino-chrysazin.	15
	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
Zr–Nb	Direct quinalizarin	125
Ti (alloys)	Cation exchange, carminic acid	92
	Distillation, 1,1′-dianthrimide	88
	Mercury cathode, sodium hydroxide precipitation, carmine (chromotrope 2B, arsenazo II).	95
	Brilliant green—BF_4^- extraction	173

Table 8.7—PROCEDURES FOR DETERMINATION OF BORON IN APPROXIMATE RANGE 0.1 TO 100 PPM—Continued

Sample	General method	Reference
Ca (CaO)	Distillation, curcumin	11, 283
	Direct carminic acid	135
Mg (compounds)	Distillation, curcumin	283
	Sodium carbonate and hydroxide precipitation, mannitol titration.	38
Al	Distillation, curcumin	291
	Cation exchange, 1,1′-dianthrimide	292
	Direct quinalizarin	118
Al–Si	Direct 1,1′-dianthrimide	301
Steel	Distillation, mannitol (coulometric) titration.	225
	Distillation, mannitol titration	302–304
	Distillation, curcumin	13, 305
	Distillation, tetrabromochrysazin	306
	Distillation, carminic acid	307, 308
	Mercury cathode, carminic acid	308, 309
	Mercury cathode, 1,1′-dianthrimide	144
	Mercury cathode, quinalizarin	310
	Cation exchange, mannitol titration	26
	Cation exchange, 1,1′-dianthrimide	311
	Lead-ion precipitation, sorbitol titration	312
	Sodium hydroxide precipitation, invert sugar titration.	313
	Sodium hydroxide precipitation, quinalizarin.	314
	Direct quinalizarin	315, 316
	Direct carmine	317
	Direct 1,1′-dianthrimide	144
	Methylene blue—BF_4^- extraction	71, 318
	(B^{10} burn-up) ammonium hydroxide precipitation, flame photometer (Li).	208
Na	Ethyl alcohol extraction, curcumin	64
C (graphite)	Distillation, curcumin	11, 14, 159, 319
	Cation exchange, curcumin	320, 321
	Direct curcumin	285
	Direct carminic acid	135
	Neutron absorption	216
CO_2	Absorption in sodium hydroxide, distillation, curcumin.	322
D_2O	Mannitol titration	226, 323
	Direct curcumin	324
	pH change with mannitol	191
F^- salts	Distillation, curcumin	20
	Distillation, cation exchange, carmine	325
	Ethyl ether extraction, carminic acid	66
	Azomethine formation	186

Table 8.7—PROCEDURES FOR DETERMINATION OF BORON IN APPROXIMATE RANGE 0.1 TO 100 PPM—Continued

Sample	General method	Reference
NO_3^- salts	Formic acid reduction, carminic acid	289
Reagents:		
Oxalic acid	Distillation, curcumin	326
Aluminum nitrate nonahydrate.	Distillation, curcumin	327
Ammonium hydroxide.	Distillation, curcumin	328
Bis-$\beta\beta'$-butoxyethyl ether.	Distillation, curcumin	329
Hydrazine nitrate	Distillation, curcumin	330
Iron powder	Distillation, curcumin	331
Potassium bromate	Distillation, curcumin	332
Nitric acid	Distillation, curcumin	333
Potassium bromide	Distillation, curcumin	334
Sodium dichromate	Distillation, curcumin	335
Sodium hydroxide	Distillation, curcumin	336, 337
Hydrazine dihydrochloride.	Distillation, curcumin	338
Hydrochloric acid	Distillation, curcumin	339
Sodium carbonate	Distillation, curcumin	337
Aluminum sulfate	Distillation, carmine	340
Ammonium fluoride	Distillation, carmine	340
Hydrogen peroxide	Direct carmine	286

sufficient sodium hydroxide to convert the boron to tetraborate upon evaporation. Samples of boron–stainless steel, boron carbide, boron carbide–uranium dioxide, boron–uranium dioxide, boron carbide–zirconium, boron–zirconium, and boron–Zircaloy–uranium have been treated in this manner.

In the technique of Williams, Campbell, and Magliocca,[23] developed for the separation of boron from glasses, a mixed catalyst of U_3O_8 and sodium metasilicate nonahydrate is added to the sample before pyrohydrolysis. This procedure has been adopted by Eberle [24] to isolate the boron from a wide variety of minerals, elemental boron, and boron carbide; undoubtedly it is satisfactory for a wide variety of boron-containing materials. An ion-exchange separation was incorporated into the procedure, described below, to ensure the absence of rubidium and strontium, which hinder the mass spectrometric analysis.

Pyrohydrolytic Separation of Boron From Minerals and Other Materials for Mass Spectrometric Isotopic Analysis.

Procedure.[24] A mixture of 0.5 g of pulverized mineral, 0.1 g of sodium metasilicate nonahydrate and 3.0 g of powdered U_3O_8, is ground in an

agate mortar to less than 300 mesh. The mixture is transferred to a platinum boat, and the boat is placed in a platinum reaction tube at room temperature. The reaction tube is connected to a steam generator, and the exit end of the condenser on the other end of the reaction tube is dipped into 100 ml of water held in a 1-liter platinum dish cooled in an ice bath. The reaction tube, held in a Burrell high-temperature furnace, and the steam generator are heated simultaneously. The reactor tube is maintained at 400 to 500°C until steam begins to pass through; then the temperature is quickly raised to 1300°C. About 500 ml of distillate is collected over a period of 60 min.

The distillate is passed through a 2-in. bed of Dowex 50–X8 (50 to 100 mesh, H^+ form) held in a 1½-in. Teflon tube fitted with a porcelain filter crucible at the lower end to support the resin. The column is washed with four 25-ml portions of water. The pH of the effluent is adjusted to 9.3 to 9.4 with dilute sodium hydroxide solution.

The solution is evaporated to dryness on a steam bath. The residue is dissolved in 1 to 2 ml of water for the mass spectrometric analysis.

Samples of elemental boron and boron carbide weighing 50 mg are treated similarly except for the omission of the auxiliary catalyst sodium metasilicate. The ion-exchange step can also be omitted.

8–8 IMPURITIES IN ELEMENTAL BORON AND BORON CARBIDE

Little work has been carried out on the determination of impurities in elemental boron since the early days of the Manhattan Project. Judson [238] has outlined the procedures available at that time for the determination of several elements:

tantalum	gravimetric, tannin.
tungsten	gravimetric, anti-1,5-di-(*p*-methoxyphenyl)-1-hydroxylamino-3-oximino-4-pentane (Ref. 239).
	gravimetric, cinchonine.
molybdenum	gravimetric, α-benzoinoxime.
carbon	combustion.
water	loss in drying.
silica	dehydration.
iron	titrimetric, ceric.
	colorimetric, thiocyanate.
nitrogen	Kjeldahl.

Oxygen, hydrogen, and nitrogen have been determined by microvacuum fusion methods with an iron bath [240] or no metal bath.[241]

[Aluminum, calcium, chromium, copper, iron, magnesium, manganese, lead, silicon, tin, and titanium are determined spectrographically with an a-c arc.[242] The sample is converted first to oxide with hydrogen peroxide–nitric acid. Nickel (1 per cent) is used as an internal standard.]

Rare earths are separated by the method of Hettel and Fassel,[243] which employs a cation-exchange resin separation together with the usual fluoride and hydroxide precipitations. Yttrium oxide is added before the separations as a carrier and subsequent spectrographic internal standard.

Rynasiewicz and Consalvo[244] have reported the impurity analysis of boron carbide. These authors used the mass-balance method to validate the accuracy of their boron determination on standard boron carbide samples. The impurities determined and the methods used were as follows:

total carbon___ combustion, gravimetric.[345]
free carbon____ X-ray diffraction.[335]
silicon_____ colorimetric, molybdenum blue.[346]
iron_____ colorimetric, o-phenanthroline.[347]
nitrogen_____ Kjeldahl.
hydrogen_____ vacuum fusion and vacuum extraction.
oxygen_____ vacuum fusion and inert-gas fusion.

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CHAPTER 9

HEAVY WATER

By C. E. Anderson and D. G. Ebenhack*

Heavy water (D_2O) as a reactor moderator must be maintained in an extremely pure state to ensure efficient and successful reactor operation. Hence analytical control of heavy water requires accurate and precise determinations not only of deuterium oxide but also of specific impurities, some of which may be present in concentrations as low as a few parts per billion.

There are many excellent references dealing with the determination of deuterium oxide and its impurities which cover in detail the theoretical aspects of the particular analyses, the techniques, and the equipment required. Therefore this chapter will only review the analytical methods that are employed in the routine control of heavy-water moderator.

9–1 LABORATORY TECHNIQUES

Most equipment used in the analysis of heavy water is not unique; it is usually found in any well-equipped laboratory. However, because the exchange of deuterium with protium (H^1) is very serious when the D_2O concentration approaches 100 mole %, it is imperative that equipment and techniques be employed which will minimize, and, whenever practical, prevent the exposure of heavy water to sources of protium contamination. Many inaccuracies in analyses arise from improper treatment of the sample and equipment.

9–1.1 Equipment Conditioning

Laboratory equipment for transferring and containing heavy water must be scrupulously cleaned to eliminate any traces of grease or protium-containing compounds and then conditioned to eliminate any traces of light water. The conditioning can be accomplished by rinsing the equipment with $\geq$99 mole % D_2O, drying it in a 150°F oven, and then storing it in a dry box or desiccator until it is to be used. In some instances, drying under vacuum may be in order.

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9–1.2 Transferring and Storing Samples

Heavy water should be transferred in a dry box or by means of a semiclosed system whenever practical. One satisfactory method for transferring small samples is by means of a hypodermic syringe. A siphon arrangement is sometimes used for large quantities. Whenever a transfer that exposes the material to the atmosphere must be made, a blanket of a dry inert gas, usually helium, is maintained over the heavy water throughout the transfer.

Containers for storage of samples should be completely filled with the sample, or a dry inert gas should be introduced to replace the air above the sample. For storing small quantities of heavy water for an extended period of time, a pyrex glass ampoule is the preferred receptacle. The ampoule should be flame sealed after receiving the heavy water. Polyethylene, glass, or metal containers can be used for transporting heavy water from an operating facility to the laboratory and for short-term storage if the container has been properly conditioned. A comparison of the storage stability of 50 ml of heavy water in sealed pyrex ampoules, screw-cap glass bottles, and polyethylene bottles is shown in Fig. 9.1.

9–2 DETERMINATION OF ISOTOPIC CONCENTRATION

There are many methods for the isotopic analysis of heavy water. Most of these are applicable, with some modification, over the entire concentration range from normal abundance (0.0147 mole % D_2O) to 100 mole % D_2O. The selection of an analytical method for routine use is usually based on three factors: the availability of equipment, the frequency and urgency of analysis, and the precision required.

Heavy-water analysis methods can be divided into two main categories: analysis by determination of a physical property of D_2O (e.g., density methods) and analysis by instrumental means (e.g., mass spectrometer). Some methods have been well established and are used routinely; these include the pycnometer and the float temperature, among the density methods, and the mass spectrometer and infrared spectrometer, among the instrument methods. Other methods, although not so well known or so frequently used, are available; some of these (emission spectroscopy, nuclear magnetic resonance, cryoscopy, and refractometry) are described briefly in this chapter.

9–2.1 Density Methods

Three density methods are discussed: the gravimetric method (pycnometer), the float temperature method, and the displacement method (Westphal balance).

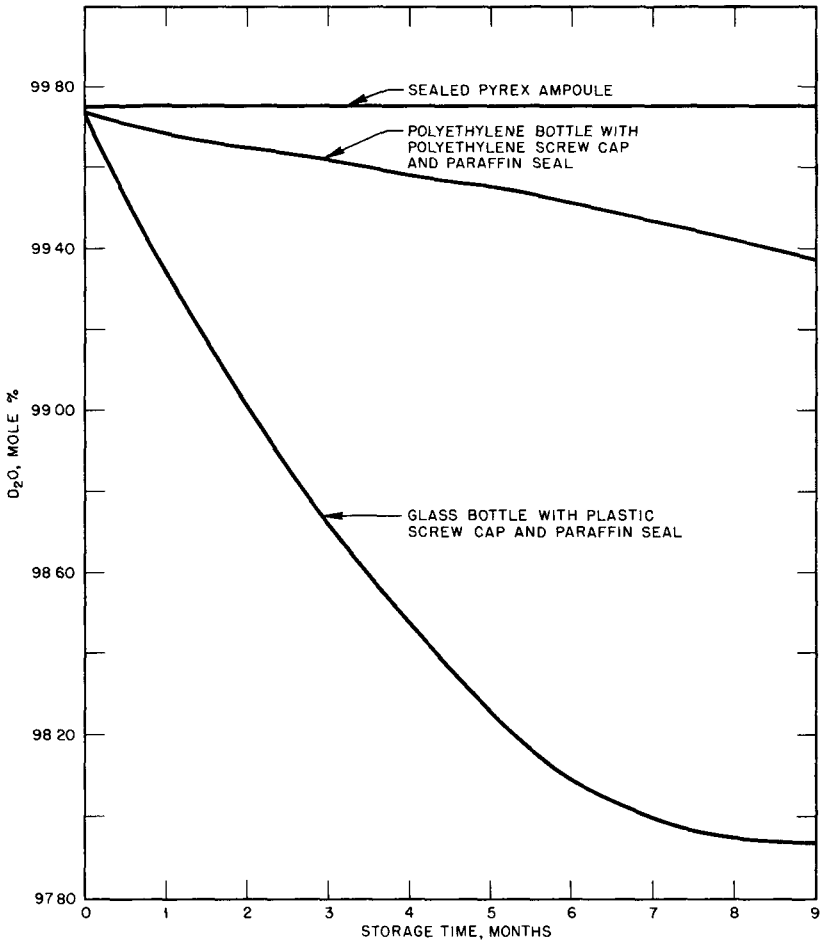


Fig. 9.1—Storage stability of heavy water in 50-ml containers. (Normalized curves, based on mass spectrometric data.)

(a) *Gravimetric Method (Pycnometer)*. This is one of the classical methods for determining D_2O content, and it is still useful for very precise work, such as establishing standard samples and confirming results obtained by other methods. The method is time consuming and requires a fair degree of skill for highest accuracy; but the equipment is relatively simple and inexpensive, and, if only a few analyses are required, the pycnometer method is ideal. Routinely, a precision of ± 0.02 mole % D_2O is obtainable at concentrations of ≥ 95 mole % D_2O, and, with care, a precision of ± 0.01 mole % can be attained.

One of the most important considerations in the pycnometer method, as in any density method, is the purity of the sample. The sample

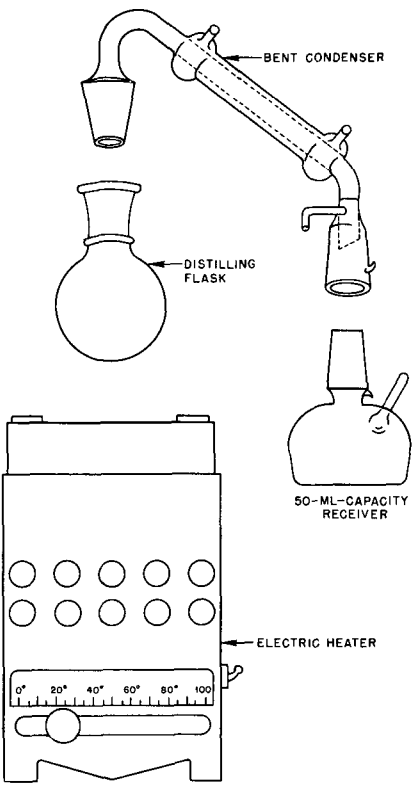


Fig. 9.2—Distillation assembly.

must be free of dissolved and particulate matter. An error of 0.0001 in specific gravity introduces an error of approximately 0.1 mole % in the analysis results. One of the more common ways of purifying the sample is by digestion with an oxidizing agent (such as a peroxide or alkaline permanganate), followed by distillation. Depending upon the condition of the sample, a more vigorous purification may be in order. Three important aspects of any cleanup procedure are: (1) particular care must be exercised to ensure complete distillation since light water–heavy water mixtures fractionate readily; (2) all vessels and chemicals used in purifying the samples must be free of any protium-containing compounds; and (3) contamination by exposure to atmospheric moisture must be avoided.

Procedure.[1] About 50 mg each of dry potassium permanganate and sodium peroxide are added to a 300-ml distilling flask (Fig. 9.2). A hypodermic syringe and needle are used to transfer approximately 35 ml of product from the sample container to the flask. A few chips of dry carborundum are added to the flask, and the sample is distilled to dry-

ness. (Flaming of the flask may be necessary to transfer the last portions of sample to the receiver.) The distillation equipment is vented through a silica gel drying tube to prevent dilution by atmospheric moisture. Contamination of the sample with grease from the ground-glass joints is to be avoided; serious contamination of samples has resulted from careless use of lubricants. A minimum amount of a good silicone grease is recommended.

After distillation the sample is transferred, by means of a hypodermic needle inserted in the side arm of the receiving flask, to a 25-ml Reischauer pycnometer (which has been calibrated and weighed, taking all standard weighing corrections). The pycnometer is stoppered and placed in a nominal 25.00°C±0.001°C constant-temperature bath, and the meniscus is adjusted to the calibration mark. The pycnometer is then removed from the bath, dried, allowed to reach room temperature, and weighed against a tare pycnometer (which has been filled with freshly boiled and cooled normal water, sealed, and weighed, taking all standard weighing corrections). The mole % D_2O, uncorrected for O^{18}, is calculated from the density of the sample, as follows:

$$A = B - C \tag{9.1}$$

$$d = A/E \tag{9.2}$$

$$\triangle d = d - d_1 \tag{9.3}$$

$$\text{Mole \% } D_2O = \frac{(927.35)(\triangle d)}{1-[(0.0329)(\triangle d)]} \tag{9.4}$$

where

A = true weight of sample in grams
B = total of tare and brass weights
C = true weight of sample pycnometer
d = density of sample at 25°C in grams per milliliter
E = true volume of sample pycnometer in milliliters
$\triangle d$ = difference between density of sample and density of protium oxide
d_1 = density of protium oxide at 25°C in grams per milliliter (lighter in density than ordinary water by 1.6×10^{-5} g/ml)

In any determination of D_2O content by density and by most other methods involving a physical property, the abundance of the O^{18} isotope must be considered since, in a number of the processes used for extracting D_2O (e.g., distillation), the product is enriched in the heavier isotopes of oxygen as well as in deuterium. The natural abundance of O^{18} is reported [1] as 0.198 mole % and that of O^{17} as 0.042 mole %. For routine work the change in the abundance of O^{17} has a negligible effect on the determination of the D_2O concentration; but any change in the O^{18} content is usually significant, and any D_2O determination must include the appropriate O^{18} correction. For work of highest precision, the O^{18} correction should be applied in the calculation [1] of sample density (0.0000012 specific gravity units per 0.001 mole % O^{18}).

Two general approaches used to determine the O^{18} content are (1) determination of O^{18} as it exists in the sample and application of a correction to the D_2O results, and (2) reduction of the O^{18} content to normal abundance. The most convenient method is to determine the O^{18} by equilibration with CO_2; this is accomplished by determining the mass 46 to mass 44 ratio of the CO_2 by a mass spectrometer after equilibration

with the D_2O sample. The equilibrium constants[1] for the carbon dioxide–heavy water reaction have been established, and the formula generally used is:

$$\text{Mole } \%\ (O^{18})_{water} = \frac{100\ R_x}{(K_a K_b)^{1/2} + R_x} \tag{9.5}$$

where

$$(K_a K_b)^{1/2} = 2.088$$

$$R_x = \frac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{18}} = \frac{m/e\ 44}{m/e\ 46}$$

Briefly, the equilibration procedure consists in shaking 5 ml of purified sample with approximately 20 cm^3 of CO_2 at atmospheric pressure for 5 hr at 25°C. No catalyst is required. The equipment preparation and sample purification are similar to those used in other heavy-water procedures. It is especially desirable that nitrogen dioxide or any compound containing NO_2 be absent.

The other, and usually less desirable, approach to the oxygen isotope problem is to normalize the O^{18} content of both the sample and a standard by bubbling anhydrous sulfur dioxide through the sample and standard. The time necessary to normalize is determined experimentally; in most cases it will be several hours at a gas flow of 15 to 20 liters/hr. Obviously, with this much gas any traces of moisture in the SO_2 (commercial anhydrous SO_2 usually contains some water) must be eliminated by use of a trap or drying tube. Also, the effluent gas from the sample container must be trapped to recover any sample vapor carried over.

(b) *Float Temperature Method (Float Bath).* Determining density by a float is an old technique. The particular adaptation of this principle which has been used for determining heavy water is quite simple; however, it requires well-trained personnel, a great deal of patience, and extremely clean equipment. For routine control it has been largely replaced by other methods, but it is still useful in establishing standards at concentrations of less than 1 mole % D_2O.

In principle the float method works as follows: the temperature at which a small quartz float has the same density as a sample, i.e., when the float is suspended below the surface of the sample, neither rising nor falling, is compared with the temperature at which the same float has the same density as a standard sample. The temperature difference (corrected for the coefficient of expansion of water, quartz, and heavy water) is then used to calculate the difference in density of the sample and the standard; this density difference is then used to calculate the mole % of heavy water in the sample.

Although this method has been used primarily in determining concentrations of D_2O of less than 5 mole %, it can be used over the entire concentration range if the proper precautions are taken for maintaining standards free of protium contamination. For best

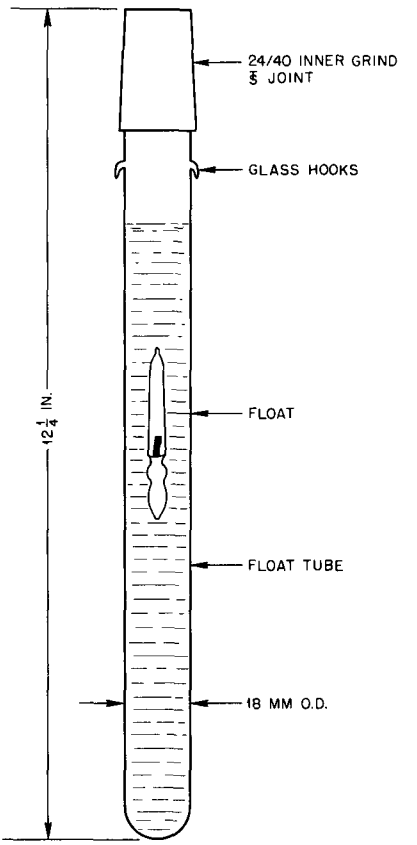


Fig 9.3—Float and float tube.

results the D_2O concentration of the standard should be as close as possible to that of the sample.

As in all density methods, the sample must be extremely pure, and the cleanliness of the equipment must be rigidly controlled. This is particularly true of the floats themselves. They must be cleaned and conditioned to the D_2O concentrations being analyzed; this is done by soaking them and then properly storing them in comparable material. In the very low D_2O concentration range (near normal abundance), dilution with moisture from the atmosphere is not important; however, above 0.05 mole % D_2O, atmospheric dilution becomes a factor and must be controlled.

The float must be so designed that it has approximately the same density as the sample and standard at normal temperatures. Figure 9.3 shows one successful design in which fused quartz is used. The

distillation apparatus required is similar to that used in the pycnometer method (Fig. 9.2), except that the receiving vessel is the tube used for floating the sample (Fig. 9.3).

A precision of ± 0.01 mole % at the 95 per cent confidence interval is attainable at concentrations in the ≥ 90 mole % D_2O range, and a precision of ± 0.0002 mole % is attainable at 0.015 mole % D_2O.

Procedure. Gases and other impurities are removed from the sample by completely distilling it directly into the float tube in exactly the same manner as in the pycnometer method. The float tube is then immersed in a water bath controlled at ± 0.001°C by a thermostat. The float is very carefully placed in the sample, and the temperature of the sample is adjusted until the float remains motionless for 200 sec. The position and movement of the float are observed with a cathetometer or telescope. The float is then removed, rinsed in a portion of standard D_2O, and then placed in another float tube containing a standard of approximately the same D_2O concentration as the sample. Again, the temperature is adjusted until the float becomes motionless. Sufficient time must be allowed for the water bath and standard to reach equilibrium. Assuming that the sample and standard are very close in D_2O concentration and the same float is used, the equation for calculating the mole % of heavy water becomes

$$\text{Mole \% } D_2O = 927.35 \times [(\Delta T \times d_3) + K] \tag{9.6}$$

where

ΔT = difference in temperature between standard and sample

d_3 = average change in density per degree for reference water at 25.9°C ($=262.6 \times 10^{-6}$)

K = difference in density of normal water and pure protium oxide ($=16 \times 10^{-6}$)

(c) *Displacement Method.* The density of heavy-water samples can be determined by displacement (with, for example, the Westphal balance). Although not so accurate as the pycnometer or float bath methods, this is an excellent method when time is a factor and precise measurements are not required. This method utilizes less expensive equipment than the pycnometer or float bath and requires less skill on the part of the operator. The precision of the method is ± 0.10 mole % at ≥ 90 mole % D_2O.

The procedure consists simply in suspending a sinker in a heavy-water standard and then in the sample. At a particular temperature, the buoyant force exerted on the sinker by the sample is compared with the buoyant force exerted by the standard. Once again, the sample must be free of dissolved and suspended impurities. Although the precision of the method normally does not warrant it, corrections for the O^{18} content of the sample and for the surface-tension effect on the wire suspension should be considered for highest accuracy. A

simplified formula that can be used to calculate the mole % of heavy water is

$$\text{Mole \% } D_2O = (A - B) \times 927.35 \tag{9.7}$$

where

A = density of the sample
B = density of normal water at the temperature at which the sample was measured

9–2.2 Mass Spectrometer

Mass spectrometry will not be discussed here except as it applies to the control of heavy water. For a discussion of the theory and general operation of mass spectrometers, see Chap. 13.

(a) *General.* The determination of the isotopic distribution of hydrogen by mass spectrometer was one of the original techniques used in the study of hydrogen isotopes. One of the earlier types of mass spectrometers used extensively for heavy-water control was the Nier instrument.[1] This instrument measures the ratio of the HD to D_2 mass peaks or the HD to H_2 mass peaks; therefore the problem of preparing a representative hydrogen gas product from the sample must be resolved. Two general methods are available: (1) the sample of water can be decomposed chemically if care is taken to decompose the entire sample to prevent fractionation of the D_2-H_2 mixture, or (2) the liquid sample can be equilibrated with a standard deuterium gas (or with hydrogen gas if the sample contains only traces of D_2O), and the equilibrated gas can be analyzed for D_2 content. Although these methods of sample preparation and this type of mass spectrometer are still employed, they have been largely replaced by other mass-spectrometric procedures and equipment that are more adaptable for rapid routine control work. The precision of these gas mass spectrometers is ± 0.02 mole % at the ≥ 98 mole % D_2O range.

(b) *Heavy-water Mass Spectrometer.* One of the mass spectrometers [2, 3] now being used most successfully for the routine control of heavy water is the Consolidated Electrodynamics Corporation model 21–330. This instrument is a continuous-recording isotope-ratio mass spectrometer specifically designed to measure the relative abundance of hydrogen isotopes in water vapor. Its greatest advantage is its ability to accept a sample of water vapor, thus eliminating the need for converting the sample to a gaseous product. This mass spectrometer is designed to collect, simultaneously and separately, ions having mass to charge ratios of 19 and 20 (representing HDO^+ and D_2O^+) or 18 and 19 (representing H_2O^+ and HDO^+). These two ion-beam signals are sent to a direct-reading ratio recorder that records the mole % D_2O. Since the ratios recorded are not an absolute measure of the relative abundance of the respective molecules, standards must

be used whose values have been determined by other methods, such as pycnometer. Results obtained by pycnometer, Nier ratio (3/4) spectrometer, and the CEC 21–330 instrument are compared in Table 9.1.

Table 9.1—COMPARISON OF RESULTS BY DIFFERENT METHODS

Sample No.	Heavy water, mole %		
	Pycnometer	CEC 21–330 mass spectrometer	Nier ratio (3/4) mass spectrometer
1	99. 73	99. 74	99. 72
2	99. 75	99. 75	99. 75
3	99. 75	99. 76	99. 75
4	99. 76	99. 76	99. 75
5	99. 67	99. 68	99. 68

The precision of measurements on the CEC 21–330 instrument varies with the concentration. Some typical precision data on routine control analyses are shown in Table 9.2.

Table 9.2—PRECISION OF CEC 21–330 MASS SPECTROMETER

Concentration range, mole % D_2O	Number of determinations	Precision (95% confidence interval), mole % D_2O
0.05 to 0.15	45	0. 0046
0.50 to 2.00	60	0. 028
13.0 to 17.0	40	0. 10
Above 99	150	0. 02

The CEC 21–330 instrument, mainly because it is subjected to water vapor, has an appreciable "memory" owing to the retention of trace amounts of the last material analyzed on the internal surfaces of the sample-introduction system and ionization chamber of the spectrometer. When the next sample is introduced, a small portion of this retained material is released from the internal surfaces and contaminates the material being analyzed. With samples of similar concentration, the effect is negligible. Therefore it is desirable to limit the samples being analyzed by one instrument to a narrow D_2O concentration range. If this is not possible, frequent flushing with standards of known D_2O concentration is required.

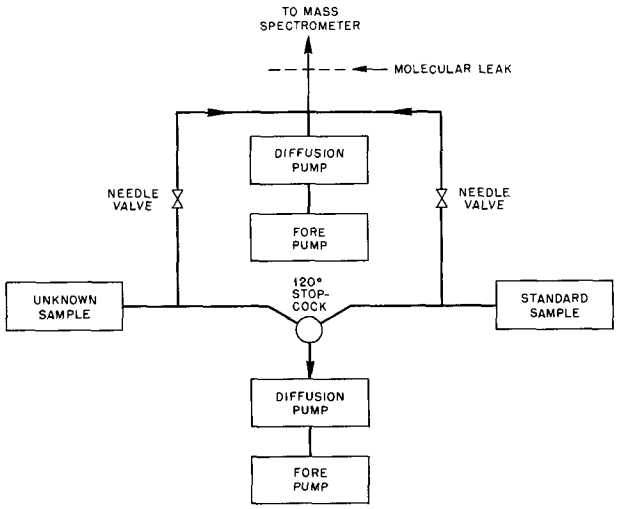


Fig. 9.4—Continuous-flow introduction system.

One modification of the CEC 21–330 mass spectrometer introduction system has been made which has minimized the memory effect, particularly at high concentrations of D_2O, and has substantially reduced the time of analysis, enabling an operator to analyze a sample in 2 to 3 min. In the original design of the introduction system, a small sample (less than 0.1 ml) was introduced into the instrument with a capillary dipper and mercury seal. With the modified arrangement a much larger quantity (several milliliters) is continuously vaporized and allowed to pass through the introduction system into a separate pumping system, with only a small side stream of vaporized sample being introduced into the ionization chamber by means of a molecular leak. The pressure is controlled at 100 μ or less by a needle valve. Isotopic separation does occur when the sample and standard are vaporized, but the effect is canceled if the concentrations of sample and standard are similar. A block diagram of the continuous-flow introduction system is shown in Fig. 9.4.

In the analysis of D_2O by a mass spectrometer, as in all other methods of heavy-water analysis, contamination of the sample with light water is always possible, and even probable, unless the necessary handling precautions are taken. However, one big advantage over the gravimetric and density methods is that no extensive cleanup of the sample is necessary. A specially designed sample boat (Fig. 9.5), which is essentially a hollow two-way stopcock, is used for presenting the sample to the instrument. Approximately 3 to 4 ml of sample is transferred from the sample bottle to the outer bulb of the boat by a

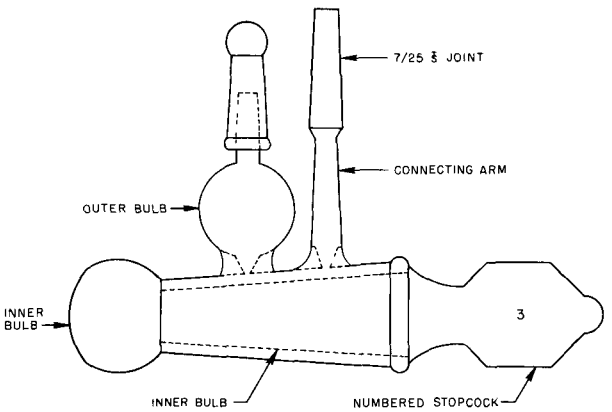


Fig. 9.5—High-range mass-spectrometer sample boat.

hypodermic syringe and then admitted to the inner bulb, which has been previously evacuated. Enough sample is left in the outer bulb to form a seal from the atmosphere. The sample boat is then connected to the mass spectrometer introduction system (Fig. 9.4) and the sample of standard is introduced into the instrument as required.

Procedure. From a set of previously prepared standards, the one nearest the estimated D_2O value of the sample is selected. The sample is transferred, by means of a hypodermic syringe or in a closed dry box, to special sample boats (Fig. 9.5), which are then connected to the introduction system (Fig. 9.4). After evacuation of the introduction system manifold, the standard is introduced into the system. The sample flow is controlled at a pressure consistent with good mass-spectrometer operation, nominally 100 μ. When the recorder has maintained a constant value for 30 sec, the sample flow is stopped, the instrument is evacuated, and the unknown sample is introduced at the same pressure. After 30 sec of steady output as indicated by the recorder, the unknown sample is evacuated from the instrument, and the standard is introduced again. An average value for the standard is calculated, and, by comparison of this value with the true value of the standard, a correction factor is determined. This correction factor is applied to the unknown sample reading to obtain the corrected value for the unknown.

There are numerous variations to this general scheme, depending on the range of concentrations being determined, the memory effect to be overcome, the concentration spread between standard and sample, and other factors. In some laboratories where the D_2O concentration of the samples varies very little, as many as 10 samples have been run between introductions of the standard.

Of course, any results by this method are only as good as the standard values. Since some slight fractionation occurs as the standard

samples vaporize and since the handling that standards experience in daily use tends to contaminate them, rigid control of the standards, including frequent verification of their true values, is necessary if reliable results are to be obtained.

9–2.3 Infrared Spectroscopy

The analysis of heavy water by infrared spectroscopy is a comparatively recent development, but one which promises to become one of the more important methods, particularly for "in-line" monitoring of heavy water at the ≧99 mole % concentration.

The precision of the method is excellent at ≧99.7 mole % and at less than 0.3 mole %, but it rapidly becomes worse as the mixture approaches equal parts of light and heavy water. The infrared measurements are made on the HDO absorption band, usually at 2.95 μ. This is the region of greatest sensitivity with samples of greater than 99 or less than 1 mole % D_2O since the equilibrium reaction for heavy water–light water mixtures is such that, at these concentrations, essentially all the lesser hydrogen isotope [4, 5] is present as HDO.

The advantages of the infrared spectrometer as a laboratory batch analyzer compared with the mass spectrometer are (1) lower instrument cost, (2) no memory effect, and (3) better precision (±0.002 mole % at the ≧99.7 mole % D_2O range).[4, 5] Its advantages over the pycnometer method are (1) less analysis time, (2) less demand on operator skill, and (3) less rigorous purification of the sample.

Automatic infrared in-line monitoring has the additional advantages of (1) eliminating the light-water contamination problem experienced with batch sampling, (2) monitoring the heavy-water concentration continuously rather than intermittently, and (3) substantially reducing attention time. Unlike the mass spectrometer, the infrared spectrometer is temperature sensitive, i.e., the temperature of the sample being analyzed is critical and should be controlled for maximum precision. Also, the sample should be free of any contaminants that might interfere with the infrared wave transmission.

Although the sensitivity of the method is ±0.002 mole % at the 99.7 mole % concentration range, standardization of the instrument with standard samples is required, and the accuracy of the measurement is limited by the accuracy of the standards, usually ±0.01 mole % as determined by pycnometer. In most procedures a double-beam differential absorption technique [4] is used. The sample cell, which usually has a capacity of less than 1 ml, is flushed several times by repeatedly introducing a small amount of sample with a hypodermic syringe or in a dry atmosphere. The reference cell is filled with H_2O

or is replaced by an optical absorber, such as soda glass, with the proper absorption characteristics. The analytical results are obtained either from a recording device calibrated to read directly in mole % D_2O or from a recorder whose reading can be converted to mole % from a calibration curve. Calibration is accomplished by analyzing known standards introduced in the same manner as an unknown sample. Frequency of calibration depends upon operating experience with the particular instrument being used and upon the degree of precision required.

9–2.4 Other Methods

Four other methods, emission spectroscopy, nuclear magnetic resonance, cryoscopy, and refractometry are briefly described in this section.

(a) *Emission Spectroscopy.* Development work on a spectrographic method of analysis for hydrogen isotopes has been conducted by Tomkins and Fred [6] and more recently by Broida and associates.[7] The method is discussed in the chapter on spectrochemical methods (Chap. 12). In the work of Broida et al., the vapor from an aqueous sample containing light water–heavy water is pumped at a nominal pressure of 400 μ through a glass tube in which a high-frequency electrodeless discharge is maintained. The light emitted from the discharge tube contains lines of the Balmer series of hydrogen and deuterium. The emitted light is dispersed by a monochromator, and the relative intensities of the beta lines of the Balmer series are measured. The ratio of intensities of the hydrogen and deuterium lines is a function of the relative concentration of the isotopes. Standardization against known standards is required.

A precision of 0.1 to 3.0 per cent has been obtained under different conditions of experimentation. The method has the advantages of using a small sample (less than 1 ml) and of not requiring sample purification (since the water vapor is analyzed). The method is sensitive to sample flow rate, pressure, temperature, and discharge-tube temperature. Some memory effect is present, and some fractionation takes place when the sample vaporizes.

(b) *Nuclear Magnetic Resonance.* Nuclear magnetic resonance [8] can be used for the determination of heavy-water purity, although the accuracy with presently available equipment and techniques is considerably less than that of most of the better-known methods. Most of the work of adapting this technique to D_2O analysis is in the development stage, and no established routine methods or precision data exist. Since the technique is intrinsically more sensitive to the proton than to the deutron, by a factor of approximately 200, and since the

minor component is measured, less precise measurements are experienced at low concentrations of D_2O than at high concentrations.

(c) *Cryoscopy.* Although the difference in the freezing points of heavy water and light water (heavy water freezes at 3.802°C) has been evaluated as a means of determining heavy water,[9] only in recent years have techniques been developed that make the method comparable in precision to other procedures, and then only in the 0 to 5 mole % D_2O range.[10] This recent work, in which the Fiske osmometer was used, is based on the principle that slightly supercooled solutions can be rapidly frozen, by agitation, and that the temperature of the ice crystals will remain constant long enough to make an accurate reading. A thermistor was used, and a precision of ±0.014 mole % D_2O was obtained at the 0 to 5 mole % D_2O range.

(d) *Refractometry.* A significant difference (0.0048 at a wave length of 5461 A at 20°C) exists between the index of refraction of ordinary water and that of heavy water. This difference, which can be measured by either a refractometer or an interferometer, can form the basis for the isotopic analysis of water. A higher accuracy is more easily obtainable with the interferometer than with the refractometer since the refraction of one liquid is compared with that of another having nearly the same composition and temperature coefficient at that refractive index. The temperature must be controlled within ±0.01°C for accurate refractometer measurements.[1] For precise results all impurities must be removed. Any of the purification methods mentioned previously can be applied here.

(e) *Miscellaneous.* Several other methods for determining deuterium have been developed and used to a limited extent. As in the better-known methods, advantage is taken of the differences in some particular physical property of light and heavy water or hydrogen and deuterium gas. Thermal conductivities, viscosities, and vapor pressures, for example, have all been used with some success.[1]

9–3 DETERMINATION OF IMPURITIES

In a heavy-water-moderated reactor the efficiency of the reactor operation and the maintenance of the reactor system, as well as the control of any moderator purification equipment, require a knowledge and quantitative determination of the moderator impurities. Since heavy water is normally free of contaminants before its use as a reactor moderator, the impurities present, except for light water, are corrosion or radiation products resulting from exposure to the reactor complex.

The analytical methods used can be grouped in three major categories: (1) determination of individual cationic and anionic impurities, (2) determination of the radioactive species present, and (3) determination of changes in the physical properties of the moderator

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which are indicative of the level of contamination. The methods employed are standard analytical techniques and are therefore only briefly described in this chapter to indicate the specific methods that have been used successfully. Because the concentrations of the contaminants are normally in the parts per million or parts per billion range, methods of highest sensitivity must be used, and extreme care must be exercised in handling the samples to prevent contamination.

9–3.1 Cationic and Anionic Impurities

As a rule, ionic impurities are determined by chemical methods; however, emission spectroscopy is preferred in some specific situations.

(a) *Emission Spectroscopy.* The emission spectrograph is used for determining cations in the parts per billion range when extreme precision is not required or when no adequate chemical methods exist. The ability to detect cations in this concentration range is made possible by a 50 to 100 volume concentration of an acidified sample in quartz equipment. Quartz ware is recommended to prevent contamination from the impurities found in conventional glassware, and acidification is recommended to prevent the loss of cations due to deposition on the evaporation equipment. The method has been used for the determination of boron, cadmium, manganese, iron, magnesium, chromium, nickel, aluminum, copper, cobalt, calcium, uranium, sodium, and lithium.

> *Procedure.* Approximately 1 liter of sample is introduced into a round-bottom quartz flask. Two to three drops of hydrofluoric acid (1+100) are added to the sample, and the sample is carefully evaporated just to dryness. The "soft" residue is redissolved in 10 ml of 6*N* spectrographically pure hydrochloric acid; then 200 μl of the concentrate is evaporated on a paraffin-coated graphite electrode (in some applications, copper or silver electrodes have been used [11]). The impurity-element spectra are excited and recorded by the use of a conventional spark source and spectrograph. Conventional spectrograph techniques are used throughout the procedure. The concentrations of the impurity elements are estimated by comparison with standard films. The precision of the method is a factor of 2 (+100 per cent to −50 per cent).

(b) *Chemical Methods.* Since most of the impurities in heavy water occur in trace quantities, very little preliminary separation or pretreatment is required. Interference found in individual methods are usually eliminated by minor adjustments of a particular method. Spectrophotometric, nephelometric, and flame photometric methods are particularly adaptable to the determination of such ions as sodium, lithium, aluminum, iron, chromium, cadmium, nickel, copper, mercury, peroxide, chloride, nitrate, sulfate, and silica, when present in the parts per million range. All working curves are made from pure chemicals.

(1) *Sodium-Lithium.*[12, 13] Flame photometry is a rapid, accurate method for the determination of sodium or lithium. In dilute solutions, interfering ions that normally inhibit the lithium-flame excitation (such as calcium and strontium) become negligible; however, for best lithium results the free-acid concentration must be no greater than 0.12 equivalents per liter of solution, and the sodium content should not exceed 25 mg/liter. No interfering ions have been encountered with this method in determining sodium. For best accuracy and sensitivity a photomultiplier attachment used with the phototube is recommended.

Procedure. As required by the flame photometer, the appropriate amount of sample (usually several milliliters) containing approximately 2.5 mg of lithium or sodium per liter is placed in the atomizer. The sample is excited in a hydrogen-oxygen flame, and the percentage of transmission is noted at a wave length of 671 mμ for lithium and 590 mμ for sodium.

(2) *Aluminum.*[14] Heavy water samples are treated with an acid dye (sold under the trade name Pontachrome Blue-Black R) which produces a red fluorescence with aluminum at a pH of 4.9. The fluorescence, which is proportional to the concentration of aluminum, is measured with a fluorophotometer, such as the Lumetron, model, 402–EF.[15] The method is sensitive to 0.001 to 0.025 mg of aluminum. Iron in concentrations of less than 0.3 ppm in the final volume will not interfere.

Procedure. An aliquot of sample containing 0.001 to 0.025 mg of aluminum and not more than 0.015 mg of iron is placed in a 50 ml beaker, and the volume is adjusted to approximately 30 ml by distilled water and 5 ml of 10 per cent ammonium acetate. The pH of the solution is adjusted to 4.9±0.1 with 6*N* ammonium hydroxide or 6*N* sulfuric acid. The solution is transferred quantitatively to a 50-ml volumetric flask, and 1.5 ml of 0.1 wt.% Pontachrome Blue-Black R dye is added. The solution is diluted to 50 ml, mixed, and allowed to stand for at least 1 hr and not more than 2 hr. The percentage of fluorescence is measured using a fluorophotometer.

(3) *Iron.*[16, 17] Ammonium thioglycolate reacts with ferrous and ferric iron in a solution having a pH of 6 to 11 to give a reddish-purple color proportional to the iron concentration when it is between 0.005 and 0.5 mg. The color developed is stable for about 2 hr. More than 10 mg of copper in the final volume causes a loss in the color of the iron complex, but this can be corrected by the addition of excess ammonium thioglycolate. Cyanide and mercurous ions interfere.

Procedure. An aliquot of sample containing at least 0.01 mg of iron is pipetted into a 50-ml volumetric flask, and the volume is brought to about 30 ml with distilled water. To the flask are added 5 ml of 1 vol.%

neutral thioglycolic acid and enough 6*N* ammonium hydroxide to make the solution basic, plus a 2 ml excess of 6*N* ammonium hydroxide. The solution is diluted to 50 ml with distilled water and mixed. The absorbancy of the sample is measured in a spectrophotometer at a wave length of 530 mμ by absorption cells with a 50-mm light path.

(4) *Chromium.*[18] Hexavalent chromium in an acid solution reacts with diphenylcarbazide to form a soluble red-violet colored complex. Interference by molybdenum and mercury is minimized by proper adjustment of the acidity of the solution with sulfuric acid. Ferric iron is also an interfering element but is removed by the addition of ammonium hydroxide. Potassium bromate in the presence of a small amount of manganese as a catalyst is used to oxidize chromium to a valence of six. After oxidation of the chromium, any bromine remaining in the solution is removed by boiling the solution with ammonium sulfate and adding hydrochloric acid. As little as 0.001 mg of chromium can be detected by this method, but the preferred concentration range is 0.005 to 0.010 mg.

Procedure. An aliquot of sample containing approximately 0.005 mg of chromium is placed in a 125-ml Erlenmeyer flask and diluted to about 20 ml with distilled water. To the flask are added 3 ml of 60 g/liter potassium bromate, 0.5 ml of 0.1 mg/ml manganese, and 2 ml of 5*N* sulfuric acid. The solution is boiled for 5 min. While the solution is boiling, 1 ml of 20 wt.% ammonium sulfate and 1 ml of 10 wt.% hydrochloric acid are added slowly. Thirty seconds after the solution becomes colorless, it is allowed to cool; then 5 ml of concentrated ammonium hydroxide is added. The solution is again boiled for 2 to 3 min to remove the excess ammonia, and it is then filtered quantitatively into a 50-ml volumetric flask. To this flask are added 2 ml of 5*N* sulfuric acid and 0.5 ml of 4 g/liter diphenylcarbazide in 95 vol.% ethyl alcohol. The solution is diluted to 50 ml with distilled water and allowed to stand for 15 min to develop maximum color. The absorbancy of the sample is measured in a spectrophotometer at 540 mμ with a 50-mm light path.

(5) *Cadmium.*[16, 17, 19] Dithizone in chloroform will extract cadmium from a strongly basic solution (pH 12.5). The reddish-pink cadmium dithizone complex formed in the chloroform layer is stable for at least 2 hr. Improved separation from interferences is achieved through the use of potassium cyanide and tartaric acid. Loss from decomposition is controlled by using hydroxylamine hydrochloride and reducing the time of contact of the chloroform with the alkali. A maximum of 5 mg of cobalt, copper, iron, manganese, and nickel can be tolerated without serious effect on color development. The range of the method is 0.001 to 0.005 mg of cadmium.

Procedure. An aliquot of sample containing approximately 0.002 mg of cadmium is placed in a 125-ml separatory funnel, and enough dis-

tilled water is added to bring the volume to 25 ml. Then, with mixing after each addition, 1 ml of 20 per cent potassium tartrate, 5 ml of 10 per cent sodium hydroxide–1 per cent potassium cyanide, and 1 ml of 20 per cent hydroxylamine chloride are added. Next, 15 ml of chloroform containing 80 mg/liter of dithizone is added, and the two phases are shaken together for 1 min. The chloroform layer is drained into a second separatory funnel containing 25 ml of cold 20 g/liter tartaric acid solution. The aqueous solution remaining in the first separatory funnel is washed with 10 ml of chloroform, and this chloroform wash is then added to the second separatory funnel. The contents of the second separatory funnel are shaken for 2 min, and the chloroform-dithizone layer is discarded. To the aqueous layer remaining are added 0.25 ml of 20 per cent hydroxylamine chloride, 15 ml of chloroform containing 8 mg/liter of dithizone, and 5 ml of 10 per cent sodium hydroxide–0.05 per cent potassium cyanide solution. The funnel is shaken for 1 min, and the chloroform layer is filtered through a glass-wool plug into a dry 20-mm absorption cell. The absorbancy of the developed color is measured in a spectrophotometer at 520 mμ.

(6) *Nickel.*[16, 17] In an alkaline solution, dimethylglyoxime reacts with nickel in the presence of an oxidizing agent to give a pink-colored slightly soluble complex that is proportional to the nickel concentration when it is between 0.01 and 0.1 mg. Aluminum and cobalt will interfere if present. Iron interference is prevented by the addition of citric acid.

Procedure. An aliquot of sample containing at least 0.01 mg of nickel is pipetted into a 50-ml volumetric flask and diluted to approximately 35 ml with distilled water. In sequence, with thorough mixing after each addition, 5 ml of 10 per cent citric acid solution and 2.5 ml of saturated bromine water are added, and the pH is adjusted by adding concentrated ammonium hydroxide until the solution is basic. To the basic solution, 1 ml of 10 g/liter dimethylglyoxime in 95 per cent ethyl alcohol is added. The volume is increased to 50 ml with distilled water, and the solution is mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 535 mμ with a 50-mm light path.

(7) *Copper.* Sodium diethyldithiocarbamate reacts with small amounts of copper to produce a golden-brown suspension in acidic, ammoniacal, or neutral solution. Since the colored compound is a colloidal suspension, gum arabic has a stabilizing effect. Iron causes no interferences when present in amounts of 2 ppm or less. The method is sensitive over the range of 0.01 to 0.1 mg of copper.

Procedure. An aliquot of sample containing approximately 0.02 mg of copper is pipetted into a 50-ml volumetric flask and diluted to approximately 30 ml with distilled water. To the flask, with mixing after every addition, are added 0.5 ml of a 50 g/liter gum arabic solution, 5 ml of concentrated ammonium hydroxide, and 5 ml of 0.1 percent

sodium diethyldithiocarbamate. The volume is increased to 50 ml with distilled water, and the solution is mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 440 mμ with a 50-mm light path.

(8) *Mercury.*[16, 17] Dithizone dissolved in carbon tetrachloride will extract mercury from an aqueous solution, forming an orange-colored complex. The colored complex is stabilized by the addition of acetic acid, and the extraction is more efficient in a sulfuric acid solution. In an acidic solution, silver, copper, gold, and palladium will also react with dithizone. The green color of the dithizone reagent exhibits maximum light absorption at a wave length of 620 mμ. For greatest sensitivity the decrease in the intensity of the green-colored dithizone reagent, due to the formation of the mercury complex, is measured, rather than the orange color of the mercury complex itself.

Procedure. To 480 ml of previously neutralized sample in a 2-liter separatory funnel are added 20 ml of 25*N* sulfuric acid and 5 ml of 6*N* acetic acid. The mercury is extracted by shaking the sample solution for 10 min with 10 ml of 0.005 per cent dithizone in carbon tetrechloride. The absorbancy of the dithizone solution is immediately measured in a spectrophotometer at 620 mμ with a 10-mm light path.

(9) *Peroxide.* At temperatures between 60 and 70°C, hydrogen peroxide reacts rapidly with acidified ferrous sulfate, oxidizing the ferrous ion to ferric. With the pH of the solution held between 4 and 6 by an acetate buffer, orthophenanthroline forms a colored complex with unreacted ferrous ion. A comparison of the intensity of the colored complex of unreacted ferrous ion in the sample with a blank containing no peroxide determines the amount of peroxide.

Procedure. An aliquot of sample containing approximately 0.01 mg of hydrogen peroxide is pipetted into a 50-ml volumetric flask containing 3 ml of 4 μg/ml ferrous sulfate solution. The contents of the volumetric flask are heated to 60 to 70°C for 10 min; then 2 ml of acetate buffer solution is added, and the pH of the solution is adjusted to 4 to 6 by either 0.1*N* ammonium hydroxide or 0.1*N* sulfuric acid. Next, 1 ml of 5 g/liter orthophenanthroline is added. The solution is diluted to 50 ml with distilled water and mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 510 mμ with a 50-mm light path.

(10) *Chloride.* The addition of silver nitrate to an aqueous sample containing chloride to which has been added methyl alcohol, nitric acid, and sodium sulfate produces a turbidity that is proportional to the amount of chloride in the sample. The preferred concentration range is 0.005 to 0.10 mg of chloride per 50 ml of solution. The particles of silver chloride form agglomerates and settle out on standing, particularly at the higher concentrations.

Procedure. An aliquot of sample containing an estimated 0.01 to 0.1 mg of chloride is pipetted into a 50-ml volumetric flask and diluted to approximately 35 ml with distilled water. To the flask are added 5 ml of methyl alcohol, 5 ml of 0.35*M* sodium sulfate–2.3*M* nitric acid solution, and 1 ml of 0.075*N* silver nitrate. The solution is diluted to 50 ml with distilled water, mixed, and allowed to stand for at least 10 min but not more than 1 hr. The absorbancy of the sample is measured in a spectrophotometer at 450 mμ with a 50-mm light path.

(11) *Nitrate.* Phenoldisulfonic acid reacts with nitrates, producing a yellow color proportional to the nitrate concentration. The color formed with the phenoldisulfonic acid is intensified by the addition of ammonium hydroxide. Chlorides up to 30 ppm can be tolerated. The method is usually used in the range of 0.01 to 0.1 mg of nitrate but is sensitive to 0.001 mg of nitrate.

Procedure. An aliquot of sample containing approximately 0.05 mg of nitrate is pipetted into a 3-in. evaporating dish, and 2.5 ml of 0.1*N* sodium hydroxide is added to the dish. The solution is evaporated to dryness on a steam bath. After the residue has cooled, 1 ml of phenoldisulfonic acid is added, and the solution is allowed to stand for 10 min. Then 7.5 ml of distilled water is added and the mixture is heated on a steam bath until any remaining residue is dissolved. The solution is transferred to a 50-ml volumetric flask containing 25 ml of distilled water, and 7.5 ml of 6*N* ammonium hydroxide is added. The solution is diluted to 50 ml with distilled water and mixed. The absorbancy of the sample is measured in a spectrophotometer at 410 mμ with a 50-mm light path.

(12) *Sulfate.*[20] This method depends upon the formation of highly insoluble barium sulfate, which is precipitated in the presence of excess salt and acid and is held in suspension by glycerol. The percentage of light transmitted through the suspension, as measured in a spectrophotometer, is inversely proportional to the sulfate concentration. In some procedures the amount of scattered light is measured. The nominal concentration range is 0.05 to 0.7 mg of sulfate per 50 ml of volume.

Procedure. An aliquot of sample containing approximately 0.3 mg of sulfate is pipetted into a 50-ml volumetric flask and diluted to approximately 30 ml with distilled water. Then, with mixing after each addition, 5 ml of 16 g/liter sodium chloride–8.7 g/liter hydrochloric acid solution, 5 ml of 33 vol.% glycerol solution, and approximately 0.3 g of barium chloride crystals are added. The contents of the flask are diluted to 50 ml with distilled water, mixed, and allowed to stand for 10 to 15 min. The absorbancy of the sample is measured in a spectrophotometer at 450 mμ with a 50-mm light path.

(13) *Silica.*[21] Soluble silica reacts with ammonium molybdate in an acid solution to form a yellow ammonium silico-molybdate complex.

This yellow complex is reduced with 1-amino-2-naphthol-4-sulfonic acid reagent to form molybdenum blue. The intensity of the color is proportional to the amount of dissolved silica present. Tartaric acid prevents interferences from phosphates.

Procedure. To a 100-ml volumetric flask, 50 ml of sample and 1 ml of 7.5 per cent ammonium molybdate in sulfuric acid are introduced. The contents of the flask are mixed thoroughly and allowed to stand for 5 min. Then, 4 ml of 10 per cent tartaric acid solution is added, the solution is mixed, and immediately 1 ml of a 0.15 per cent 1-amino-2-naphthol-4-sulfonic acid solution in a 10 per cent sodium bisulfite–7 per cent sodium sulfite solution is introduced. The flask contents are diluted to 100 ml with distilled water, mixed, and allowed to stand for 20 min for color development. The absorbancy of the sample is measured in a spectrophotometer at 700 mμ with a 50-mm light path.

9–3.2 Radioactive Contaminants

Since heavy water as a reactor moderator is exposed to an intense field of radiation, it is natural to expect that a significant amount of the impurities present will be converted to radioactive species and that some degradation of the heavy water itself will occur. In addition, any reactor fuel failures will, in most reactor designs, contribute fission-product activity to the heavy water. Quantitative identification and control of these radioactive impurities are important, not only for the reasons stated previously concerning all impurities but also because of the associated radiation hazards to personnel. Table 9.3 lists the radioactive nuclides that have been detected and identified in heavy-water moderator used in a reactor complex in which the materials of construction are primarily stainless steels and aluminum and in which fuel failures have occurred with the release of fission products.

Methods for determining individual radioactive isotopes include radiochemical separation and gamma scintillation spectrometry. Methods for determining tritium are discussed separately; these are generally based upon measurement of tritium beta activity.

(a) *Radiochemical Separation.* One means of determining the individual nuclides is by chemical separation, followed by gamma or beta counting. Although accurate and precise results are possible, this technique requires extreme care to obtain effective separation since the concentrations of the individual nuclides are usually very low. The method is also time consuming if several nuclides are to be separated, a consideration of particular importance if short-lived isotopes are involved. Obviously, it is impossible to list a universally adaptable

Table 9.3—RADIOACTIVE NUCLIDES OCCURRING AS IMPURITIES IN HEAVY-WATER MODERATOR

Isotope	Half life
From Structural Materials	
Na^{24}	15 hr.
Mn^{56}	2.6 hr.
Co^{60}	5.3 years.
Cr^{51}	26.5 days.
Fe^{59}	45 days.
Ni^{65}	2.5 hr.
Cu^{64}	12.8 hr.
Al^{28}	2.3 min.
From Fuel Failure	
Zr^{95}	65 days.
Nb^{95}	35 days.
Ru^{103}	40 days.
From Heavy Water	
H^3	12.3 years.

separations scheme. Dissolved and suspended contaminants, elemental groupings, individual concentrations, and many other factors must be considered. Figure 9.6 shows a sequential scheme of separation that has been used routinely when fission-product activity is absent.[22] Although theoretically this scheme or similar schemes should isolate the various nuclides, particularly with the use of inactive carriers, separation is seldom quantitative; therefore the purity of the separate radioactive precipitates or solutions should be confirmed by gamma spectrometry or by analysis of decay curves.

(b) *Gamma Spectrometry.* Of the several approaches to the quantitative or qualitative determination of individual radioactive isotopes in heavy-water moderator, probably the most versatile, efficient, and accurate method is gamma scintillation spectrometry.[23, 24] This method has gained wide acceptance and is now being used routinely in many laboratories. Spectrometers are being manufactured in a sufficient variety of designs to fit almost any requirements.

In brief, a gamma scintillation spectrometer consists of (1) a scintillator, usually a sodium iodide (thallium-activated) crystal that emits light when struck by a gamma photon, (2) a phototube that converts the light energy into electrical energy and provides some amplification.

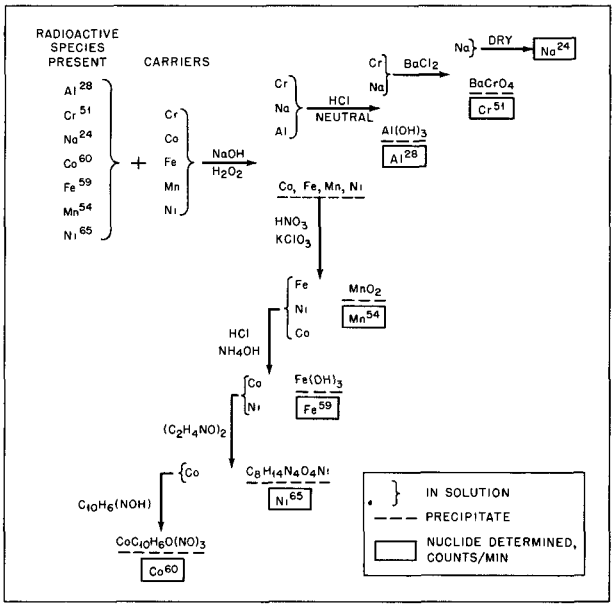


Fig. 9.6—Typical radiochemical analysis.

and (3) a pulse-height analyzer that further amplifies the electrical signal and sorts the electrical pulses according to their amplitude. Since the pulse heights are very nearly proportional to the energies of the different gamma photons, the gamma energy spectrum can be analyzed from the pulse-height distribution.

Pulse-height analyzers are designed with a single channel or with a number of channels. With a single-channel analyzer, only one pulse height can be examined at a time; whereas the multichannel instruments allow the simultaneous examination of several pulse heights. If the interest is in only one or two particular nuclides, the single-channel analyzer will suffice. Usually, however, the activity present in heavy-water moderator comes from many different radioactive isotopes, and for efficiency and accuracy the multichannel analyzers are preferred.

A 3- by 3-in. crystal has been found to be ideal for the detector. For the best resolution and for a minimum of interference from light leakage, the crystal should be mounted as an integral part of the phototube. Spurious scattered radiation arising from interaction with surrounding material must be controlled; graded shielding of the detector is suggested to reduce secondary and background radiation to the lowest possible level.

Although tedious chemical separations are not usually required in preparing heavy-water samples for pulse-height analyses, some preliminary separation is occasionally needed if gamma energies cannot be resolved by the analyzer or if high-energy gammas in relatively large abundance mask the low-energy spectrum. In some instances, differences in half lives can be used to advantage in eliminating interferences. In complex mixtures the contribution of secondary energy peaks of one nuclide to the primary peaks of other nuclides can be resolved by suitable calibration and the proper mathematical treatment. The time required to perform final computations can be substantially reduced through the use of high-speed computers. In one instance calculations that required two days with a desk calculator were completed in 30 min by electronic computers.

(c) *Tritium.* In heavy-water-moderated reactor systems, tritium is formed from deuterium by neutron capture. Since the tritium concentration is a function of the neutron flux, it is subject to wide variations; hence methods must be available to detect a wide range of concentrations. Most of the tritium is present as tritiated heavy water, but a small amount exists as the gas. Generally, the analytical methods are based upon the measurement of tritium beta activity.

(1) *Tritium Oxide: Ionization Chamber.* In this method the sample of heavy water is decomposed by metallic calcium, the gaseous decomposition products are transferred to an evacuated ion chamber, and the ionizing current produced by the beta radiation from the tritium decay is measured by a vibrating-reed electrometer (Fig. 9.7). Since the rates of reaction of calcium with the different hydrogen isotopes vary, either the entire sample must be decomposed and all the gaseous product introduced into the ion chamber, or the standards used in calibrating the electrometer must be similar in composition to the material being analyzed. The current produced is a linear function of the tritium concentration in heavy water. The lower limit of sensitivity is approximately 0.1 μc/ml.

Procedure. About 3 g of calcium metal and 3 or 4 granules of calcium chloride are placed in a 125-ml acetylating flask. After the electrometer background on air at atmospheric pressure is determined, the entire system is evacuated, and approximately 5 ml of sample is added to the sample buret. The sample is introduced to the system dropwise until the pressure in the system returns to 1 atm. Then the ion chamber is isolated from the rest of the apparatus, the current produced by the beta radiation is measured, and the concentration of tritium is determined from a standard calibration curve.

(2) *Tritium Oxide: Scintillation Counting.* In recent years the technique of measuring low-energy beta emitters in liquid scintillators has been adapted for the determination of tritium in water.

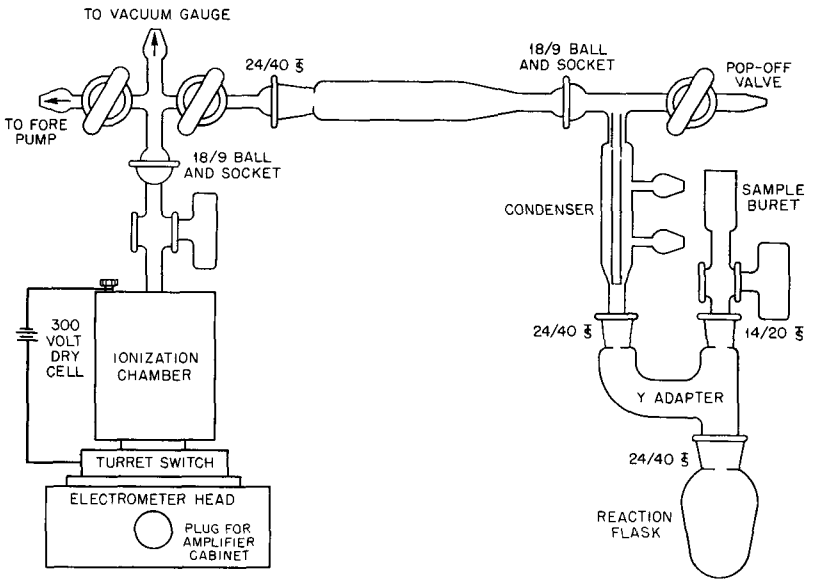


Fig. 9.7—Vibrating-reed electrometer and associated equipment.

The liquid scintillator–phototube system is combined with a pulse-height analyzer to provide discrimination of the tritium-decay-activated pulses from other radioactive contaminants. This is an extremely sensitive method; tritium oxide below 0.00005 μc/ml can be detected. The thermal noise produced by the photomultiplier must be controlled to obtain this low limit of sensitivity. This is accomplished by cooling the samples and phototube and by using a coincidence arrangement of two photomultipliers to screen out the thermal noise pulses originating from the individual phototubes.

Procedure. A scintillation solution is prepared by dissolving 50 g of naphthalene, 4 g of 2,5-diphenyloxazole, and 0.1 g of *p*-bis 2-(5-phenyloxazole)-benzene in 1 liter of 2,4-dioxane. Twelve milliliters of this scintillation solution and three milliliters of sample are mixed in a 16-ml polyethylene vial, placed in the refrigerated detection compartment of the spectrometer, cooled for 30 min to approximately 5 to 10°C, and counted.

(3) *Tritium Gas.* Ion-chamber techniques can be used to determine gaseous tritium. The current produced by the beta radiation is measured by an electrometer and converted to tritium concentration by comparison with a standard calibration curve.

9–4 DETERMINATION OF PHYSICAL PROPERTIES

Because heavy-water moderator must be maintained in a high state of purity for efficient reactor operation, the equipment and methods

used for determining its physical properties must be capable of accurately detecting extremely small changes; good, reliable equipment of the highest sensitivity should therefore be used. Usually, pH (or pD), conductivity, and turbidity are determined. If turbidity is high, the size of the particulate matter may be of interest.

9–4.1 pH

Because heavy water as a moderator is usually a highly unbuffered pure material and hence readily absorbs atmospheric gases and other contaminants, accurate pH values are difficult to obtain. In-line analyses are preferable but, if a bench type pH meter is used, consideration must be given to providing proper grounding for the meter and adequate shielding to protect the sample from atmospheric contamination. A low-resistance large-surface-area glass electrode is recommended in all applications. A sensitivity of 0.02 pH unit is desirable.

9–4.2 Conductivity

Since heavy water as a moderator is very pure, its specific conductance is very low and can be used as a means of measuring dissolved ionic impurities. A conductivity cell and bridge capable of measuring values in the 0- to 50-micromho range are desirable.

9–4.3 Turbidity [15]

Turbidity can be determined visually by comparing the sample against turbidity standards with the use of Nessler tubes or instrumentally by passing a beam of light through the sample and measuring the scattered or absorbed light. Although it is known that the particle size of suspended matter and the color of the sample have a very pronounced effect on the absorption and scattering of light, it is believed that the photoelectric method is as good as, or better than, other methods for routine control. The concentration range of interest is usually 0 to 100 ppm as silica, based on American Public Health Association turbidity units. For highest sensitivity, nephelometric measurements are usually employed. With this technique a precision of 0.1 ppm in the 0- to 5-ppm range is possible.

9–4.4 Particle Size

Information concerning the size of particulate matter is important in designing equipment for turbidity removal or control. There are many techniques for determining particle size, but unfortunately the diameter of the particles found in moderator is quite often in the 0.1- to 10-μ range, and particles in this size range and in concentrations

of 0 to 100 ppm can be characterized by only a few of the standard techniques. The optical microscope can be used; the electron microscope is suitable but is expensive and requires considerable skill for proper operation.

Light scattering,[25, 26] although not quantitative, provides information concerning the particle-size range and the average particle size. With this method the intensity of scattered light is measured over an angular range, and the measurements are converted to a special graphical form, forming a composite curve in which the individual particle-size groups appear as steps in the change of intensity with angle. This procedure is effective in the 0.2- to 50-μ-diameter range.

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CHAPTER 10

REACTOR COOLANTS

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The coolants used for nuclear reactors consist of gaseous coolants such as helium and carbon dioxide; liquid coolants, such as water and deuterium; and liquified coolants, such as sodium, sodium–potassium (NaK) alloys, and polyphenyls. Analytical control of the feed coolants, as well as of the circuit coolants, is important, both from the standpoint of the possible presence of high absorption-cross-section impurities and the radiation stability and chemical compatability of these coolants with other materials in the reactor. The presence of impurities in the coolant that can be activated by capture of thermal neutrons to produce gamma activity are of special interest to the analyst.

Nuclear Coolant Reactions: In a water-cooled reactor the primary coolant is exposed to a high neutron flux as it is circulated. The H^2, O^{16}, O^{17}, and O^{18} nuclides in the water interact with the neutrons to form unstable nuclides that emit beta, gamma, or neutron radiation. The most important recations are $O^{16}(n,p)N^{16}$, $O^{16}(n,\alpha)N^{13}$, $O^{17}(n,p)N^{17}$, $O^{18}(p,n)F^{18}$, $O^{18}(n,\gamma)O^{19}$, and $H^2(n,\gamma)H^3$.

Nitrogen–16 has a 7.35-sec half life and emits beta particles having energies of 3.32, 4.39, and 10.40 Mev and gamma rays of 6.13 and 7.10 Mev. This nuclide has a great effect on reactor-shielding requirements because its radiations are the most intense and penetrating in the system. Nitrogen–17 has a 4.14-sec half life and emits a 3.7-Mev beta particle and a 1-Mev neutron. Its activity and that of O^{19}, which has a 29.4-sec half life, are also important in defining shielding requirements. Tritium has a 12.4-year half life and emits a very weak beta particle. This particle may be absorbed directly through the skin and exchanged with body fluids to form tritiated water. The concentration of the other radionuclides (10-min N^{13} and 1.9-hr F^{18}) limit accessibility to the reactor compartment shortly after shutdown.

The coolant in a gas-cooled reactor is usually helium, carbon dioxide, or nitrogen. The activation of helium is small because only the He^3 isotope (0.00013 per cent abundant in natural helium) is involved: $He^3(n,p)H^3$. In carbon dioxide-cooled reactors, the oxygen undergoes the same reactions as the oxygen in water. In addition, carbon undergoes the reactions $C^{12}(n,\gamma)C^{13}$ and $C^{13}(n,\gamma)C^{14}$. Car-

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bon–13 is stable and carbon–14 is a low-energy beta emitter with a 5600-year half life. Therefore no extra shielding is required for these isotopes.

Primary Coolant Impurities: Although purified to the practical engineering limit for plant usage, primary coolant water contains up to 0.5 ppm of impurities consisting mainly of iron, silica, and sodium. The most important nuclear reaction involved is $Na^{23}(n,\gamma)Na^{24}$. Sodium–24 has a 15-hr half life and is a beta–gamma emitter. Its activity limits accessibility to the system shortly after shutdown.

Make-up water, although deaerated, conveys small amounts of air that consists of 78 per cent nitrogen, 21 per cent oxygen, and 0.9 per cent argon with traces of the other noble gases into the primary system. The oxygen nuclear reactions are discussed above for water. The major reaction in make-up water is $N^{14}(n,p)C^{14}$. The predominant activated gaseous impurity is Ar^{41} produced by the reaction $Ar^{40}(n,\gamma)Ar^{41}$. Argon–41 is a 1.8-hr beta–gamma emitter and is a radiological health hazard if it escapes into the reactor-compartment air. The most probable escape of this isotope would be primary-to-secondary leakage into the steam system.

The impurities in high-purity helium used in gas-cooled reactors are about 0.006 per cent nitrogen, 0.002 per cent oxygen, 0.005 per cent water, and 0.005 per cent hydrogen. Nuclear reactions involving these elements are discussed above. A carbon dioxide coolant contains, in general, impurities of nitrogen, oxygen, and argon. A nitrogen coolant contains small amounts of oxygen and hydrogen, which may undergo the nuclear reactions mentioned above for these nuclides.

Corrosion: In a water-cooled reactor, corrosion occurs on the surfaces of the primary system. Corrosion products flake off from the metal and are transported through the system. They are generally insoluble and circulate as particulate "crud" through the system. Some cruds, however, exhibit a phase distribution between the soluble and insoluble form. Proper control of the water chemistry may promote the formation of a smooth resistant oxide coating on the metals that will minimize further corrosion.

The activation of corrosion products in the coolant may occur by one or more of three processes:

1. Activation of corrosion products circulated through the core by the coolant flow.
2. Activation of corrosion products formed in the reactor core and redeposited elsewhere in the system.
3. Deposition of corrosion products from elsewhere in the system within the core area, followed by activation and subsequent transport out of the core area.

Even though aluminum or zirconium is present as cladding of fuel elements, most of the activated corrosion products are formed from stainless steel in the primary system. Most activated corrosion products are formed by (n,γ) reactions with a stable isotopic form of the element, e.g., $Mn^{55}(n,\gamma)Mn^{56}$ and $Co^{59}(n,\gamma)Co^{60}$. Other nuclear reactions, such as $Ni^{58}(n, p)Co^{58}$ and $Al^{27}(n, \alpha)Na^{24}$, also may occur.

Because of the deposition phenomenon, complete purification of the primary system with, for example, ion-exchange resins is limited, and the system walls become increasingly contaminated with long-lived activities as operation time increases. Ready access to system components for maintenance becomes difficult because of the radiation. The major long-lived activated corrosion products include 45-day Fe^{59}, 5.2-year Co^{60}, 71-day Co^{58}, 291-day Mn^{54}, 28-day Cr^{51}, 65-day Zr^{95} (for reactors with zirconium components), 45-day Hf^{181} (from hafnium impurities in zirconium or from control rods), and 13-year Eu^{152} and 16-year Eu^{154} (from europium control rods). Activities contributing to radiation hazards at shorter intervals after shutdown include 2.6-hr Mn^{56}, 13-hr Cu^{64}, 15-hr Na^{24} (from aluminum), 24-hr W^{187}, and 9.3-hr Eu^{152} (from europium control rods). Carbon dioxide, nitrogen, and helium coolants used in gas-cooled reactors cause little or no corrosion to the primary system.

Erosion: Erosion is differentiated from corrosion in that erosion is the mechanical disintegration of the interior metal surfaces of the system, whereas corrosion is the chemical disintegration of these surfaces. The activated products from erosion are of the same type as the activated products from corrosion, but they are formed from abrasion in both water- and gas-cooled reactors.

Fission Products: Fission fragments have a kinetic recoil energy that enables them to penetrate cladding 0.1 to 1 mil thick. If the cladding (normally several mils thick) should be reduced to this range by various factors, fission products may enter the coolant. Fission products may also diffuse through the cladding into the coolant. Gaseous nuclides have the highest diffusion rates. Because a finite amount of time is involved in the diffusion of gaseous fission products through the cladding, only fairly long half-lived (of the order of days) products and their daughters escape into the coolant by this mechanism. These two modes bring only relatively low amounts of fission products into the reactor coolant and are of minor concern under normal operating conditions.

The rupture of a fuel element or a cladding defect releases large amounts of fission products into the coolant and may increase activities to a significant level. It is imperative that such occurrences be discovered as soon as possible. Contamination of the surface of a fuel element with even a few parts per million of fissionable nuclides may

also cause relatively large amounts of fission products in the coolant. Stringent controls must be taken during fuel fabrication to keep fissionable-nuclide contamination to a minimum. Gross iodine activity indicates total fission products being released since 8.05-day I^{131} is obtained from the products of the fission of U^{235}.

Fission-product activity in the primary coolant (water or gas) should be kept as low as possible, not only to minimize radiation levels, but also to minimize waste-disposal problems caused by long-lived fission products such as Sr^{90}.

Primary-system Debris: The minor amounts of debris that accumulate in the primary system before start-up, after refueling, and when primary-system components are replaced, may be circulated through the system and activated. Cleanliness during fabrication and reactor assembly can prevent most of this debris from entering the system.

Coolant Additives: The materials added to the coolant to maintain proper water conditions may become activated. An example is the activation of the lithium hydroxide that is used in coolants for pH control. Tritium may be formed by the reaction $Li^6(n,\alpha)H^3$. In a gas-cooled reactor, impurities in the moderator may enter the coolant by corrosion or erosion and become activated.

10–1 WATER-COOLED REACTORS

By C. J. Rodden

10–1.1 Introduction

Reactors may be cooled with water either by using a once-through system such as is employed in the Hanford reactors or by recirculation of the water as is done in pressurized-water reactors. It is beyond the scope of this book to consider problems relating to water treatment, corrosion, and materials selection. There have been engineering evaluation studies considering these problems.[1] The problems of the once-through coolant are fewer than those of the recirculated coolants.

Design specifications for water purity in the primary systems of nuclear power reactor plants are generally more stringent than those for conventional plants operating at comparable temperatures and pressures because of the problems associated with carrying highly radioactive materials throughout the plant.

The methods of analysis for the initial cooling water are not discussed. The analysis of water has been considered in various reviews that give the necessary references to manuals, books, and journal articles.[2, 3] Standard methods for the examination of water are given in detail in an American Public Health Association publication.[4] In recirculating-water reactors, the greatest number of analyses by far are the so-called "conventional determinations" of pH, chloride content, conductivity, lithium hydroxide content (if this material is used),

and isotopic purity (for reactors cooled by heavy water). These analyses are made routinely and are essential for adequate coolant control. Many of the measurements are made automatically. Analyses dealing with radioactive contamination are done only at intervals or after a rupture or similar incident. Indicative of this type of analyses are those performed for reactors such as the ones for the Army nuclear-power plants (SM–1, SM–1A, PM–2A, and PM–3A)[4] and the Shippingport Atomic Power Station.

A description of the Shippingport Pressurized Water Reactor is given in the book of the same title published for the Atoms for Peace Conference in Geneva in 1958 by the Addison–Wesley Publishing Company, Inc., Reading, Mass. Chapter 8 of this book discusses cooling systems.

Examples of the waters used in reactors which are of interest are the primary-system charging water, primary coolant water, canal water, component-cooling water, and neutron-shield-tank water from a pressurized-water reactor. Although turbine and service waters are analyzed, they will not be considered here.

The *charging water* for the primary system is demineralized, deaerated water that is stored under a steam blanket to exclude air. It should contain less than 0.14 ppm of oxygen and 0.1 ppm of chloride and should have a conductivity not exceeding 1.5 μmho/cm and a pH between 6.0 and 8.0 at 25°C.

The *primary-coolant water* is charging water treated with lithium hydroxide to give a pH of 9.5 to 10.5. This pH is maintained by a lithium hydroxide resin in the purification demineralizer. The oxygen concentration is maintained below 0.14 ppm and the hydrogen concentration between 25 to 35 ml per kilogram of water. Analyses are made for conductance, pH, lithium, hydrogen, and oxygen. The 15-min and 120-hr activity measurements are also made. The demineralizer inlet and outlet are analyzed for Kr^{88}, Cs^{138}, Br^{84} and I^{131}. In addition, at one stage or another, Cs^{136}, Cs^{137}, I^{132}, I^{133}, and H^3 are determined. Also the primary-coolant gas activity and Xe^{133} are determined.

The *canal-water* system is initially filled with demineralized nondeaerated water. Make-up water, taken from the primary-coolant charging system, should have a pH between 6 and 8 and should contain less than 2 ppm of solids as SiO_2. The conductivity should not exceed 5 μmho/cm. The radioactivity of the influent and effluent of the demineralizer is monitored.

The initial fill and subsequent makeup for the *component-cooling-water* system and the *neutron-shield-tank water* is made with the primary-system charging water. Potassium chromate is added as a corrosion inhibitor and maintained at a concentration of 500 to 1000

ppm as chromate. Potassium hydroxide is added to adjust the pH to a range of 8.3 to 9.5. Analyses are made for pH, chromate, gross iodine, K^{42}, and gross gamma activity. Continual measurements and recordings are made of pH, electrical conductivity, dissolved oxygen, soluble radioactivity, and insoluble-crud radioactivity.

10–1.2 Analytical Control of Coolant Water

The reliability of the instruments that continually measure and record the concentration of the various constituents given above is checked by taking water samples and analyzing them in the laboratory. Since hydrazine is used to control the oxygen content, it, in addition to hydrogen, is determined. Crud samples from the demineralized influent and effluent are analyzed for iron and total weight of crud. The major radionuclides in the crud include Fe^{59}, Co^{58}, Co^{60}, Ta^{182}, Ta^{183}, Zr^{95}, Hf^{175}, Hf^{181}, Nb^{95}, Mn^{54}, and Mn^{56}. Resin beds are analyzed for fission products and major induced activities. The fission products include Cs^{138}, Cs^{136}, Cs^{137}, I^{131}, Sr^{89}, and Sr^{90}; the major induced activities are Fe^{59}, Co^{58}, Co^{60}, Ta^{182}, Ta^{183}, Hf^{175}, Hf^{181}, Zr^{95}, Cr^{51}, Mn^{54}, and Nb^{95}. In addition, determinations of a number of other radioactive elements that are present are made when required.

A list of the radiochemical determinations that may be made is given in Table 10.1; the half-lives of various nuclides and the types of radiation they emit are given in Table 10.2; and the carriers employed in the radiochemical separations are given in Table 10.3.

Table 10.1—RADIOCHEMICAL DETERMINATIONS

In primary coolant	In crud	In resin bed
Br^{84}	Ba^{140}	Co^{58}
Cs^{136}	Ce^{137}	Co^{60}
Cs^{137}	Ce^{141}	Cr^{51}
Cs^{138}	Ce^{144}	Cs^{136}
Cs^{139}	Co^{58}	Cs^{137}
F^{18}	Co^{60}	Cs^{138}
I^{131}	Fe^{59}	Fe^{59}
I^{132}	Hf^{175}	Hf^{175}
I^{133}	Hf^{181}	Hf^{181}
Kr^{88}	Mn^{54}	I^{131}
N^{13}	Mn^{56}	Mn^{54}
Na^{24}	Nb^{95}	Nb^{95}
H^{3}	Sr^{89}	Sr^{89}
Xe^{133}	Sr^{90}	Sr^{90}
15-min gross gamma activity	Ta^{182}	Ta^{182}
120-hr gross gamma activity	Ta^{183}	Ta^{183}
	Y^{90}	Zr^{95}
	Zr^{95}	

Table 10.2—NUCLIDES*

Nuclide	Half life	Energies, Mev	
		Beta†	Gamma
Ar^{41}	1.83 hr	1.20 (99%)	1.30 (99%).
Ba^{139}	85.0 min	2.22 (66%), 2.38 (15%), 0.82 (19%).	1.43.
Ba^{140}	12.8 day	1.02 (60%), 0.49 (25%), 0.60 (10%), 0.89 (5%).	0.53 (25), 0.03 (15), 0.16 (7), 0.42 (5).
Br^{82}	35.9 hr	0.44	0.77 (10), 0.62 (5), 0.55 (4).
Br^{83}	2.33 hr	0.94	0.050 (20%).
Br^{84}	31.8 min	4.21 (3)	0.87 (10), 3.93 (2.5).
Ce^{141}	32.5 day	0.435 (70%), 0.58 (30%)	
Ce^{143}	33 hr	1.12 (40), 1.40 (37), 0.50 (12).	0.057 (vs), 0.294(s), 0.668(m), 0.351(m).
Ce^{144}	290 day	0.304 (72%), 0.17 (22%), 0.223 (3%).	0.134 (10), 0.08 (5).
Cs^{134}	2.3 year	0.65 (70%)	0.605, 0.797.
Cs^{136}	13.0 day	0 34 (93%), 0.657 (7%)	0.067, 0.153, 0.162, 0.265. 0.335, 0.822, 1.04, 1.24, 1.41, 2.35, 2.49.
Cs^{137}	30 year	0.523 (92%), 1.19 (8%)	
Cs^{138}	32 min	3.4	1.43 (10), 0.463 (3.6), 1.01 (3.4), 2.21 (2.5), 2.63 (1.2), 0.55 (1.1).
Cs^{139}	9.5 min	3.17	
Cr^{51}	27.8 day	ϵ	0.323 (10%).
Co^{58}	72.0 day	ϵ; β^+0.475	1.62 (2%), 0.81 (98%.)
Co^{60}	5.27 year	0.309 (100%)	1.173 (100%).
Eu^{152}	13 year	ϵ	0.344, 0.244, 0.72, 0.96, 1.09.
Eu^{154}	16 year	145 (95%), ϵ	0.123, 0.78, 1.12, 1.4.
F^{18}	1.87 hr	β^+0.649	
Hf^{175}	70 day	ϵ	0.343 (10).
Hf^{181}	46 day	0.410	
I^{131}	8.05 day	0.608 (87%), 0.335 (9%), 0.25 (3%).	0.364 (81%), 0.637 (9%), 0.284 (6.3%), 0.72 (3%).
I^{132}	2.33 hr	2.12 (18%), 1.5 (24%), 1.2 (23%).	0.67 (10), 0.78 (8), 0.528 (2), 0.96 (2).
I^{133}	20.8 hr	1.4 (94%), 0.5 (6%)	0.53 (94%), 0.85 (5%).
Fe^{59}	45.1 day	0.462 (54%), 0.27 (46%)	1.10 (57%), 1.29 (43%).
Kr^{88}	2.8 hr	0.52 (68%), 2.8 (20%), 0.9 (12%).	0.028 (10), 0.191 (10), 2.4 (10), 0.85 (6).
Mo^{99}	67.0 hr	0.45 (13%), 1.23 (87%)	0.74, 0.18.
Nb^{95}	35 day	0.162	0.764.
N^{13}	9.98 min	β^+1.19	
K^{42}	12.47 hr	3.54 (82%), 1.98 (18%)	1.53 (11%).

See footnotes at end of table.

Table 10.2—NUCLIDES—Continued

Nuclide	Half life	Energies, Mev	
		Beta†	Gamma
Pr^{144}	17.5 min	2.98 (97%), 0.8 (2%)	0.695 (10), 2.18 (5).
Rb^{88}	17.8 min	5.3 (75%), 3.6 (15%), 2.5 (10%).	1.85 (10), 0.91 (6), 2.7 (1).
Na^{24}	15.0 hr	1.39 (100%)	1.368 (10), 2.754 (10).
Sr^{89}	50.4 day	1.46	
Sr^{90}	28 year	0.543	
Ta^{182}	112 day	0.51	0.0677 (13), 1.122 (12).
Ta^{183}	5.2 day	0.615 (95%)	0.246 (10), 0.354 (4), 0.1079 (3.5).
Te^{132}	77.7 hr	0.22	0.231.
Tc^{99}	6.04 hr		0.14 (99%).
Xe^{133}	5.27 day	0.345	0.081.
Y^{90}	64.4 hr	2.28 (100%)	1.75.
Zr^{95}	63.3 day	0.364 (54%), 0.40 (43%), 0.88 (2%).	0.754 (54%), 0.722 (43%).
Zr^{97}	17.0 hr	1.91	0.66 (10), 0.75 (9).

*From William H Sullivan, *Trilinear Chart of Nuclides*, U.S. Government Printing Office, Washington, D.C.

†β^- except as indicated by β^+ in column.

(a) *Determinations in Coolant Analysis.* The specific conductance of coolant waters is determined by standard methods [4] as a check on recording instruments. The pH of the various coolant waters is also determined to check recording instruments. Suspended solids in canal water is measured by a turbidimeter. Chromate in component cooling water is determined by titration with 0.025*N* sodium thiosulfate after the water is acidified and potassium iodide is added. Chloride is determined by titrating with 0.0014*N* mercuric nitrate using diphenylcarbazone–bromphenol blue indicator. Adjustment of the pH to 3.25 to 3.35 is necessary. Hydrogen is determined by the Blacet–Leighton procedure [5] using a portion of the gas as extracted in the determination of total gas (see below). Iron is determined by a spectrophotometric method using *o*-phenanthroline. Lithium is determined by a flame spectrophotometric method. Hydrazine is determined by a spectrophotometric method using *p*-dimethylaminebenzaldehyde in an acid solution. Dissolved oxygen is determined by the Winkler procedure [4] in which the permanganate, formed by treating the coolant water with manganese hydroxide, reacts with iodide. The iodine produced is titrated with sodium thiosulfate.

The solution of the crud and resin samples are discussed under the radiochemical determinations because the analyses performed on these materials are essentially radiochemical in nature.

Table 10.3—CARRIER SOLUTIONS

Carrier reagent, 10 mg/ml	Material and weight	Dissolve in and/or dilute with
Ammonium	NH_4Cl, 3 g	100 ml of water.
Antimony	Sb_2O_3, 1.20 g	100 ml of dilute HCl.
Arsenic	As_2O_5, 1.53 g	100 ml of dilute HCl.
Barium	$Ba(NO_3)_2$, 1.9 g	100 ml of water.
Bromine	KBr, 1.49 g	100 ml of water.
Cerium	$Ce(NO_3)_3 \cdot 6H_2O$, 3.10 g	100 ml of water.
Cesium	$CsNO_3$, 1.5 g	100 ml of water.
Chromium	$K_2Cr_2O_7$, 2.8 g	100 ml of water.
Cobalt	$CoCl_2 \cdot 6H_2O$, 4 g	10 ml of HCl and 90 ml of water.
Copper	Cu metal, 1 g	25 ml of HNO_3 and 75 ml of water.
Fluoride	NaF, 1.8 g	100 ml of water.
Iodide	KI, 1.3 g	100 ml of water.
Iron	*Fe metal powder*, 1 g	50 ml of HCl and 50 ml of water.
Lanthanum	La_2O_3, 1.2 g	50 ml of HNO_3 and 50 ml of water.
Manganese	MnO_2, 1.6 g	25 ml of HCl and 75 ml of water.
Nickel	Ni metal powder, 1 g	25 ml of HNO_3 and 75 ml of water.
Niobium	$K_8Nb_6O_{19} \cdot 16H_2O$, 2.6 g	Heat with HNO_3; dissolve oxide in 20 ml of saturated oxalic acid; make to 100 ml with water.
Palladium	$PdCl_2 \cdot 2H_2O$, 2 g	100 ml of water.
Potassium	KCl, 1.9 g	100 ml of water.
Rubidium	RbCl, 1.4 g	100 ml of water.
Sodium	NaCl, 2.542 g	100 ml of water.
Strontium	$Sr(NO_3)_2$, 2.4 g	100 ml of water.
Tantalum	Ta, 1.0 g	100 ml of water containing oxalic acid after dissolving in HNO_3 and HF and precipitating with NH_4OH.
Tellurium	TeO_2, 1.25 g	100 ml 4*N* HCl.
Tungsten	$Na_2WO_4 \cdot 2H_2O$, 1.8 g	100 ml of water.
Yttrium	Y_2O_3, 1.25 g	25 ml of HNO_3 and 75 ml of water.
Zirconium	$ZrO_2Cl_2 \cdot 8H_2O$, 3.54 g	5 ml of HF and 95 ml of water.

Determination of Total Gas (Volumetric). The extraction apparatus consists of a simple gas train employing a Toepler pump to transfer the gas to a measuring buret. The sample system is evacu-

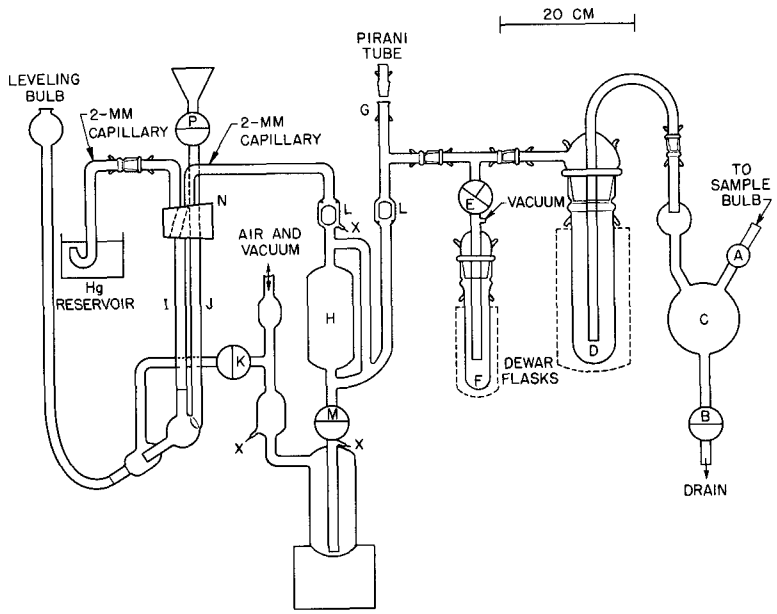


Fig. 10.1—Gas-extraction apparatus, *A*, sample inlet; *B*, stopcock to drain; *C*, water retainer; *D*, cold trap; *E*, *K*, *M*, *N*, *P*, stopcocks; *F*, vacuum cold trap; *G*, Pirani gauge connection; *H*, Toepler pump; *I*, gas buret to contain 5 ml in straight portion; *J*, air leg; *L*, check valves, mercury tight; *X*, Toepler-pump electrical leads.

ated, the sample is introduced, and the evolved gas is transferred and measured in a measuring buret.

Procedure. The Dewar flask around D in Fig. 10.1 is filled with a dry ice–trichloroethylene mixture. The Dewar flask around F is filled with liquid nitrogen. The Toepler pump, H, and the gas buret I are filled with mercury to the point that the tip of the capillary is covered by the mercury in the reservoir. The leveling bulb is in the raised position, with the tube to K filled with mercury. All stopcocks are closed except E, which is opened, and the system is evacuated to below 10^{-2} torr through the vacuum attachment tube below E. The pressure is measured on the Pirani gauge. Stopcock E is then closed.

The sample bomb containing the coolant sample is connected to A, and the system is evacuated by opening E and then slowly opening the sample-inlet cock, A. When pressure is again 10^{-2} torr or less, stopcock E is closed and the Toepler-pump stopcock, M, is opened. The Toepler-pump electrical connections are made. The sample bomb is inverted, and the sample is transferred by opening the sample bomb and allowing the sample to flow into the sample bulb. The sample inlet, A, is now closed. The gas evolves from the sample and the Toepler pump runs until the original pressure is obtained. The leveling bulb is lowered to the bottom, and the gas is transferred to the gas buret I through N, which is then closed as is the Toepler-pump stopcock, M. The leveling

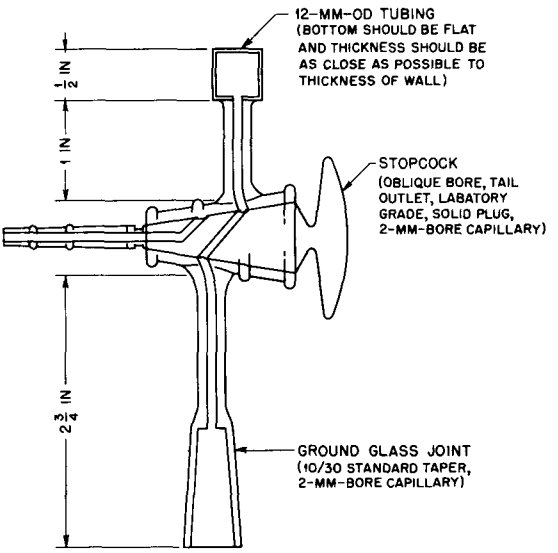


Fig. 10.2—Counting vessel for Ar^{41} and Xe^{133} determination.

bulb is raised to its initial position; and P, the air-leg stopcock, is opened. The leveling bulb is lowered so that the level in J is the same as the level in I, and the volume is measured. The barometric pressure and temperature are measured, and the gas per kilogram of sample is calculated. The gas sample is retained for subsequent analysis. The sample is collected in a Blacet–Leighton gas-analyzer thimble through the 2-mm side arm from the gas buret.

(b) *Radiochemical Analyses.* The radiochemical analyses performed are given below in alphabetical order.

(1) *Argon–41.* Argon–41 and fission gases such as Xe^{133} and Kr^{88} are radiological health hazards with respect to accessibility into the reactor compartment and inhalation. Under normal conditions the predominant gaseous activity will be due to Ar^{41}. The Ar^{41} analysis is performed manually in certain pressurized-water reactors. In the boiling-water reactor, a similar analysis is usually performed with in-line instrumentation.

Argon enters the primary coolant as a component of air, either entrapped in filling, or dissolved in make-up water. The activated Ar^{41} is removed from a water sample along with other gaseous products. Argon–41 has a gamma activity of 1.30 Mev.

Procedure. The gas is stripped from the water sample in a buret as described in Sec. 10–1.2(a). After the gas concentration has been measured, a portion of the gas is transferred to a Blacet–Leighton gas-analyzer thimble,[5] and the volume of the gas is measured. A counting vessel (see Fig. 10.2) is evacuated, and then the ground-glass joint is filled to the cock with mercury by suction applied through the side arm.

The sample in the Blacet-Leighton thimble is transferred to the counting chamber. Argon–41 activity is measured by means of a gamma-ray scintillation detector at a suitable distance to prevent overloading the counting apparatus. A pulse-height analysis is made to determine the count rate at the 1.3-Mev photopeak within 2 hr after sampling. A decay curve is constructed to determine the purity of the Ar^{41} by means of its 110-min half life. In an alternate procedure [6] a sample of the coolant is counted before and after removing gases by bubbling air through the sample.

(2) *Barium.* Barium and strontium occur as fission products. The barium activity is primarily composed of 85-min Ba^{139} and 12.8-day Ba^{140}. Both are beta and gamma emitters. Barium and strontium are precipitated as nitrates from fuming nitric acid, and barium is then separated from strontium by precipitation as barium chromate from an acetate-buffered solution.

Procedure. The sample is added to a centrifuge tube containing 2 ml of barium carrier solution and 2 ml of strontium carrier solution (see Table 10.3). Fuming nitric acid is added, and after digestion the solution is centrifuged. The residue is dissolved in water, and the barium and strontium are again precipitated with fuming nitric acid. The precipitate is dissolved in water; and, after the addition of 8 drops of an iron carrier (Table 10.3), ammonium hydroxide is added. After centrifugation the supernatant is acidified with 6*N* HNO_3 using methyl red as an indicator, and then 1 ml of 6*N* acetic acid and 2 ml of 6*N* ammonium acetate are added. After the resultant solution is heated to boiling, 1.5*M* potassium chromate is added dropwise until precipitation is complete. A couple of drops of Aerosol are added, and the solution is centrifuged. The barium chromate is dissolved in 6*N* HCl, a HCl–ether solution (4+1) is added, and after digestion the solution is centrifuged. The precipitated barium chloride is dissolved in water, and 1 ml of strontium carrier solution (Table 10.3) is added. After the addition of methyl red indicator, the solution is treated with 1 ml of 6*N* acetic acid and then 2 ml of 6*N* ammonium acetate. Potassium chromate is again added to precipitate barium chromate, and the solution is again centrifuged. (This time is noted.) The barium chromate is dissolved in 6*N* HCl and made up to 10 ml with water. Barium sulfate is precipitated from the near-boiling solution with 12*N* H_2SO_4. The barium sulfate is weighed and mounted for beta counting.

The Ba^{139} and Ba^{140} activities are determined with a beta proportional counter. The 85-min Ba^{139} is determined from its decay curve taken over a period of 1.5 hr. The 12.8-day Ba^{140} is determined from its decay curve, taken after the La^{140} has grown to equilibrium between the second and fourth weeks. The Ba^{139} activity must be corrected for the Ba^{140}–La^{140} activity by calculation of their respective degrees of decay and growth at the Ba^{139} counting times.

(3) *Bromine.* Bromine found in coolants after use will be composed principally of Br^{83} and Br^{84} with minor amounts of Br^{82}. Elemental iodine and bromine can be separated from fission elements by extraction into CCl_4. After reduction of these elements to bromide

and iodide, the iodide is oxidized to elemental iodine while the bromide is unaffected. After the iodine is extracted with CCl_4, the bromide is oxidized to elemental bromine with $KMnO_4$ after which it is extracted with CCl_4. Bromine is removed from the CCl_4 with $NH_2OH \cdot HCl$ and finally precipitated as AgBr.

Procedure. The sample is added to a centrifuge tube containing 10 ml of 2*M* Na_2CO_3, and 10 mg of bromide carrier solution and 10 mg of iodide carrier solution (Table 10.3) are added. A stream of H_2S is passed into the solution, and the excess H_2S is removed by boiling. The solution is transferred to a separatory funnel, and 10 ml of CCl_4 is added. After the solution has been acidified with HNO_3, 3 ml of 0.1*M* $NaNO_2$ is added, and the contents are shaken. The CCl_4 layer containing iodine is discarded. The extraction is repeated until the organic layer is colorless. A few drops of 1*M* $KMnO_4$ are added to the aqueous layer to oxidize the bromide, and the elemental bromine is extracted with CCl_4. The bromine is removed from the CCl_4 layer by adding 10 ml of H_2O followed by 1*M* $NaHSO_3$ to decolorize the organic phase. The oxidation and extraction is repeated. The aqueous layer is transferred to a centrifuge tube, and the bromide is precipitated with 2 ml of 0.1*M* $AgNO_3$. Two milliliters of HNO_3 is added, and the suspension is boiled. It is then filtered on a tared filter paper, washed with water and ethanol, dried in a vacuum, and weighed. The paper is then backed with a very thin plastic backing and counted either by beta or gamma counting for Br^{83} and Br^{84} or for Br^{84} by pulse-height analysis.

The bromine isotopes activity can be determined by means of a beta proportional counter. The Br^{84} activity may also be determined with a gamma-ray scintillation detector and a pulse-height analyzer. In the proportional counter the Br^{84} decay is determined by counting through a 440 mg/cm^2 aluminum absorber for a period of 2 hr. The Br^{83} is determined from its decay curve without an absorber for a period of 4 to 8 hr. Based on its decay curve, any Br^{82} is measured after 1 day if required. If a gamma-ray spectrometer is used for the Br^{84}, the decay curve is measured over the 0.87-Mev gamma-ray photopeak. Gamma pulse-height analysis for Br^{84} is made every 0.5 hr for 1.5 hr.

(4) *Cerium.* Cerium and the other rare earths are first separated as insoluble fluorides from the sample. The cerium is then oxidized to the quadrivalent state and extracted with methyl isobutyl ketone from an HNO_3 solution. This effectively separates cerium from the rare earths. After precipitation from alkaline earths with NH_4OH, the cerium is precipitated as oxalate from a nitric acid solution and then converted to oxide for weighing and counting.

Procedure. To the sample are added 20 mg of cerium carrier solution (Table 10.3), 5 ml HNO_3, and 1 ml of saturated $NaBrO_3$ solution. The solution is heated, and 30 per cent peroxide is added until the solution is light brown. The solution is heated to remove bromine, and 5 mg of zirconium carrier solution (Table 10.3) and 0.5 ml of HF are added. After it is centrifuged and washed, the precipitate is stirred with 2 ml of saturated H_3BO_3 and 5 ml of HNO_3; then 2 ml of 2*M* $NaBrO_3$ is added.

The cerium is extracted with 50 ml of methyl isobutyl ketone that has been equilibrated with 50 ml of 9*M* HNO_3 containing 2 ml of 2*M* $NaBrO_3$. The hexone layer is washed with 10 ml of 9*M* HNO_3 containing a few drops of 2*M* $NaBrO_3$. (The water layer is neutralized with NH_4OH and is either discarded or saved for the rare earth determination. This procedure is followed to prevent explosions due to decomposition of hexone in acid.)

The cerium is backwashed from the hexone with 5 ml of water containing a few drops of H_2O_2. The hexone is washed three times with water. The aqueous solution containing the cerium is made basic with NH_4OH. The precipitate is centrifuged down and redissolved by adding 6*N* HNO_3 and boiling the solution. The solution is neutralized, and 1 ml of 2 per cent HNO_3 is added. Saturated $(NH_4)_2C_2O_4$ is then added, and the solution is cooled in ice. The resultant precipitate is centrifuged, washed, and dissolved in 1 ml of 6*N* HNO_3. The solution is diluted to 15 ml, and the cerium is reprecipitated with ammonium oxalate. After centrifugation, the precipitate is transferred to a tared filter disk, washed with ethanol, dried in a vacuum dessicator, weighed, and mounted for beta counting.

The cerium activity is determined with a beta proportional counter. Cerium–144 is determined from an absorption curve of its Pr^{144} daughter, using aluminum absorbers with a density of 100 to 1600 mg/cm^2, at least 5 days after sampling to allow the Ce^{143} to decay to a low level. Cerium–141 may be determined from the difference between the total beta activity at zero absorber and the Ce^{144}–Pr^{144} total activity as estimated by comparison with a pure standard Ce^{144}–Pr^{144} absorption curve.

(5) *Cesium.* Cesium and rubidium are separated from interfering fission-product activity by means of sodium carbonate. The cesium is separated from rubidium as $Cs_2Bi_2I_9$ followed by a Cs_2PtCl_6 precipitation.

Procedure. To the sample are added 20 mg of cesium carrier solution and 5 mg each of rubidium, barium, strontium, and iron carrier solution (Table 10.3). The solution is neutralized with 12*N* NaOH, and 1 ml of 1*M* Na_2CO_3 is added; after this the precipitate formed is centrifuged and discarded. The solution is acidified with glacial acetic acid, keeping the volume to less than 15 ml, and 1 ml of HI–BiI_3 reagent (10 g BiI_3 per 50 ml of 55 per cent HI) is added. The solution is cooled in an ice bath, the precipitate is centrifuged, and the supernatant is discarded. The precipitate is washed with 1 ml of 2*N* HCl and 7 ml of water, and after seperation the supernatant is discarded. The precipitate is dissolved in 2 drops of 12*N* NaOH and 5 ml of water; the mixture is centrifuged and the supernatant is transferred to another centrifuge tube. Five milliliters of HNO_3 is added to the supernatant, and the solution is boiled to expel iodine. After cooling in an ice bath, 10 ml of ethanol and 10 drops of 10 per cent $H_2P_2Cl_6$ are added. After centrifugation, the precipitate is washed with ethanol and transferred to a tared filter paper. It is then vacuum dried, weighed, and counted.

Cesium–138 is resolved from residual Cs^{139} by a decay curve of beta activity measured over a period of 1½ hr through a 300 mg/cm^2 aluminum absorber. The Cs^{139} is determined in a separate procedure.

A beta decay curve of the long-lived isotopes Cs^{136} and Cs^{137} is made without an absorber over a period of a week. A gamma-ray spectrum taken the day following the preparation of the sample is used to determine the ratio of the activity of the Cs^{136} and Cs^{137}. The Cs^{134} is not considered.

The specific activity of Cs^{139} is determined by analyzing for the Ba^{139} daughter activity that grows in. The barium is initially scavanged by precipitation as the carbonate. The cesium is then allowed to decay for a specified time, and the barium that grew in is separated.

Procedure. The sample is added to a centrifuge cone containing 20 mg of barium and 20 mg of cesium carrier solution, (Table 10.3). The barium is precipitated with $2M$ Na_2CO_3, and the time is recorded. The precipitate is centrifuged and discarded, and 20 mg of barium carrier (Table 10.3) is added to the supernatant. The solution is acidified with $6N$ HNO_3 and allowed to stand 35 min. The barium is precipitated with $2M$ Na_2CO_3, and the time for precipitation is recorded. The precipitate is dissolved in $6N$ HNO_3 and water, and the procedure as indicated under barium is followed to complete the determination.

The Ba^{139} activity is measured by means of a beta proportional counter from a decay curve as of the time of the second separation from the Cs^{139}. The Cs^{139} activity is corrected for decay to the original sampling time, taking into account the limited growth of the Ba^{139} and the rapid decay of the Cs^{139} during the 35 min between the first and second separation of the barium.

(6) *Chromium.* Chromium is separated from fission and activation products by a $BaCrO_4$ precipitation and an ether extraction of CrO_5. Radiobarium is separated by a $BaSO_4$ precipitation. The chromium is then precipitated as $BaCrO_4$ for weighing and counting.

Procedure. To an Erlenmeyer flask are added 40 mg of chromium carrier solution (Table 10.3), the sample, and 0.5 ml of HNO_3, after which the solution is evaporated to dryness. After the residue is taken up in 1 ml of HNO_3 and 5 ml of H_2O, 3 ml of saturated $NaBrO_3$ solution is added, and the solution is heated to oxidize the Cr^{3+} to $Cr_2O_7^{-2}$. The solution is then transferred to a centrifuge cone and made basic with NH_4OH. Then 0.1 ml of iron carrier solution is added (Table 10.3), after which the solution is centrifuged. The supernatant is evaporated to one-half its volume and then acidified with HNO_3. To this solution is added $1M$ $NaNO_2$ until the $Cr_2O_7^{+2}$ is reduced to Cr^{+3}. Excess NO_2^- is removed by heating, and NH_4OH is added until $Cr(OH)_3$ precipitates. Excess NH_4OH is removed by heating. The solution is centrifuged, the supernatant is discarded, and the precipitate is washed with H_2O. After dissolution in HCl and reprecipitation with NH_4OH, the $Cr(OH)_3$ is dissolved in 5 drops of HNO_3, the solution is diluted to 15 ml, and 3 ml of saturated $NaBrO_3$ solution is added. The chromium is precipitated with a saturated solution of $Ba(NO_3)_2$. To the solution are added 2 ml of $6M$ ammonium acetate and 1 ml of $6M$ acetic acid. The solution is centrifuged, and the supernatant is discarded. The washed precipitate is dissolved in 5 drops of HCl and 10 ml of water. A volume of 1 to 2 ml of saturated $NaBrO_3$ is added. The solution is cooled, a few drops

of cold H_2O_2 are added, and the CrO_5 is extracted with 90 ml of cold ethyl ether. The ether layer is washed with 10 ml of H_2O containing 3 ml of HCl per liter. The chromium is back-extracted into water by shaking the ether layer with 15 ml of H_2O containing 3 to 4 drops of NH_4OH. After being transferred to a centrifuge tube, the solution is warmed in a water bath to remove ether; and 2 ml of 6*M* ammonium acetate and 1 ml of 6*M* acetic acid are added. The solution is heated to boiling, and the $BaCrO_4$ is precipitated with saturated $Ba(NO_3)_2$. The solution is centrifuged, the supernatant is discarded, and the precipitate is washed with water. The precipitate is transferred to a weighed filter paper, washed with water and ethanol, and dried at 110°C. It is then weighed and mounted for counting.

The 0.32-Mev gamma ray of Cr^{51} is measured by means of a gamma-ray scintillation spectrometer and the peak-integration method or a spectrum stripping technique.

(7) *Crud and Ion-exchange-resin Solution.* Crud is the jargon applied to the insoluble corrosion products that flake off metal surfaces and are transported through a cooling system. The name, however, has been used to such an extent that its use has become almost universal. In some instances [6] the coolant is removed from the system and filtered to obtain the crud, whereas in others the coolant is passed through a crud probe that filters out the crud in the influent and effluent water of the demineralizer. The major radionuclides in the crud are given in Table 10.1. The resin from the demineralizer contains both crud and resin; and, when the analysis of the resin alone is required, a separation is necessary. This separation is made by taking advantage of the magnetic properties of the crud.

Since the crud consists chiefly of insoluble corrosion products that may be activated by the means indicated in the introduction to this chapter, the chief problem is in the dissolution and separation of the elements found in the crud.

The resin bed contains soluble radioactive elements removed from the coolant in addition to some of the elements found in the crud.

After separation of the resin and crud, they are put into solution and the radio assays of the various isotopes are made as outlined.

Separation of Resin and Crud. The sample of the resin and crud is transferred to a graduated cylinder, the resin is allowed to settle, and its volume is measured. The mixture is then transferred to a beaker with water, stirred with a power stirrer, and a strong magnet is placed near one side of the beaker to attract the crud. The water and crud are decanted through a filter paper in a Büchner funnel. The resin is again wet with water and stirred. More water is added and the procedure above is repeated. Sufficient acetone to cover the resin is added, and it is stirred vigorously to knock the crud off the resin. More acetone is added, and the crud is separated with a magnet as described above except that the crud around the glass near the magnet

is separated with a dropper. The crud and acetone are decanted and filtered through the same filter paper as used before.

Dissolution of the Crud. The crud from the crud filter probe or from the resin bed is transferred to a porcelain crucible and ignited over a Meker burner at red heat. A 0.5-g sample of crud is weighed and counted in a platinum planchet after a few drops of 2 per cent Zapon are added to the sample and the planchet is backed with aluminum.

The rest of the crud sample is treated with 50 ml of fuming HNO_3 and 20 ml of $HClO_4$ in a beaker, and the mixture is fumed to a volume of 5 ml. After the cooled solution is taken up in 6*N* HCl, it is filtered and washed, with the filtrate and the washings being collected in a polyethylene bottle. One milliliter of HF is added to the bottle. The beaker is washed with 3*N* HF, and the washings are transferred to a platinum crucible. The residue and filter is again treated with 50 ml of fuming HNO_3 and 20 ml of $HClO_4$ in a beaker. The solution and residue is transferred to a centrifuge tube with 6*N* HCl and is then centrifuged. The supernatant is decanted into the polyethylene bottle, and the residue in the centrifuge tube is transferred to the platinum crucible with 3*N* HF and 2*N* $HClO_4$. The contents of the crucible are evaporated to fumes and cooled; then 3 ml of HF is added, after which the solution is again fumed. After the contents of the crucible is taken up in 6*N* HCl, any residue remaining is retreated as above and finally fused with Na_2CO_3 and dissolved in 6*N* HCl. All solutions are transferred to the original polyethylene bottle and made up to 100 or 200 ml. This combined solution is used for the necessary radioisotopic analysis.

Dissolution of Ion-exchange Resin. The ion-exchange resin may be decomposed by wet combustion or ignition. In the wet ashing method, H_2SO_4 and HNO_3 are used. Any residue is decomposed with HF and H_2SO_4. The final filtered solution is made to 3*M* in HCl. In the ignition method the resin is ignited at a final temperature of 800°C, and the residue is taken up in HNO_3 and $HClO_4$, and the solution is fumed. After the addition of water, any residue is decomposed by fuming with HF, HNO_3, and $HClO_4$. The solution is made up to 3*M* in HCl as above.

(8) *Cobalt.* The reactions $Ni^{58}(n,p)Co^{58}$ and $Co^{59}(n,\gamma)Co^{60}$ are responsible for the radioactive cobalt present in the sample. The precipitation of cobalt as potassium cobaltinitrite has proved satisfactory. Additional decontamination is obtained by the extraction of the cobalt thiocyanate complex into amyl alcohol. Cobalt is precipitated as sulfide, oxidized with HNO_3, and finally reprecipitated with KOH.

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Procedure. To the sample in a centrifuge tube are added 20 mg of cobalt carrier solution and 10 mg of nickel carrier solution (Table 10.3), and the solution is treated with 10*N* KOH. The precipitate is centrifuged and washed and the supernatant is discarded. The precipitate is dissolved with 3 ml of 6*N* acetic acid; and, after the solution is diluted to 25 ml, the cobalt is precipitated with 6 ml of KNO_2–acetic acid reagent (3*N* acetic acid saturated with KNO_2). The precipitate is allowed to digest for 20 min, and then it is centrifuged and washed with water. The supernatant is discarded. The precipitate is dissolved in 2 ml of HCl, the solution is boiled to near dryness, and 10 mg of nickel carrier solution is added (Table 10.3). A precipitation is made with 10*N* KOH. The precipitate is centrifuged and washed. After the dissolution and precipitation of the cobaltinitrite is repeated, the $K_3Co(NO_2)_6$ is dissolved in 5 ml of HCl, and the solution is evaporated to near dryness. To the residue are added 5 mg of palladium carrier solution and 5 mg of copper carrier solution (Table 10.3). The solution is diluted to 20 ml with 0.1*N* HCl, heated, and H_2S is passed into it. The sulfide is centrifuged, and the filtrate is collected in a centrifuge cone. Palladium and copper carrier solutions are added as above, and the precipitation is repeated.

The solution is evaporated to near dryness, diluted to 25 ml, and 10 mg of iron carrier solution (Table 10.3) and 0.5 ml of HCl are added. The iron is precipitated with NH_4OH. The solution is centrifuged, and the precipitate is discarded. The supernatant is acidified with HCl, iron carrier solution is added, and the precipitation is repeated. A third iron precipitation also is made. The supernatant is acidified to about 1*N* in HCl and 15 g of ammonium thiocyanate is added. The thiocyanate complex of cobalt is extracted into 50 ml of (1+1) amyl alcohol–ethyl ether mixture. The organic layer is washed with ammonium thiocyanate solution (1 g in 2 ml of H_2O). The cobalt is back-extracted into 20 ml of H_2O containing 6 ml of NH_4OH. The aqueous layer is transferred to a centrifuge cone, and CoS is precipitated with H_2S. The precipitate of CoS is dissolved in 3 ml of HNO_3, the solution is boiled and diluted to 10 ml, and then 1 g of KNO_2 is added, after which the cobalt is precipitated with 10*N* KOH. The precipitate is filtered and ignited in a porcelain crucible at 700°C. The residue is transferred to a tared filter disk, weighed, and mounted for counting.

A gamma-ray scintillation spectrometer is used to measure simultaneously and to resolve the 0.51-Mev positron annihilation radiation from Co^{58} and the 1.17- and 1.33-Mev gamma rays from Co^{60}. A peak-integration technique or a spectrum stripping technique is used to estimate the amount of each isotope.

(9) *Fifteen-minute Activity.* The activity levels of a primary coolant sample or a degassed sample from a pressurized-water reactor and a boiling-water reactor 15 min after sampling indicate the short-lived radioactive level in the coolant and determine accessibility to the reactor compartment shortly after reactor shutdown. In addition, samples taken upstream and downstream of the primary coolant demineralizer determine the efficiency of the ion-exchange resin. The boiling-water-reactor primary coolant samples taken before and after condensation indicate the activity carry-over. The sample is counted

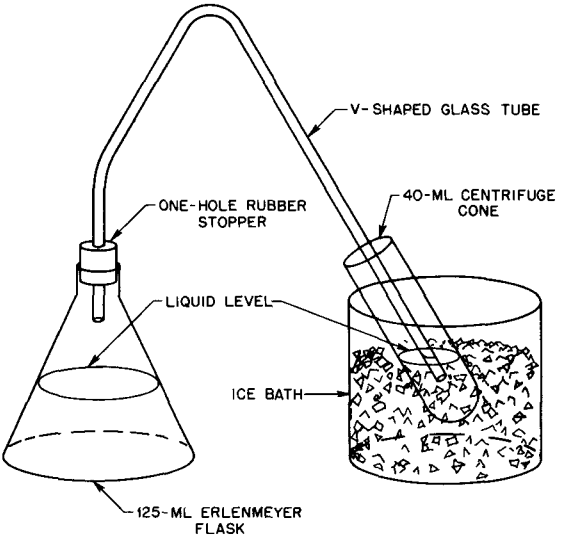


Fig. 10.3—Fluoride distilling apparatus.

in a well counter or is dried and counted in a Geiger–Mueller counter. The level of short-lived activity in the ion-exchange influent and effluent is determined by well-counting a water sample as soon after sampling as is practicable. The sample is counted after each of four successive 15-min intervals.

(10) *Fluorine–18.* Fluorine is separated from halides by the precipitation of the insoluble chlorides, bromides, and iodides with silver. The fluorine is then precipitated as lanthanum fluoride.

Procedure. To the sample are added 10 mg of fluoride carrier solution, 10 mg of iodide carrier solution (Table 10.3), and 0.3*M* $AgNO_3$ to precipitate the iodide. The precipitate is centrifuged down, the supernatant is transferred to the still shown in Fig. 10.3, and 50 ml of H_2SO_4 is added. The distillate formed by heating the solution to fumes is collected in a solution containing 50 mg of lanthanum carrier (Table 10.3). The LaF_3 precipitate is filtered on a weighed glass-fiber filter, washed with alcohol and ether, and weighed. The sample is then counted.

Fluorine–18 activity is measured either with a beta proportional counter or a gamma-ray scintillation spectrometer using the 0.51-Mev annihilation radiation. The activity is followed for 1 hr, and a decay curve is constructed. The curve is extrapolated to sampling time.

(11) *Iodine Activity (Gross and* I^{131} *and* I^{133}). The gross-iodine procedure is used to supplement in-line fission-product monitors in the pressurized-water reactor and the boiling-water reactor. The iodine activity levels indicate total fission-products levels. High

levels may limit discharge of primary coolant and may indicate a fuel-element failure. The gross-iodine activity consists chiefly of I^{131} with small amount of I^{133}. The activity of both these nuclides can be determined if desired.

Iodine is effectively separated from other fission products by the extraction of elemental iodine into CCl_4. Separation of iodine from bromine is accomplished by reduction of BrO_3^- and IO_3^- to Br^- and I_2. The elemental iodine is then extracted in CCl_4.

Procedure. Into a separatory funnel are placed the sample, 20 mg of iodine carrier solution, and 20 ml of bromine carrier solution (Table 10.3). The solution is made basic with 5 ml of 2*M* Na_2CO_3. To the solution is added 1 ml of a 5 per cent sodium hypochlorite solution. After the solution is acidified with HNO_3, 3 ml of 1*M* hydroxylamine hydrochloride solution is added, and iodine is extracted with CCl_4. The CCl_4 layer is shaken with 10 ml of water containing a few drops of 1*M* $NaHSO_3$. The CCl_4 is discarded. To the aqueous layer is added 1 ml of 6*N* HNO_3 and a few drops of 1*M* $NaNO_2$. The iodine is extracted with 10 ml of CCl_4. The iodine in the CCl_4 layer is extracted into water with 5 ml of water containing a few drops of 1*M* $NaHSO_3$. The water layer is diluted to 50 ml, and 2 ml is placed in a vial for counting. Two milliliters of the remaining solution is transferred to an Erlenmeyer flask, and 10 ml of water and 5 ml of HNO_3 are added. After a known amount (10 ml) of standardized 0.01*M* $AgNO_3$ and 1 ml of saturated ferric alum in 1*N* HNO_3 are added, the excess silver is titrated with 0.01*M* KSCN.

Because, in the determination of iodine in the resin, the ignition of the resin results in loss of iodine, it is necessary to analyze the dried resin. The analysis is done by adding 20 mg of iodine carrier (Table 10.3) and 10 ml of 2*M* Na_2CO_3 followed by 1 ml of a 5 per cent NaClO solution. After the solution is heated in a hot-water bath, it is filtered and the procedure is carried out as described above.

The nuclides I^{131} and I^{133} are measured by means of a gamma-ray scintillation spectrometer and the peak-integration method or the spectrum stripping method. A decay curve of each gamma count rate taken over a period of several days is used to estimate the count rate at sampling time.

(12) *Iron.* Iron is separated from fission products by a sulfide precipitation from a tartrate solution followed by an anion-exchange separation. The iron is finally extracted into isopropyl ether.

Procedure. To the sample are added 10 mg of iron carrier solution (Table 10.3) and 2 ml of saturated tartaric acid solution. The solution is made basic with NH_4OH and saturated with H_2S. The precipitate is centrifuged and then washed with dilute NH_4OH saturated with NH_4NO_3. The sulfide precipitate is dissolved in 0.5 ml of HCl, the H_2S is removed by boiling, and the solution is evaporated to near dryness after the addition of 0.5 ml HNO_3 and 2 ml HCl. The residue is dissolved in 10 ml HCl and poured onto a Dowex-1 anion resin column (1X8, 50 to 100 mesh in a 8-cm by 13-mm tube) previously equilibrated with 10 ml of HCl. The solution is allowed to run through the column, and the resin is washed with 10 ml of HCl followed by 15 ml of 6*N* HCl.

The iron is eluted from the resin with 10 ml of 0.5*N* HCl. To the effluent are added 5 mg of copper carrier solution and a drop each of antimony, arsenic, and tellurium carrier solutions (Table 10.3); and the volume is made to 20 ml with 0.5*N* HCl. The solution is saturated with H_2S; and after centrifugation the supernatant is treated with 2 ml of saturated tartaric acid solution, made basic with 6*N* NH_4OH, and saturated with H_2S. The precipitate is washed again with NH_4OH saturated with NH_4NO_3 as before. The precipitate is dissolved in HCl and then evaporated to dryness. The residue is transferred with 10 ml of 8*N* HCl to a separatory funnel, and 30 ml of isopropyl ether is used to extract the iron. The iron is transferred to the aqueous phase with 10 ml of water. The solution is again precipitated with H_2S from a tartrate solution and reextracted as above. After two more extractions as above, the final sulfide precipitate is washed with acetone and ignited in a porcelain crucible. It is then transferred to a tared filter disk, weighed, mounted, and counted.

The Fe^{59} can be counted by either a beta proportional counter or a gamma-ray scintillation spectrometer. The gamma-ray peaks may be evaluated either by the peak-integration method or the spectrum stripping method.

(13) *Krypton–88.* The activity of the Kr^{88} is determined by measuring the amount of its Rb^{88} daughter that grows in over a 6-hr period. The rubidium is purified by an iron scavenge and precipitated as the chloroplatinate.

Procedure. Six hours after the sample is taken, an aliquot is pipetted into a centrifuge tube, and 20 mg of rubidium carrier solution and 5 mg of iron carrier solution (Table 10.3) are added. The iron is precipitated with 6*N* NaOH. After the solution is centrifuged, the supernatant is acidified with 6*N* HCl, and 1 ml of 0.5*M* H_2PtCl_6 and 10 ml of ethanol are added. The precipitate is washed with ethanol, transferred to a tared filter disk, weighed, mounted, and counted.

The Rb^{88} activity is measured by means of a beta proportional counter and is corrected back to the end of the Rb^{88} growth period by means of a decay curve. The Rb^{88} growth is calculated for the time allowed, and the Kr^{88} is corrected for its decay since the original sampling time.

(14) *Molybdenum.* The radioactive contaminants of concern in the molybdenum determination are those associated with molybdenum in the decay chain strontium–yttrium–zirconium–niobium–molybdenum–technetium. An effective separation from strontium–yttrium–zirconium–niobium is made by an anion-exchange process. Molybdenum is absorbed in the hexavalent state, strontium and yttrium pass through the column, and zirconium is absorbed. Zirconium is eluted with dilute HCl prior to removal of the molybdenum with dilute NH_4OH. α-Benzoin oxime is used to separate the molybdenum from niobium in an oxalate solution.

Procedure. To the sample are added 20 mg of molybdenum carrier solution (Table 10.3) and 5 ml of fuming HNO_3, after which the solution

is evaporated to dryness. Two milliliters of HCl is added, and the solution is again evaporated to dryness. This step is repeated. The residue is taken up in ice-cold HCl saturated with HCl gas, and the resultant molybdenum solution is poured onto a Dowex 1 anion resin (1X8, 50 to 100 mesh in a 10-cm by 13-mm tube) that has been converted to the acid form with HCl. The resin column is treated with 15 ml of 4*N* HCl followed by 15 ml of water. The molybdenum is eluted from the column with 3*N* NH_4OH into a centrifuge tube, 5 mg of iron carrier solution (Table 10.3) is added; and, after the solution is centrifuged, the supernatant is acidified with HNO_3 (methyl red end point). One milliliter of saturated oxalic acid, 6 drops of bromine water, and 10 ml of α-benzoin oxime reagent are added. The time of the α-benzoin oxime addition is noted. After it is cooled in an ice bath, the precipitate is removed by centrifugation. The precipitate is transferred to a porcelain crucible, ignited at 500°C, cooled, transferred to a tared filter paper with ethyl alcohol, dried, weighed, and then mounted for counting.

The Mo^{99} activity may be measured using a beta proportional counter and a decay curve taken over a period of 7 days. A gamma scintillation counter may also be used, but a wait of 24 hr is necessary to allow the Tc^{99} activity to grow in.

(15) *Niobium–95.* Niobium is separated from other fission products by extraction of the fluo complex into tributyl phosphate (TBP).

Procedure. To 3 ml of niobium carrier solution (Table 10.3) are added 3 ml of HF, the sample, which should be 4*M* in HCl, 10 mg of zirconium carrier solution (Table 10.3), and saturated $Ba(NO_3)_2$ to precipitate $BaZrF_6$. After centrifugation, the supernatant is treated with an additional 10 mg of zirconium carrier, and the $BaZrF_6$ precipitation is repeated. The precipitate is discarded. The supernatant is treated with 2 ml of saturated H_3BO_3, 20 ml of HNO_3, and 0.5 g of $KBrO_3$, and the solution is heated. Additional $KBrO_3$ in three steps is added with the solution being heated between additions. The solution is evaporated somewhat, centrifuged, and the supernatant is discarded. The precipitate is washed with hot 2 per cent NH_4NO_3. After transferring to a polyethylene centrifuge tube, the precipitate is dissolved in 2 ml of 40 per cent HF and 3 ml of 12*M* H_2SO_4. Five milliliters of TBP is added, the solution is stirred and the organic layer is separated by centrifuging. The TBP layer is treated with 5 ml of petroleum ether and 5 ml of NH_4OH. After centrifugation the aqueous layer is washed with petroleum ether, and the precipitate is centrifuged and washed with hot 2 per cent NH_4NO_3. The precipitate is transferred to a filter paper and ignited at 800°C in a weighed crucible. The residue is transferred to a counting mount. The weight is obtained by reweighing the crucible.

The Nb^{95} activity is measured by means of a gamma-ray scintillation spectrometer, and the peak-integration method or the spectrum stripping method is used on the 0.76-Mev photopeak.

(16) *Nitrogen–13.* Nitrogen–13 is separated by a Kjeldahl distillation procedure followed by a precipitation of ammonium chloroplatinate.

Procedure. To the sample is added 10 mg of ammonium carrier solution (Table 10.3), and the ammonium is distilled from the solution in a micro-Kjeldahl apparatus after the addition of NaOH. The evolved ammonia is collected in a centrifuge tube containing 2 ml of 5 per cent H_2PtCl_6 and 20 ml of ethanol. The precipitate is filtered on a weighed glass-fiber filter, washed with ethanol and ether, weighed, and mounted.

The N^{13} activity is measured either with a beta proportional counter or a gamma-ray scintillation spectrometer using the 0.51-Mev annihilation radiation. The activity is followed for 1 hr, and a decay curve is constructed. The curve is extrapolated to sampling time.

(17) *Potassium–42.* Potassium–42 activity arises from neutron irradiation of the $KrCrO_4$ used as a corrosion inhibitor. Potassium is separated by the precipitation of the tetraphenylboron derivative.

Procedure. To the sample in a centrifuge cone is added sufficient HCl to make the solution 0.2*N* in HCl. Twenty milliliters of 6 per cent sodium tetraphenylboron solution is added; and, after these materials are stirred, the precipitate is separated. The precipitate is dissolved in acetone, the solution is diluted with alcohol, and the potassium is reprecipitated. The precipitate is transferred to a tared filter disk, weighed, mounted, and counted.

The K^{42} activity is determined with a beta proportional counter by means of a decay curve taken over a period of several days.

(18) *One Hundred and Twenty-hour Degassed Activity.* The gross activity or degassed activity of a primary coolant sample from a pressurized-water reactor or a boiling-water reactor 120 hr (5 days) after sampling is from those radionuclides having half lives of the order of days and years. This activity level builds up to an equilibrium value during normal plant operation and is significant in limiting prolonged access to the reactor compartment after shutdown. The method serves as an indication of increases in corrosion product or fission-product activity. The sample from the 15-min activity analysis is allowed to decay for 120 hr and is then counted.

(19) *Rare Earths (Especially Europium).* Europium, which may be present when europium control rods are used, is separated with other rare earths by precipitation with HF in the same manner as is cerium. The rare earths are recovered from the aqueous phase after the extraction of cerium with hexone.

Procedure. The procedure as outlined for cerium is followed to the extraction step. To the aqueous layer and washings is added 10 mg of lanthanum carrier solution (Table 10.3), and the rare earths are precipitated with NH_4OH. The precipitate is washed with 5 per cent NH_4OH containing 5 per cent NH_4NO_3. The washed precipitate is dissolved in HNO_3 and the excess HNO_3 is neutralized with dilute NH_4OH. To the solution is added 10 ml of saturated oxalic solution. The precipitate is washed with water and transferred to a weighed filter disk. Then the precipitate is washed with ethanol and ether and the disk is weighed and counted.

If it is assumed that the predominant activity is due to Eu^{152} and Eu^{154}, the sample activity can be determined by using a gamma-ray scintillation spectrometer and either the peak-integration method or the spectrum stripping method. Visual inspection of the spectrum should indicate if any significant contamination by other rare earths is present.

(20) *Sodium–24.* Sodium is separated as the chloride after scavenging the solution with strontium, lanthanum, and iron carriers.

Procedure. To the sample are added 20 mg of sodium carrier solution, 5 drops each of strontium, lanthanum, and iron carrier solutions (Table 10.3), and a saturated solution of $(NH_4)_2CO_3$. The precipitate is centrifuged down, and the supernatant is treated with 2 ml of HCl and evaporated to dryness. The residue is dissolved in water, 10 ml of HCl and 10 ml of ether are added, and the solution is cooled in an ice bath. The precipitate is centrifuged down and dissolved with water, and HCl and ether are added as above. The final NaCl precipitate is filtered on a weighed glass-fiber filter, washed with ether, and weighed. The sample is then counted.

The activity of Na^{24} can be determined with either a beta proportional counter or a gamma-ray scintillation spectrometer. When using the gamma-ray spectrometer, the peak-integration method is used on the 2.75-Mev photopeak. A decay curve is taken over a period of several hours and extrapolated back to sampling time.

(21) *Strontium–89.* Barium and strontium are the important alkaline-earth fission products. Both are separated by precipitation of the nitrate from fuming HNO_3. An iron scavenge is used to separate yttrium and lanthanum daughters. Barium is separated from strontium by precipitation as the chromate.

Procedure. Into a centrifuge tube are added 20 mg of strontium carrier solution, 20 mg of barium carrier solution (Table 10.3), and the sample. The solution is evaporated to less than 5 ml and cooled; then 50 ml of fuming HNO_3 is added. After the solution is cooled and centrifuged, the precipitate is dissolved in 2 ml of H_2O. After this solution is cooled, 20 ml of fuming HNO_3 is added, the solution is again cooled, and the precipitate formed is centrifuged. The precipitate is dissolved in 10 ml of H_2O; 4 drops of iron carrier solution (Table 10.3) are added; and, after the solution is heated to boiling, CO_2-free NH_4OH is added to the phenolphthalein end point. After centrifugation the supernatant is transferred to another centrifuge cone and the time for zero Y^{90} separation is noted. After the supernatant is acidified with $6M$ HNO_3, 2 ml of $6M$ NH_4OAc and 1 ml $6M$ HOAc are added. The solution is heated to boiling, and 2 ml of $1.5M$ $K_2Cr_2O_7$ is added. After a centrifuging step, the supernatant is transferred to a beaker, and 2 ml NH_4OH is added. After this solution is heated to the boiling point, 20 ml of saturated $(NH_4)_2CO_3$ solution is added. After the solution is cooled the $SrCO_3$ formed is transferred to a weighed filter paper. The precipitate is washed with water and then with ethanol. After the precipitate is dried at 110°C, the paper and its contents are weighed, mounted, and cooled.

Strontium–89 activity is measured with a beta proportional counter. The growth of the Y^{90}, which grows in from Sr^{90}, and the decay of Sr^{89} are followed for a period of 1 week. The decay curve must be corrected for the Sr^{90}–Y^{90} activity by performing a Y^{90} separation at the end of this period as given under Sr^{90}.

(22) *Strontium–90.* The yttrium daughter is separated as the oxalate from a sample of Sr^{90} after a period of 2 weeks.

Procedure. The filter paper from the separation as given in the procedure for Sr^{89} that has aged for 2 or more weeks is ignited and the residue is dissolved in 6*N* HNO_3. After the solution is evaporated to near dryness, 20 mg of yttrium carrier solution (Table 10.3) and 5 ml of fuming HNO_3 are added. The solution is evaporated to near dryness, and 10 ml of saturated Na_2CO_3 and 1 g of solid Na_2CO_3 are added. After this solution is boiled, the precipitate formed is centrifuged and dissolved in 6*N* HNO_3. The solution is diluted to 10 ml and $Y(OH)_3$ is precipitated with NH_4OH. After a centrifuging step, the precipitate is dissolved in 2 ml of 6*N* HCl. This solution is diluted to 15 ml, and 20 ml of saturated $(NH_4)_2C_2O_4$ is added to the hot solution. The $Y_2(C_2O_2)_3$ is centrifuged down, and the precipitate is transferred to a filter paper and washed with alcohol and ether. The filter paper and its contents are ignited in a muffle furnace. The Y_2O_3 is transferred to a tared filter paper with methanol, dried, weighed, and counted.

The activity of Y^{90} is simply measured with a beta proportional counter, and a decay curve is taken over a period of several days.

(23) *Tantalum.* Tantalum and niobium are separated from other fission products by precipitation of the hydrated oxide. The tantalum is then separated from niobium by extraction of the fluo complex into diisopropylketone.

Procedure. The sample is added to 20 mg of tantalum carrier solution (Table 10.3) containing 1 ml of HF. One gram of solid NH_4NO_3 and 5 drops of 1 per cent $Fe(NO_3)_3$ solution are added, and the solution is made basic with NH_4OH. After a centrifuging step, the precipitate is washed by heating with HNO_3. The precipitate is dissolved in a small volume of 12*N* H_2SO_4 which is 0.4*N* in HF. The solution is extracted with 10 ml of diisopropylketone (DIPK), and the DIPK layer is washed with a 2-ml portion of the H_2SO_4–HF mixture. To the organic layer is added 10 ml of H_2O; and the layers are separated by centrifuging after they have been shaken vigorously. The contents of the centrifuge tube are poured into the original separatory funnel, and the aqueous layer is collected in a centrifuge cone. A second extraction with 10 ml of water is made, and this aqueous layer is added to the first one. The aqueous solution is made basic with NH_4OH, and the precipitate is separated by centrifuging. The precipitate is washed with 10 ml of hot HNO_3. The residue is treated twice more with the H_2SO_4–HF mixture, and the extraction with DIPK is repeated.

The final precipitate is transferred to a filter with the aid of 10 ml of absolute methanol and is then ignited at 900°C. The Ta_2O_5 is ground with 1 ml of methanol and transferred to a weighed platinum disk. A couple of drops of HF are added, and the disk is ignited over a Meker burner. It is then cooled, weighed, and counted.

The tantalum activities are counted with a gamma-ray scintillation counter. A decay curve taken over a period of 2 weeks is used to resolve the Ta^{182} and the Ta^{183}. Both are extrapolated back to sampling time, and the amounts of each are calculated.

(24) *Tellurium.* Tellurium is separated as the element after the removal of selenium by volatilization with HBr.

Procedure. To the sample are added 10 mg of tellurium carrier solution (Table 10.3) and then 10 ml of HBr. The beaker is covered with a watch glass and heated on a hot plate to near dryness. The HBr treatment is repeated twice using 5 ml of HBr. The residue is taken up in 5 ml of 3*N* HCl and then transferred to a centrifuge cone. The solution is made basic with 6*N* NaOH, and 2 mg of iron carrier solution (Table 10.3) is added. The solution is centrifuged, and the supernatant is made 3*N* in HCl and heated. Solid sodium bisulfite is added until no more black precipitate forms. A few drops of 1 percent Aerosol solution are added; and, after it is centrifuged and washed with 5 ml of H_2O, the precipitate is dissolved in HCl and HNO_3 and evaporated to dryness. The residue is dissolved in 10 ml of hot H_2O, and 6*N* NaOH is added until a white precipitate appears. Then 10 drops of the NaOH are added in excess. An additional 2 mg of iron carrier solution is added, and the solution is centrifuged. The supernatant is adjusted to 3*N* in HCl and then heated. Solid $NaHSO_3$ is added to precipitate the tellurium. The time of bisufite addition is noted. After it is washed with H_2O and ethanol, the residue is weighed, mounted, and counted.

The Te^{132} and I^{132} activities are measured with a beta proportional counter after a wait of 20 hr for the I^{132} to approach equilibrium. The counting is continued for 2 hr to obtain a decay curve for the Te^{132} and is extrapolated back to sampling time.

(25) *Tritium.* In certain instances the determination of tritium is desired. The sample of coolant water is dropped onto metallic calcium. The evolved hydrogen and tritium are collected in a Geiger–Muller tube, to which subsequently ethylene and argon are added. The sample tube is counted simultaneously with another tube containing inert hydrogen. The detailed procedure is given in Ref. 7.

(26) *Xenon–133.* The radioactive gases xenon, krypton, and argon, as well as inert hydrogen and nitrogen, are stripped from the coolant. The gas mixture is then counted.

Procedure. The gaseous components of the coolant are stripped and collected in the gas buret of the gas-extraction apparatus as given in Sec. 10–1.2(a). A measured amount of gas sample is transferred to the counting chamber as given for the Ar^{41} determination described in Sec. 10–1.2(b)(1). The sample in the counting chamber is stored under water for 1 week to permit decay of short-lived krypton and argon. The sample is then counted.

The Xe^{133} activity is measured by means of a gamma-ray scintillation detector and a pulse-height analyzer, using an NaI(Tl) crystal and a distance combination that gives a reasonable counting rate. A usual

combination is a 3- by 3-in. crystal and about a 20-cm distance between the sample and the crystal.

(27) *Zirconium–Hafnium.* The zirconium and hafnium are separated by a barium fluozirconate (fluohafnate) precipitation. After the fluozirconate (fluohafnate) is dissolved, the zirconium-hafnium is separated by a cupferron precipitation. Since there is no simple radiochemical procedure for isolating trace amounts of hafnium from equal or greater amounts of zirconium, the hafnium is not determined. If zirconium is not used as cladding material and if hafnium is used as control rods, the same procedure for zirconium is applied to the hafnium except a hafnium carrier is used in place of zirconium. The zirconium sample may consist of Zr^{95} and Zr^{97}, whereas hafnium samples may contain Hf^{175} and Hf^{181} in addition to the above zirconium radionuclides.

Procedure. To a lusteroid tube are added 50 mg of zirconium carrier solution (Table 10.3) and the sample. The solution is made 4*M* in HNO_3 and 5*M* in HF. To this solution is added 5 ml of saturated $Ba(NO_3)_2$ solution, and the precipitate is centrifuged down. The precipitate is dissolved in 4 ml of saturated H_3BO_3 solution and 2 ml of HNO_3 followed by 10 ml of H_2O. The barium fluozirconate is again precipitated by adding 1 ml of saturated $Ba(NO_3)_2$ solution and 1 ml of HF. The precipitate is redissolved and reprecipitated as above. The final precipitate is dissolved in 4 ml of H_3BO_3, 4ml of HCl, and 10 ml of H_2O. Three drops of H_2SO_4 are added, and the solution is centrifuged. The supernatant is precipitated with NH_4OH (phenolphthalein end point), and the precipitate is dissolved in 2 ml of HCl. After this solution is diluted to 15 ml and cooled, 4 ml of a 6 per cent cupferron solution is added.

The precipitate is centrifuged down and washed with cold 1*M* HCl and then with methanol. The precipitate is transferred to a filter paper and cautiously ignited to 800°C in a porcelain crucible. The ZrO_2 is transferred to a tared 4-ml vial, weighed, and counted.

The zirconium activity, whether it is present alone or as part of a hafnium-zirconium mixture, is measured with a gamma-ray spectrometer by comparison with standards that have been freshly separated from the Nb^{95} daughter (this measurement need be done only once). The hafnium, if present in quantities greater than the zirconium by a factor of 10, can be measured by an integral gamma count above the 30-kev level. Any zirconium activity is then subtracted on the basis of the above gamma-ray spectra. Any 17-hr Zr^{97} present is negligible.

10–2 GAS-COOLED REACTORS

By C. J. Rodden

Of the many reactors now in operation, those of the Calder Hall type, which use carbon dioxide as a coolant, are the best examples of those employing gas coolants. The use of helium as a coolant is limited. Analytical methods using gas-chromatographic techniques

for the analysis of impurities in helium when used as a blanket or carrier gas have been described.[8] The analyses performed on carbon dioxide are given as being indicative of gas-cooled reactors. The following discussion is taken from the work of Woodman and coworkers as reported at the Fourth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 12–14, 1960 (Ref. 65).

The gaseous coolant in a reactor must possess a number of characteristics in addition to the important requisite of good heat-transfer properties and this situation is reflected in some of the analytical requirements. Neutron economy considerations dictate that the coolant itself shall have a low absorption cross section and that impurities with high cross sections shall be kept below specified, very low concentrations. It is important that the coolant shall have high radiation stability and that it shall be chemically compatible with other materials in the reactor; analyses throwing light on radiation breakdown and interaction with, say, the graphite moderator, are, therefore, likely to be called for.

10–2.1 Analytical Control of Feed Gas

The gas is delivered to the reactor site in 10-ton-capacity road tankers in the liquid form. Samples are taken from each tanker on arrival and are rapidly examined to determine the percentage of gas not absorbed by a solution of KOH. This examination gives a quick measure of the purity of the gas; it must be made before the gas can be cleared for feeding into the storage tanks. The liquid carbon dioxide is sampled while it flows through a copper spiral immersed in hot water to give continuous gasification under controllable conditions. It is, of course, important to sample the liquid and not the gaseous ullage since fractionation is known to occur. A measured volume of the gas is then collected over brine and absorbed with a KOH solution; the residual gas is measured in a calibrated portion of the absorption vessel and removed, if required, for subsequent analysis by mass spectrometry or gas chromatography.[9]

The analysis of the residual gas includes the determination of argon, hydrogen, nitrogen, methane, ethane, propane, and ethylene. The most important of these is argon since Ar^{40} has a capture cross section of 0.53 barns for thermal neutrons, yielding Ar^{41} with a half life of 1.8 hr. The presence of argon, therefore, has a significant influence on shielding problems when the gas is fed into the circuit as coolant. Initially argon was determined by neutron-activation analysis,[10] but it was soon found more convenient to analyze the residual gas, along with all the other gaseous impurities listed above, by conventional mass-spectrometric techniques.

Another impurity that could have profound effects on the performance of the coolant is boron. Boron in the feed gas is determined by absorption in sodium hydroxide and subsequent distillation as methyl borate followed by absorptiometric estimation of the boron with curcumin.[11]

Moisture is determined on the feed gas by the conventional magnesium perchlorate absorption method.[12]

On occasion, gas-chromatographic analysis of residual-gas samples has been found to be a useful complementary technique to conventional mass spectrometry; for example, the chromatography approach enables one to characterize and estimate traces of dimethyl ether in the parts per million region when it is present as an unexpected impurity. In fact, it is quite feasible to dispense with mass spectrometry as a control technique and use the much cheaper gas-chromatographic method.[13]

Table 10.4 summarizes a typical feed-gas analysis.

Table 10.4—TYPICAL FEED-GAS ANALYSIS [65]

Component determined	Typical result, ppm
Ar	3
H	<1
O	35
N	75
CH_4	1
C_2H_6	<1
C_3H_8	<1
C_2H_4	5
H_2O	40
B	<0. 1
Residual gas, vol.%	0. 2

10–2.2 Circuit-Gas Analysis

The principal sampling points for the circuit gas of a Calder Hall type reactor are shown in Fig. 10.4.

Sampling of the circuit gas has to be carried out at pressures of the order of 100 psi and at a temperature of about 150°C. These conditions are fairly readily accomplished by using a cylinder fitted with a valve at each end coupled to the sampling point by means of a flexible pressure line incorporating a T-piece and a valve. The line and cylinder are flushed out with the sample gas, and the cylinder is finally filled with gas at the pressure of the system being sampled.[14]

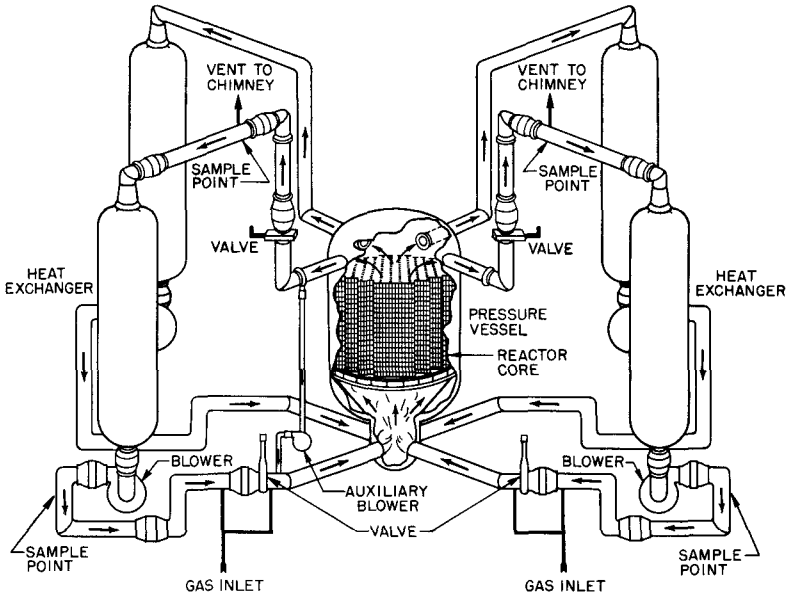


Fig. 10.4—Position of sampling points on a Calder Hall type reactor.

Following a fresh charge of gas to a reactor, a periodic determination of residual gas, i.e., percentage of gas not absorbed in KOH, is usually carried out as supporting evidence of normal satisfactory start-up. Carbon monoxide determinations are made for a similar reason. The method for these determinations is basically the conventional iodine pentoxide procedure. The gas sample is dried by passing it through silica gel and Anhydrone and then through iodine pentoxide at 140°C to 150°C; the resulting iodine is absorbed in potassium iodide and titrated with sodium thiosulphate.[15]

Carbon monoxide can also be determined by infrared monitors installed on a limited scale on the reactors. More important, perhaps, than continuous monitoring of the coolant for carbon monoxide is the application of an infrared analyzer for the detection of combustion. For this purpose the instruments have to be modified to allow differential measurements to be made of gas leaving a channel against the bulk gas entering the bottom duct to the reactor. This technique permits distinction between an ordinary burst without combustion and a burst with combustion. The instrument sensitivity is such that on a background of several thousand parts per million of carbon monoxide an increase of 150 ppm would give full-scale deflection.

Mass-spectrometric analysis of the residual gas enables one to follow the changes in the levels of other gaseous impurities, in particular

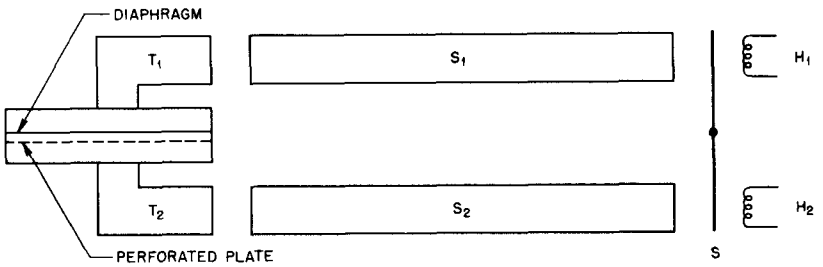


Fig. 10.5—Infrared gas analyzer.

the fall in nitrogen and argon contents soon after start-up. The initial start-up values and the time taken for the levels to fall to those of the feed gas obviously depend on the degree of purging before final pressurizing of the gas circuit and the rate of any leakage of coolant from the reactor.

Moisture determinations are frequently carried out during start-up and under normal operating conditions. A variety of methods for such a determination are available. As a reference method the Anhydrone absorption procedure is preferred.[12] A modification of the Karl Fischer method has been used,[16] but it is subject to interference from some impurities likely to be present in circuit gas. Also this method involves manipulative difficulties and it is rather slow. Therefore it is generally less suitable than other methods. For quick spot checks on moisture, one of the commercially available hygrometers, such as the Alnor hygrometer, has been found quite satisfactory. For continuous monitoring of moisture level, infrared instrumentation has been installed.[65] Their present lower limit of detection is about 20 ppm whereas normal operational levels after start-up fall well below this, usually not exceeding 10 ppm. A diagram of the infrared gas analyzer installed is shown in Fig. 10.5. It is similar to the Perkin–Elmer TRI–NON instrument. The gas to be analyzed is passed continuously through the sample tube, S_1; absorption in S_1 is compared with the absorption in a similar tube, S_2, mounted parallel to S_1 and usually filled with dry air. Energy from two nichrome heaters, H_1 and H_2, is passed through both tubes and the portion transmitted is received by the two chambers, T_1 and T_2, which contain a sample of the gas to be measured.

The chambers T_1 and T_2 are separated by a thin diaphragm that forms one electrode of an electrical condenser. The other electrode is in the form of a closely adjacent insulated, perforated metal plate. Radiation transmitted by S_1 and S_2 is absorbed by the gas in T_1 and T_2 causing a temperature increase with a resultant increase in pressure.

If the transmission through both S_1 and S_2 is identical, the diaphragm remains stationary. When, however, a sample of gas to be analyzed is introduced into S_1, the transmission balance is broken; and the diaphragm is displaced, producing a corresponding change in the capacitance of the condenser. The application of a polarizing potential to the condenser converts the capacity change to a current change that is amplified to provide an indication related to the pressure difference between T_1 and T_2.

To obtain measurements free from zero drift, a rotating shutter S interrupts the radiation from heaters H_1 and H_2 at a frequency of about 6 cycles/sec, allowing pressure changes to be directly related to temperature changes which are themselves related to the differences in absorption of energy S_1 and S_2. Any other gas present in the sample will not affect the result unless it has absorption bands which overlap those of the gas (water vapor) being determined. In this event filter tubes containing the interfering gas or gases can be included in the two optical paths.

The C^{14} content of circuit gas is of interest for two reasons. First, it is necessary to evaluate the activity due to C^{14} prior to the occasional release of the reactor coolant; and, second, it is of interest in the study of coolant–moderator reactions. Carbon monoxide builds up after start-up to a level of the order of 0.3 to 0.4 vol.%, and the C^{14} level in the carbon monoxide is consistently some 20 times higher than it is in the carbon dioxide. This condition presumably follows from the reaction of the fresh coolant carbon dioxide with graphite moderator rich in C^{14} and implies that subsequent exchange is very slow. The result of this observation emphasizes the continuing need for an analytical procedure that can determine C^{14} in the monoxide and dioxide separately; this determination is readily achieved by absorption in KOH (with subsequent regeneration of the carbon dioxide in barium hydroxide) while the residual carbon monoxide is oxidized by iodine pentoxide to the dioxide, which is in turn absorbed in barium hydroxide. The resulting barium carbonate precipitates are gelled with an organic scintillant and the C^{14} content evaluated conventionally in a liquid scintillation counter. A typical figure for the C^{14} content of coolant carbon dioxide is 1 disintegration/min/ml.

One other determination in the circuit gas worth mentioning is that of traces of oil present, e.g., from a faulty seal in the blower. The sampling technique,[17] which perhaps is not ideal, is designed to collect oil in fine droplet form and as vaporized oil; it involves the insertion of a specially designed sampling tube with a $\frac{1}{16}$-in. hole drilled in the side $\frac{1}{8}$ in. from the end. A needle valve leads to a copper cooling spiral and two absorption vessels containing carbon

tetrachloride. After a 6-hr sampling time at a rate of 1 liter/min, the tube complete with head is detached and rinsed with carbon tetrachloride. The washings are combined with the main absorbant, and the oil content is assessed by a conventional infrared absorption procedure,[18] making the measurements at 2890 cm^{-1} (3.46 μ) (attributed to the carbon–hydrogen stretching frequency of hydrocarbons) and using as a standard the actual oil used in the blowers. The limit of detection is 5 ppm.

Determination of Radioactive Components of Circuit Gas. It is of great interest and of some importance to determine the radioactive components of circuit gas in prototype power reactors during normal operation for several reasons. First, from the aspect of shielding studies, much valuable guidance can be obtained by characterization of the various active species present. Second, from the health physics standpoint, it is important to have a knowledge of the activities present in circuit gas before a discharge "blow-down" can be authorized. Third, from the point of view of the continuing satisfactory operation of burst-cartridge detection gear, data on activities other than those of fission products is clearly useful. Finally, from the more fundamental aspect of reactor studies, including coolant–moderator interactions and canning-material performance, information on the active species present is important.

Two active components have already been mentioned (Ar^{41} and C^{14}) ; but, additionally, it would be expected that N^{16} and O^{19} would be present. Preliminary measurements of the activities of the Ar^{41}, N^{16}, and O^{19} in the coolant gas have been made by flowing the gas from a duct sampling point along a delay line and through a flow-through Geiger tube. The separate determination of Ar^{41} in the gas has reached a more advanced stage. The problem is far simpler than that for the shorter lived isotopes since normal gamma-spectrometric techniques can be used. The gas sample is contained in a 4-in.-high 1½-in.-diameter container situated on a 1- by 1½-in. NaI (Tl) crystal. The counting efficiency of this system has been calculated mathematically; and, for gas containing 4 ppm of natural argon, a typical value of Ar^{14} activity of 10 disintegrations/sec/cm^3 (at S.T.P.) is obtained.

This gamma-spectrometric study of the activity of the coolant gas with a 100-channel gamma spectrometer confirms the presence of N^{16}, Ar^{41}, and O^{19} with their energies at 6.13, 1.30, and 0.20 Mev, respectively. Gamma spectra obtained from circuit-gas filter samples are typical of irradiated graphite associated with traces of activated constructional-material corrosion products, e.g., activated iron rust.

690–457 O—64——45

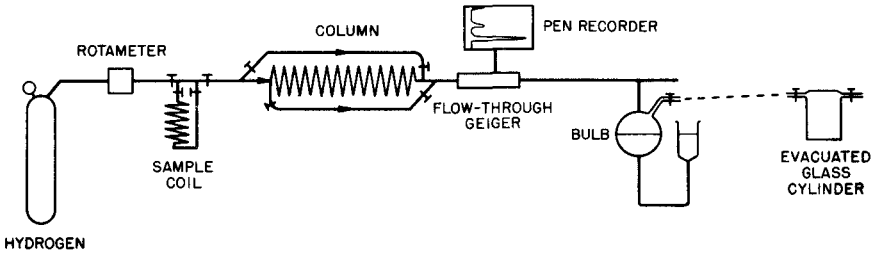


Fig. 10.6—Gas chromatograph.

Some very small contributions to the gas activity come occasionally from fission-product gases released into the coolant from burst cartridges or from cartridge contamination, and some knowledge of these contaminations is very useful in the understanding and improvement of burst-cartridge detection. For one to study the fission-product gases in the coolant without too great a delay, it is necessary to separate the Ar^{41} from the xenon and krypton isotopes by some rapid physical means.

Several techniques have been examined, and the most encouraging method investigated so far is that of passing the gas through a gas-chromatographic column. Figures 10.6 and 10.7 show the more or less conventional apparatus used and the separation achieved.[66] The sample of residual gas is introduced into the gas-chromatographic apparatus by means of the spiral system shown and is flushed through the column (8 ft by ¼-in. ID coiled copper tube filled with $^{36}/_{42}$-mesh 5A molecular sieve) with hydrogen at 150 ml/min.

Detection of the active rare gases is achieved by a flow-through Geiger tube containing a 2-in. plug of activated charcoal. The charcoal serves to hold up the gases inside the counter so that the maximum count can be obtained; this count is shown by a pen recorder. A typical separation is shown in Figure 10.7. Although the activity of Ar^{41} is orders of magnitude greater than the krypton and xenon fractions, it shows only a minimum peak height since it is not held up at all by the charcoal contained in the Geiger detection tube.

The krypton fraction is collected over water, and then the flow of hydrogen through the chromatographic column is reversed. This action quickly elutes the xenon, which is strongly adsorbed at the front of the column. The xenon fraction is also collected over water.

Both rare gases are transferred to evacuated glass cylinders of known dimensions and are then counted on a 3- by 3-in. sodium iodide crystal connected to a 100-channel pulse-height analyzer. Gamma-spectrometric scans of the krypton and xenon fractions are obtained. From these scans the activities of the particular isotopes are calculated and plotted.

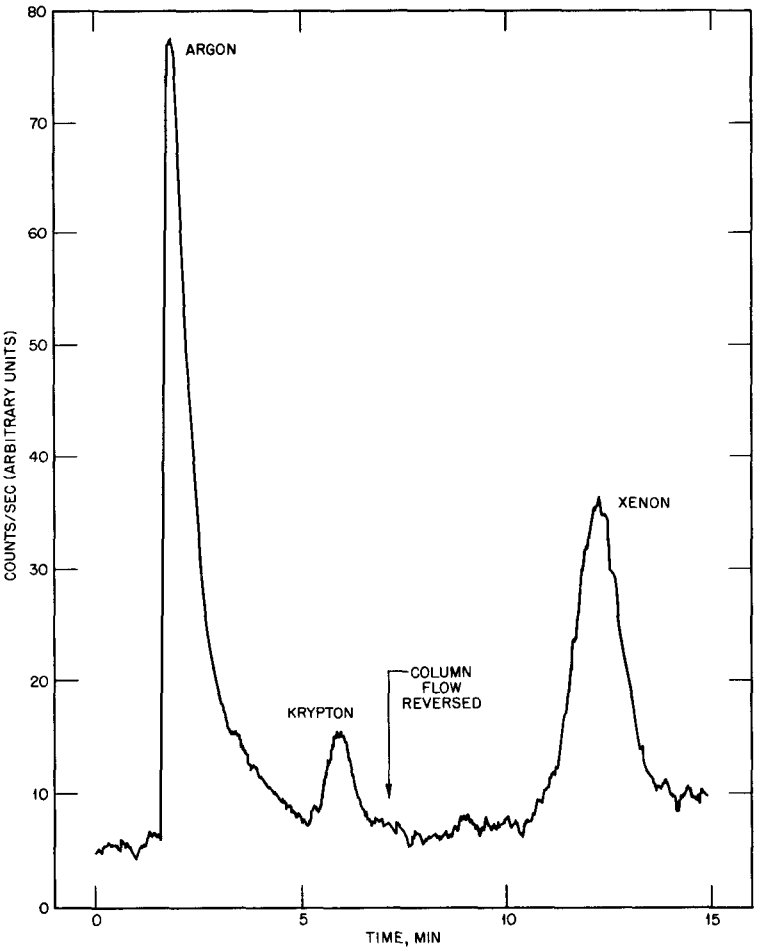


Fig. 10.7—Separation of radioactive gases by gas chromatograph.

10–3 REACTORS COOLED WITH SODIUM OR SODIUM–POTASSIUM ALLOYS

By W. C. Judd and D. Dutina

Metallic sodium contains a wide variety of impurities that are generally of low concentration. Results obtained on typical material are shown in Table 10.5. Of the impurities shown, several are particularly important. Oxygen, for example, must be kept at minimum attainable levels if sodium is to retain its noncorrosive properties. Boron, cadmium, and mercury have extremely high cross sections, and their concentration must be kept in check from the point of view

of neutron economy. Indeed, it is for this same reason that the total impurity concentration must be determined and minimized.

There has been concern over the problem of transport of activated nuclides from the structural material of the reactor core to the outer portions of the coolant system. This process takes place through normal corrosion and atom-exchange processes in coolant systems and can lead to excessive radiation levels in system components that may require service. It is necessary, therefore, to try to limit corrosion processes and to perform chemical analyses to assure compliance with necessary specifications of purity.

A variety of analytical methods have been developed to meet this need. Some of the required analyses can be performed after simply testing a standard procedure for applicability to the sample under study; others require some modification of standard procedures to tailor them to the special needs of this system. A few determinations require novel approaches of method and equipment, such as the analyses of oxygen, hydrogen, and carbon.

In the text that follows, a recommended procedure for each of the elements is given in detail. Alternate procedures, when available, are described also but in an abbreviated manner. It should be stated, however, that in many instances the recommended and alternate procedures are of equal suitability and the method chosen for detailed description simply reflects the personal inclinations of the authors of this section.

It is believed that estimations of metallic elements may be made best by spectrographic techniques. These techniques permit the simultaneous observation of a wide variety of contaminants in a single sample of sodium; thus maximum information per dollar spent on analysis is obtained. Spectrographic methods suitable for the analysis of metallic impurities in sodium have been developed by F. P. Landis and coworkers at the Knolls Atomic Power Laboratory [19] and are described in Sec. 10–3.4.

For a few of the elements, e.g., iron and boron, colorimetric methods are presented in addition to the spectrographic ones. These elements are of particular interest and importance in the field. Consequently the colorimetric methods are made available for use in those cases where it is essential to obtain greater precision than that afforded by spectrographic techniques.

10–3.1 Handling and Sampling

A complete description of the physical characteristics of and precautions in handling sodium and sodium–potassium alloy can be found in the book entitled, *Sodium, Its Manufacture, Properties and Uses.*[20]

Table 10.5—IMPURITY CONCENTRATIONS IN SODIUM

Element	Parts per million	Analytical method
Ag	0.3	Spectrographic.
Al	20	Spectrographic.
B	<4	Spectrographic; colorimetric.
Ba	2	Spectrographic.
Be	<1	Spectrographic.
C	50	Manometric.
Ca	15	Spectrographic.
Cd	<1	Spectrographic.
Cl	<20	Volumetric.
Co	<2	Spectrographic.
Cr	<1	Spectrographic, colorimetric.
Cs	<50	Flame photometric.
Cu	4	Spectrographic.
Fe	1	Spectrographic; colorimetric.
H	60	Gasometric.
In	<1	Spectrographic.
Hg	1	Spectrographic.
K	<100	Flame photometric.
Li	15	Flame photometric.
Mg	10	Spectrographic.
Mn	<2	Spectrographic.
Ni	<2	Spectrographic.
O	10	Volumetric.
P	<10	Colorimetric.
Pb	2	Spectrographic.
Pd	<3	Spectrographic.
S	30	Volumetric.
Si	<10	Spectrographic.
Sn	<15	Spectrographic.
Sr	<5	Spectrographic.
Ti	<10	Spectrographic.
Tl	<10	Spectrographic.
U	<0.7	Fluorometric.
V	<2	Spectrographic.

To avoid excessive repetition, the reader is referred to this invaluable work for the various details of sodium technology. Another useful reference is the *Liquid Metals Handbook, Sodium (NaK) Supplement.*[21] Considerable detail concerning the handling and sampling of sodium and sodium–potassium alloy can be found in it. Also the methods used at the Capenhurst Works, United Kingdom Atomic Energy Authority, are presented in Ref. 22.

The casual reader, who is not acquainted with basic properties of sodium, may be helped by the following general observations con-

cerning the properties and technology of sodium. It is a light metal (density, 0.9684 g/cm³ at 20°C) with a melting point of 97.8°C. It is highly reactive and combines with oxygen, water, etc., in a most violent manner. One product of the reaction with water is hydrogen, which can create a hazardous condition because of its potentially explosive nature in the presence of air. Sodium is a good heat-transfer agent.[23] It can be pumped by means of electromagnetic pumps, thus no moving parts in the coolant system are required. When free of oxygen, it has only slight corrosive action on stainless steel. Finally, pure sodium is commercially available in adequate supply.

When sodium is sampled for analysis, it is quite difficult to obtain a representative fraction. This problem is discussed by Mausteller and Voorhees.[23] In addition, the references to the determination of oxygen also touch on the sampling problems. Probably the most effective method of sampling large systems is by means of the sampler described by Bruggeman et al.[24] When sampling techniques are being devised or selected, due attention must be paid to the problems of homogeneity, differential freeze-out in the sample line, and particulate suspension instead of the true solution. The sodium sample obtained for analysis is generally transferred into an evacuated glass or quartz tube and allowed to cool and solidify. The tubing is then broken, and the sodium is dissolved prior to analysis. There are four dissolution media generally used: alcohol, water, mercury, and organic solvents.

Sodium–potassium alloy, in contrast to sodium, is liquid at room temperature and is violently pyrophoric. Pepkowitz [25] describes a novel and effective method of dissolving sodium–potassium alloy prior to analysis.

10–3.2 Determination of Sodium and Potassium in Sodium–Potassium Alloy

Walters and Miller [26] describe a weighing and titration method to determine the sodium and potassium content of sodium–potassium alloy. These authors also describe a freezing-point determination in the 92 to 100 per cent potassium region.

10–3.3 Chemical Analysis of Impurities in Sodium

When a sample of sodium or sodium–potassium alloy is analyzed, the usual procedure for determining the sample weight is titrating with a standard acid. Flame photometry affords a second way of determining sample weight. A measured aliquot of the solution, resulting from the dissolution step, is analyzed for sodium by a flame photometer. In the case of hydrogen and impurity determinations, the metal sample is weighed directly.

(a) *Hydrogen.* The hydrogen content of sodium or sodium–potassium alloy used as a heat-transfer fluid in a heat-exchange system should be held to a specified minimum because of possible hydriding and subsequent embrittlement of the materials of construction. The determination of an excessive amount of hydrogen in the liquid-metal coolant serves as a warning that a potential danger of hydriding embrittlement exists.

The first description of the determination of hydrogen in sodium was reported by Pepkowitz and Proud.[27] They sealed a sodium sample in an iron capsule and heated it to 700°C in a vacuum system. The hydrogen present diffused through the capsule walls and was measured by the usual vacuum-system techniques. When used to measure the hydrogen content of brick sodium, this technique exhibited a standard deviation of ±15 ppm at concentrations of approximately 60 ppm.

Holt [28] indicated that the above method did not liberate all the hydrogen. He proposed an isotope-dilution method employing a mass spectrometer for measurement of the hydrogen. In Holt's method the rapid exchange of hydrogen and deuterium in sodium and sodium–potassium alloy affords a convenient method for the determination of hydrogen. After a known amount of deuterium has been added, the sample is heated at 500°C for 5 min. The deuterides and hydrides are then decomposed, and the resulting gases are analyzed in a mass spectrometer. Although results derived with sodium were satisfactory, it was found necessary to apply a correction factor with sodium–potassium alloy to compensate for the effect of different rates of formation of the hydrides and deuterides in the cooler zones of the tube during equilibration.

Procedure.[27] This procedure requires the use of iron capsules, welding apparatus, a vacuum system, and an induction heater. This equipment is shown in photographs and in diagrams in the first five figures of Ref. 27. Brief descriptions of this equipment are included below to the extent required for comprehension, but the reader is referred to Ref. 27 for a more complete discourse.

Iron capsules, which are the shells of 6C5 metal radio tubes, and covers, which are press-fit caps stamped from 10-mil sheet iron, are degreased with acetone and oven-dried. The capsules and lids are degassed in the vacuum apparatus by heating them inductively at 700°C while continuously pumping on the system. When the pressure is reduced to 2 or 3×10^{-3} torr, pumping is stopped, the capsules are allowed to cool, and tank helium is bled into the system until atmospheric pressure is attained. The capsules are stored in a desiccator until they are used.

The sodium to be analyzed is stored and sampled in a dry box under a helium atmosphere. In the case of the raw brick metal, a sample from the center of the brick is cut, placed in one of the degassed capsules, and weighed. The lid is pressed into place, and the capsule

is removed from the dry box and immediately welded shut. The seal is made with a simple shielded arc-welding technique using a tungsten electrode.

The sealed capsule is next introduced into the vacuum system, which consists of the following parts in sequence: a pyrex furnance tube, a thermocouple gauge, a cold trap cooled with liquid nitrogen, a double McLeod gauge, quartz copper oxide tube with an external heater, and a mechanical pump. The capsule is supported on a molybdenum wire rack positioned in the pyrex furnace tube. Next, the copper oxide is degassed by heating to 400° C while pumping on the system. When the pressure is reduced to 1 to $2X10^{-3}$ torr, the system is closed to the pump, and the copper oxide is cooled to room temperature with an air blast. During this interval the tightness of the system is verified by means of the thermocouple gauge.

The coil of the induction heater is centered around the portion of the pyrex furnace holding the iron capsule. The temperature is raised to 700°C over a period of 5 min to allow the hydrogen to diffuse through the walls of the capsule as it is generated, thus preventing a build-up of excess pressure in the capsule. Heating is continued until a constant reading, H_T, is attained on the McLeod gauge (usually 15 to 20 min). The induction heater is turned off, and the copper oxide furnace is turned on. The hydrogen is oxidized to water, which is then frozen out in the cold trap, a process normally requiring 35 min. The pressure is read at intervals until a minimum reading, H_R, is reached. The copper oxide furnace is removed, and the system is brought to atmospheric pressure by running in tank helium.

The hydrogen is calculated from the two pressure readings, H_T and H_R, and from a blank, b, obtained by running an empty capsule through the procedure. The equation employed is:

$$\text{Mg of } H_2 = (H_T^2 - H_R^2)K - b$$

where K is an experimentally determined constant for the whole system. It it determined by carrying known amounts of standard sucrose through the procedure using magnesium turnings as the reducing agent.

(b) *Carbon.* When sodium is employed as a coolant in a reactor heat-exchange system made from stainless steel, the carbon content of the sodium must be kept low because stainless steels are subject to grain-boundary carburization and consequent embrittlement.

Stoffer and Phillips [29] determined carbon in sodium–potassium alloy by combustion of the sample in an atmosphere of pure oxygen. The carbon is thus converted to carbon dioxide, which is absorbed and weighed. A temperature of 950°C is necessary to assure complete recovery of the carbon dioxide.

A wet-combustion technique for measurement of the carbon in sodium, after the sodium is converted to hydroxide by contact with moist nitrogen, is reported by Farrington et al.[30] Pepkowitz and Downer [31] also discuss a procedure that involves wet combustion followed by a conductometric determination of the carbon dioxide. A

manometric method of carbon dioxide measurement following a wet-combustion procedure is reported by Pepkowitz and Porter.[32] This method is designed to measure carbon concentrations in the 0.01 per cent range in sodium. The method has a standard deviation of ± 0.001 per cent. A modification of the latter method, usable in the 10 to 300 ppm concentration range, is included in the Capenhurst compilation.[22]

Procedure.[22] The apparatus is comprised, in sequence, of a conventional gas-purifying train, a reaction tube, a system of cold traps, a manometric system, and a vacuum pump. The purifying train for the oxygen sweep gas consists of a copper oxide preheater (600°C), a sulfuric acid bubble counter, and an Anhydrone–Carbsorb adsorber. The reaction tube is fitted with a dropping funnel. The three cold traps, in order, are cooled with a dry-ice–acetone mixture, liquid nitrogen, and again liquid nitrogen. The manometer is connected by means of a 3-way stopcock in the line between the first trap and the second trap. The manometer pressure is indicated by the level of oil in the capillary tube; contact between oil and carbon dioxide is prevented by a mercury seal. The method for filling the manometer is described in Ref. 22.

Approximately 1 g of sample is weighed and transferred to the dry reaction tube, which is disconnected from the apparatus. With the funnel head attached and closed, the vessel is purged with nitrogen. Five milliliters of water are added dropwise through the funnel; nitrogen flow is continued until the sodium has dissolved. The solution is neutralized with 3.6*M* sulfuric acid, and a few milliliters in excess are added. The solution is evaporated to dryness by suspending the tube between two vertical infrared heaters while the nitrogen flow is maintained to speed up the dehydration. The reaction tube is attached to the manometric system. The cold traps and manometer are evacuated to the limit of the vacuum pump while the rest of the system is isolated. During this period the first trap, which removes water, is cooled, as is the third trap, which is designed to guard the pump. The stopcock connecting the traps to the rest of system is gradually opened.

Next, oxygen is drawn into the manometer at a sufficient rate (about 20 ml/min) to produce a 2-cm rise. After the entire system has been purged for 10 min, a flask of liquid nitrogen is placed under the second trap and the CO_2 is frozen out; the oxygen purge is continued. Through the dropping funnel, 5 ml of the oxidizing solution is added. (To form this solution, combine 13 g of chromic acid, 85 ml of orthophosphoric acid, and 165 ml of fuming sulfuric acid. This solution is gradually warmed to 140°C and then cooled to 80°C. Suction is applied during the remainder of the cooling time to remove dissolved CO_2.) The mixture is heated at incipient boiling for 5 min; oxygen is drawn through the system for an additional 5 min. Again the reaction vessel and gas train are isolated, and the remainder of the system is evacuated. Next, the third cold trap and the pump are isolated, and the connection between the manometer and the second cold trap is made by means of a stopcock. The pressure P_1 is read, the liquid-nitrogen flask is removed, the trap is warmed to room temperature, and the pressure P_2 is read. A reagent

blank is handled in the same way as the sample was handled. The carbon content of the sample is calculated from the following expression:

$$\text{Carbon (ppm)} = \frac{(P_2 - P_1) - (B - P_3)F}{W}$$

where P_1 and P_2 = pressure readings taken above the sample
B = room-temperature pressure reading of the blank
P_3 = manometer reading for the blank with the liquid-nitrogen trap in place
W = weight of sample in grams
F = calibration factor for the system

The calibration factor is determined by adding 1 ml of sucrose solution (1 mg/ml) to the reaction tube and carrying out the procedure detailed above. This procedure is repeated with successively larger aliquots until the limit of the manometric system is reached. A graph of micrograms of carbon vs. pressure is plotted. The factor F for the apparatus is calculated as

$$F = \frac{\text{Sum of micrograms of carbon added}}{\text{Sum of pressures in millimeters produced}}$$

(c) *Nitrogen.* The determination of nitrogen in sodium has not assumed the importance of the determinations of oxygen or hydrogen, but a knowledge of the nitride nitrogen concentration permits a useful estimation of the possible extent of nitriding of structural materials in the system. The nitride level has been measured by the Nessler technique.[33]

The sample is decomposed with alcohol followed by steam, and the nitride is allowed to react with water, forming ammonia. This procedure is done in a flask fitted with a delivery tube immersed in a dilute acid solution. The remainder of the ammonia is distilled into the dilute acid, the distillate is evaporated to remove alcohol, and the ammonia is determined by the Nessler method.[4, 34] The useful range of this method is 5 to 400 ppm with a standard deviation of ±10 per cent.

Procedure. The steam-distillation apparatus employed in this determination is a conventional one. It consists of a steam-generating flask closed with a one-hole stopper in which is inserted a vent tube with a stopcock. The steam leaves the flask through a side arm, which holds a stopcock and which terminates in a standard-taper joint. This joint connects with a matching joint on the reaction flask. The flask is fitted on top with a dropping funnel and is connected by means of a standard-taper joint to a water-cooled condenser. The receiver for the condensate is a 150-ml beaker. Heating of the steam generator is accomplished by an electrical heating mantle.

The complete apparatus is assembled, and the water in the steam generator is heated to a vigorous boil. Steam is passed through the apparatus for 30 min with the condenser water not running. After this steaming-out period, the receiver is removed and the steam is vented to the atmosphere. The stopcock on the steam-flask side arm is closed, the reaction flask is removed, and the tip of the side arm is

dried carefully. Twenty milliliters of 0.02*N* hydrochloric acid is placed in the receiving beaker. The beaker is placed in such a manner that the condenser tube presses against the flat bottom; this arrangement serves to break up the gas bubbles. Water flow through the condenser is started. The sodium sample (1 to 2 g) is placed in the dry reaction flask, which is then attached to the distillation assembly. By means of the dropping funnel, 15 to 20 ml of ethyl alcohol (95 per cent) is added slowly to the sample. Near the end of the dissolving period, 2 to 3 ml of water is added to speed up the reaction. The reaction rate, controlled by the rate of alcohol addition, should be such that a rapid stream of bubbles is caused to evolve from the condenser tip. The rate, however, should not be so rapid that contact of the gas and receiver solution are not maintained. If necessary, the reaction rate can be reduced by raising an ice bath around the reaction flask.

When the reaction is complete, the side arm of stopcock is opened, and the vent on the steam flask is closed. The receiving flask is lowered momentarily while steam sweeps air out of the apparatus. It is raised again so that the condenser tip is just immersed, and the steam flow is continued until a total of 50 ml of distillate has been collected. The receiver is lowered, the distillate is allowed to drip for 30 sec, and the condenser tip is rinsed with water into the receiver solution. The heat is removed, and the steam generator is vented.

The receiver solution is boiled down to a volume of 25 ml, cooled, and transferred to a 50-ml volumetric flask. One milliliter of Nessler's reagent is added. (To make this reagent add to a solution containing 61.75 g of potassium iodide dissolved in 250 ml of water sufficient saturated mercuric chloride to just make it bright red. The red precipitate is dissolved with 0.75 g of potassium iodide, and a solution of 150 g of potassium hydroxide in 250 ml of water is added. The volume is then brought up to 1 liter.) After this volume is diluted to the mark, the absorbance is measured at 410 mμ in 1-cm cells with water as a reference solution. The nitrogen concentration is obtained from a reference curve made by measuring the absorbance of solutions containing known amounts of ammonium chloride to which Nessler's reagent has been added. Blanks are run on triply distilled sodium carried through the entire procedure.

The weight of the sodium sample taken may be determined by titrating the solution remaining in the reaction flask with standard acid.

(d) *Oxygen.* When sodium or sodium–potassium alloy is used as a heat-transfer medium in a nuclear power plant, the determination and control of the oxygen content is of considerable importance. High oxygen levels lead to excessive corrosion rates and also may cause plugging of constricted passages in the system.

The first method reported for the determination of oxygen (sodium monoxide) in sodium was that of Pepkowitz and Judd.[35] This method is based upon the principle of extraction of the metallic sodium with mercury, leaving sodium monoxide as a residue in the extraction vessel. The sodium monoxide can then be dissolved in distilled water and titrated with standard acid or determined with a

flame photometer. The sodium sample weight is determined by dissolving the sodium from the mercury alloy and titrating with standard acid.

The original procedure was modified by Williams and Miller [36] and by Pepkowitz, Judd and Downer.[37] Williams and Miller were able to obtain a mean deviation of ±0.002 per cent with their refined procedure. All the authors cited in Refs. 35 to 37 describe the difficulties encountered when attempting to obtain a truly valid sample from a liquid-metal system. Bruggeman and Billuris [24] described a system for sampling sodium and performing the analysis in an argon-filled chamber attached to the heat-exchange system. This ingenious apparatus gave results with a standard deviation of ±0.001 per cent.

Another technique for determining the sodium monoxide content of sodium makes use of the Wurtz reaction.[38] Sodium metal reacts with excess alkyl halide in xylene. The products formed are sodium halide and hydrocarbon. The sodium halide and sodium monoxide are dissolved in water. An acid titration measures the amount of sodium monoxide originally present. The amount of sodium originally present can be determined by performing a halide analysis. The standard deviation of this method is ±0.005 per cent according to White, Ross, and Cowan.[38] A method for obtaining an improved acidimetric end point, which is necessary when the sample has a small oxygen content, is presented by Smythe and deBruin.[39] Silverman and Shideler [40] report a modification in the method used to dry the alkyl halide reagent and claim an improvement thereby, but the authors present no direct comparison of results obtained by the modified and the original methods. A modified version of the alkyl halide method is also reported by the Ethyl Corporation.[41] Their version describes a novel sample preparation involving the use of a blanket of hot white oil (Primol D) and isopropyl alcohol to prevent oxidation. Since the alcohol film so produced might lead to high results, it is removed prior to analysis by rinsing in a warm (70°C) mixture of white oil, *n*-butyl bromide, and *n*-hexane. Other modifications suggested are the use of a closed reaction vessel to prevent moisture absorption by the alkyl bromide reagent and the drying of the reagent over warm, powdered calcium metal. A standard deviation of ±0.0006 per cent is reported for the method.

A third type of method for the estimation of oxygen in sodium consists of distillation of the metal away from the oxide.[42, 43] The oxide is dissolved and determined by titration. This method requires more elaborate equipment and techniques than the methods discussed above.

Procedure.[41] The reactor employed is fabricated from 35-mm glass tubing. It is approximately 12 in. long and is sealed closed at one end

and fitted with a standard-taper 40/50 glass joint at the open end. The top for this reactor vessel consists of a male 40/50 joint fitted with a three-way stopcock, the arms of which are made of 9-mm tubing. Nitrogen gas, used for purging, is purified by passage through a glass tower filled with Dehydrite.

The three-way stopcock and the glass joint of the reaction vessel are lubricated with a minimum of Dow–Corning high-vacuum grease. The entire assembly is heated in an oven at 500°C for 30 min. The apparatus is then cooled just sufficiently so that it can be connected to a vacuum line and a dry nitrogen tube. The vessel is alternately evacuated and then filled with dry nitrogen several times by means of the three-way stopcock. The vacuum is maintained for approximately 30 min while the vessel cools to approximately 80 to 60°C. A Glass-Col heater, under the reactor, serves to maintain the temperature.

The reactor is filled with dry nitrogen, the head is removed, and approximately 75 ml of *n*-butyl bromide–hexane solution is filtered into it. (Four parts of *n*-butyl bromide are mixed with five parts of *n*-hexane.) Oxygen compounds are removed by extracting in a separatory funnel with successive 25-ml portions of sulfuric acid until the acid layer remains colorless. The entrained acid in the organic layer is neutralized by mixing the organic solution with solid sodium bicarbonate. The organic solution is filtered and kept stoppered in a flask that has a drying tube filled with Dehydrite attached to the stopper. The reagent is dried by boiling it gently (70°C) with ground calcium metal. The reactor is again alternately evacuated and purged with nitrogen.

The sodium sample is dropped into a 250-ml large-mouth Erlenmeyer flask containing 100 ml of white oil [dry Primol D mixed with a small volume (5 per cent) of dry xylene and boiled to expel moisture] and 1 ml of isopropyl alcohol (dried by refluxing with molten sodium and distilling). The oily solution is heated until the sodium melts, and the flask is rotated to slough off any oxide film from the molten sodium. The ball of molten sodium is split in two by squeezing the middle of the sphere with a dry pair of tweezers. The oil is cooled with a blast of air, and one ball of sodium is quickly transferred to a second flask containing white oil and isopropyl alcohol. Again the solution is heated until the sodium melts, and then it is immediately cooled. The sodium is rapidly transferred to a stoppered Erlenmeyer flask containing 50 ml of dry white oil and 50 ml of the *n*-butyl bromide–hexane solution heated to 70°C. The sodium is permitted to react with the reagent for 3 to 5 min, and some of the blue-black crust of sodium bromide is sloughed off. The sample is then transferred to the reaction vessel, which is alternately evacuated and purged with dry nitrogen until the reaction subsides. A stirring rod (12-in.-long 7-mm-diameter glass rod flattened at one end) is used to pulverize the sodium bromide mass, and the vessel is heated gently at 70°C for 30 min to ensure complete conversion of sodium to sodium bromide.

The hot solution is hydrolyzed with approximately 50 ml of distilled water and stirred to extract all the alkali-metal oxides from the two-phase system. The mixture is transferred to a 250-ml separatory funnel, and the aqueous layer is drained into an Erlenmeyer flask. The reaction flask and separatory funnel are washed with an additional 25-ml portion of distilled water, which is combined with the first

aqueous extract. The solution is titrated with standard 0.01*N* hydrochloric acid to the phenolphthalein end point. The weight of the combined oxygen is equal to the milliequivalents of acid required times 0.008.

The weight of the sodium sample may be determined on the neutral aqueous extract by means of a Volhard titration for bromide. The extract is diluted to 1 liter, and a 25-ml aliquot is placed in a 250-ml flask. Twenty milliliters of dilute nitric acid (1+9), 5 ml of benzyl alcohol, and 3 to 5 ml of ferric alum indicator are added. From a buret is added 0.2 to 0.3 ml of standard 0.1*N* potassium thiocyanate solution. Next, the solution is titrated to the disappearance of the red-brown color with standard 0.1*N* silver nitrate solution.

(e) *Lithium and Potassium.* The determination of the alkali elements in sodium has not attracted much attention, with perhaps the exception of potassium. Traces of lithium and cesium are hardly deleterious to the performance of sodium as a heat-exchange medium; hence little concern over their absolute levels is shown. Natural potassium levels in sodium are not of great concern, but because of certain developments in the technology, there is usually a need to know the potassium content of sodium.

Lithium and potassium are usually determined by flame photometer techniques.[44] The sodium sample is dissolved in water by dropping very small pieces of it into about 2 ml of water in an Erlenmeyer flask or beaker into which a stream of nitrogen gas is rapidly flowing. As more and more sodium reacts with the water, the resulting hydroxide solution becomes quite concentrated, and the sodium–water reaction then slows down. Slightly larger pieces of sodium can now be added, and a small amount of water can be added to speed up the dissolution. In this way, a 1-g sodium sample can be dissolved in about 15 min. The sodium hydroxide formed is titrated with standard hydrochloric acid; the titration neutralizes the solution and gives an estimate of the amount of sodium in the sample. The solution is evaporated and transferred to a volumetric flask and diluted to volume (10 ml for each gram of sodium).

The line intensity of an aliquot of the solution is read on the flame photometer using a didymium filter to reduce the intensity of the sodium light. Standards can be prepared easily by dissolving the appropriate amount of pure sodium chloride and adding measured amounts of alkali-metal standard solutions. The line intensities of the standards are compared with the line intensities of the sample. It is important to have identical sodium chloride concentrations in the standard and sample solutions since the aspiration rate of the solution is affected by the salt content when the solution is moderately concentrated.

An alternate method for estimating the lithium or potassium content of the sample solution is given by the method of standard addi-

tion. After the inital line intensities are observed, a measured aliquot, V_1, of a concentrated standard solution is added to a measured aliquot, V_2, of the sample solution and mixed well. The resulting line intensity is again observed; the increase in intensity is proportional to the mass of standard added. With this information it is possible to calculate the original concentration of the element in the sample solution.

Table 10.6.—WAVE LENGTHS AND SENSITIVITIES OF ALKALI METALS DETERMINED BY FLAME SPECTROPHOTOMETRY

Element	Wave length, mμ	Sensitivity, ppm
Lithium	671	15
Potassium	767	100
Cesium	852	50

Listed in Table 10.6 are the wave lengths and sensitivities for the estimations of the alkali metals in sodium by a flame-photometer technique.

(f) *Cesium.* The determination of cesium [45] in sodium can be accomplished by precipitating ammonium chloroplatinate from a chloride solution and allowing the cesium chloroplatinate to coprecipitate with it. The chloroplatinate is then dissolved in hydrochloric acid, diluted to volume, and determined with the flame photometer.

(g) *Boron.* The boron content of sodium has been measured at the 0.5-ppm level using a 2-g sample. The method utilizes the chromogenic properties of the curcumin–boron complex. Sodium is dissolved in a boron-free container and evaporated to dryness as the chloride salt. The boron is separated from the salt by extracting into acidified ethanol. The boron is estimated colorimetrically in the ethanol extract with curcumin as a reagent. The details of extraction and color development as described by Rynasiewicz et al.,[46] are given in the following procedure.

Procedure. Approximately 2 g of sodium are dissolved in 50 ml of water in a quartz Erlenmeyer flask purged with a continuous stream of nitrogen. The solution is cooled in an ice bath and nearly neutralized to the methyl red end point with the standard 4.5*N* hydrochloric acid. The volume of acid required is a measure of the sample weight. The solution is transferred to a 3¾-in. platinum dish and evaporated just to dryness under a heat lamp. The aggregated sodium chloride is broken up, and 10 per cent hydrochloric acid is added dropwise until the salt is just acid to methyl red. The boron is extracted with 15 ml of 95 per cent ethanol and decanted into a 50-ml centrifuge tube; the ex-

traction is repeated with two more portions of alcohol made acid with 1 drop of 10 per cent hydrochloric acid. The combined extracts are centrifuged for 5 min, transferred to a 2¾-in. platinum dish, and neutralized with 0.1*N* sodium hydroxide. Five milliliters of 0.1*N* sodium hydroxide and 2 ml of 3 per cent glycerol in methanol solution are added, and the mixture is evaporated to dryness under a heat lamp. Heating is continued for several minutes, after which the residue is charred gently over a Meker burner. Ignition is completed with the full heat of the burner. The platinum dish is cooled in a tray of crushed dry ice, and 2 ml of 0.1 per cent curcumin in ethanol is added down the sides of the dish. One milliliter of oxalic–hydrochloric acid reagent is added. (To make this reagent, mix 6 g of oxalic acid and 20 ml of hydrochloric acid and dilute to 100 ml with water.) The reagent is added dropwise allowing each drop to freeze before adding the next one. The dish is removed from the ice and heated in the palm of the hand, and the viscous mixture is rotated around the inside walls of the dish until most of the salt dissolves. The dish is then floated on a water bath maintained at 60±1°C. After evaporation has occurred, the dish is heated for an additional 10 min. The residue is extracted with 70 per cent ethanol, transferred to a 25-ml volumetric flask, and made to volume with 70 per cent ethanol. The suspension is shaken well, and a portion is transferred to a 15-ml centrifuge tube in which it is centrifuged at 1500 rpm for 10 min. The supernatant is decanted into a 20-mm cuvette, and the absorbance is measured at 550 mμ in a spectrophotometer using air as 100 per cent transmission. The blank on the reagents should read about 80 per cent transmission. A standard curve (boron concentration in the 0.02- to 0.32-ppm range vs. absorbance) is prepared by treating standard boron samples in the same manner as the unknown samples except for the alcohol extraction from sodium chloride. The boron in the unknown is determined from the standard curve, which is prepared with each new batch of curcumin reagent.

It should be noted that throughout the procedure, including reagent preparation, the usual laboratory glassware that contains boron is avoided because of the danger of contamination. Details on the precautions used in this regard may be found in the original paper.[46]

(h) *Sulfur.* An Ethyl Corporation procedure[47] describes a nephelometric determination of sulfur in sodium in the 30- to 300-ppm range. This procedure involves measurement of the turbidity produced by the precipitation of barium sulfate. Sulfur also has been determined at concentration levels greater than 30 ppm in sodium by a procedure that entails a reduction to hydrogen sulfide, distillation of the gas, and determination of sulfide by an iodimetric titration.[48, 49]

Procedure. A 3-g sample is dissolved in distilled water, and the sample weight is determined by titration with standard 3*N* hydrochloric acid to the phenolphthalein end point. The sample is evaporated to a volume of 2 ml. Twenty-five milliliters of a reducing mixture (4 parts of hydriodic acid, 4 parts of hydrochloric acid, and 1 part of hypophosphorous acid by volume) is boiled for 20 min in a distillation flask attached to a still. An apparatus of the type shown in Fig. 8.4 of Ref. 49 is suitable for this purpose. During this preboiling a stream of nitrogen

purified through Ascarite is bubbled through the solution at the rate of one bubble per second. The flask containing the reducing mixture is detached and cooled. The sample is added, and the flask is reattached to the still. Twenty milliliters of 0.01*N* sodium hypochlorite in 2*N* sodium hydroxide is introduced into an absorption tube that is attached to the outlet of the still. The flask is heated sufficiently to maintain a steady gentle boil for a period of 20 min, during which time the nitrogen sweep is maintained as during the preboiling of the reducing mixture. Rapid boiling must be avoided to ensure that all the evolved gas condenses. The sodium hypochlorite solution is transferred to a 500-ml iodine flask, 3 g of potassium iodide are added, and the solution is acidified with 6*N* sulfuric acid. After the solution is mixed well, it is allowed to stand 5 min; and then it is titrated with standard 0.01*N* sodium thiosulfate to a starch end point. A reagent blank is carried through the procedure.

(i) *Chloride.* Chloride may be determined turbidimetrically [47] at concentrations of 50 to 500 ppm in a 1-g sample of sodium. Turbidity is produced by the addition of silver nitrate to the sample dissolved in a water–methanol mixture.

Chloride also may be determined by a modification of the mercurimetric titration commonly employed in water analyses.[50, 51] The chloride in the dissolved sample is determined by titration with a standardized solution of mercuric ion. The end point of the reaction is signaled by the formation of a blue-violet complex cation between the excess mercuric ion and the diphenylcarbazone added as an indicator. The procedure is applicable down to a concentration range of 50 ppm in a 1-g sample.

Procedure. Approximately 1 g of sodium is dissolved in water under a stream of nitrogen. The solution is titrated with standard 3*N* nitric acid to the equivalence point as determined with a pH meter. The volume of nitric acid required is a measure of the sample weight. The solution is transferred to a porcelain evaporating dish, and 10 drops of a mixed indicator [diphenyl carbazone (0.5 g) and bromphenol blue (0.05 g) in 100 ml of 95 per cent ethyl alcohol] are added. The pH is adjusted with 0.05*N* sodium hydroxide and 0.05*N* nitric acid until a yellow color is just attained. The solution is then titrated with standard 0.01*N* mercuric nitrate until a blue-violet color just persists. This stage marks the equivalence point for the titration. A reagent blank is titrated in an identical manner. The mercuric nitrate is standardized by titrating aliquots of a standard sodium chloride solution to the same end point.

(j) *Chromium.* Chromium in sodium is determined colorimetrically using diphenylcarbazide as the chromogenic agent. In one procedure [52] the chromium is oxidized to the hexavalent state with potassium permanganate in a sulfuric acid medium. Sodium azide is added to destroy the permanganate color, and the chromium diphenyl carbazide color is developed. The chromium can be estimated at concentrations of 1 ppm in a 1-g sample.

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Mann and White [53] describe a method for determining chromium in sodium at a concentration level of 0.5 ppm using a 4-g sample of sodium. The chromium in the hexavalent state is complexed with tri-*n*-octylphosphine and extracted into benzene. Oxidation is accomplished either with bromine water in a hydrochloric acid solution or with argentic oxide in a sulfuric acid solution. The chromium is then determined directly in the benzene phase by spectrophotometric measurement of the chromium–diphenylcarbazide complex.

Procedure.[53] Sufficient sodium is dissolved in water to yield 1 to 10 μg of chromium. However, no more than 4 g of metal should be dissolved in any case. The solution is titrated to a pH of 7 with standardized 6*N* hydrochloric acid, and the weight of the sample is obtained from the volume of acid required. Sulfuric acid is added in sufficient quantity to produce a final solution that is 5 vol.% in sulfuric acid and has a total volume less than 80 ml. Next, 3 ml of sulfuric acid and 100 mg of argentic oxide are added. The solution is stirred well and then boiled vigorously for 5 min. The solution is cooled, diluted with water to 50 ml if necessary, and transferred to a 125-ml separatory funnel. Sulfuric acid (5*M*) is added to make the solution 1*M*. Five milliliters of 0.2*M* tri-*n*-octylphosphine oxide in benzene is added, and the flask is shaken for 2 min. The phases are allowed to separate, and the organic phase is collected in a test tube containing nonindicating silica gel. Two milliliters of diphenylcarbazide solution (0.25 per cent in absolute alcohol) are transferred to a 10-ml volumetric flask. Next, a 3-ml aliquot of the organic extract is added, and the sample is diluted to volume with ethanol. The procedure for color development just described should be carried out in the sequence given and without interruption. The absorbance of the solution is measured within 1 hr. The measurement is made at 550 mμ against a reference solution that contains only the reagents that have been taken throughout the entire procedure. The chromium concentration is obtained by comparing the absorbance with that of standard solutions of chromium that have been carried through the same procedure.

(k) *Iron.* Rodgers et al.[54] describe a procedure for the analysis of iron in sodium. A large sample is dissolved in methyl alcohol; the resultant solution is neutralized with hydrochloric acid and then evaporated. The salts are dissolved in water, and tartaric acid is added. Ferric sulfide is precipitated with hydrogen sulfide water from an ammoniacal solution. The sulfide is dissolved, the iron is oxidized to the ferric state, and the absorbance of the ferric thiocyanate complex is measured.

Iron also may be estimated colorimetrically at the 1-ppm concentration level on a 1-g sodium sample by means of the standard 2,2′-dipyridyl method.[55] Iron in the dissolved sample is reduced to the ferrous state, the reagent solution containing acetic acid–sodium acetate as a buffer is added, and the absorbance of the pink ferrous complex is measured. The procedure is not sensitive below about 1 ppm.

The ferrous color is measured in the presence of sodium chloride, the solubility of which is equivalent to approximately 1 g of sodium in 10 ml of solution. This factor limits concentrating the sample to improve the sensitivity. Cobalt, nickel, and copper, which may interfere with the iron determination, are not normally present at sufficient concentration levels to warrant separation.

Procedure. Approximately 1 g of sodium is dissolved in water under a blanket of nitrogen. Glass spatulas are used to cut the sodium to prevent contamination of the sample. The solution is titrated to the phenolphthalein end point with standardized 3*N* hydrochloric acid. The volume of hydrochloric acid required is a measure of the sample weight. Three additional drops of hydrochloric acid are added, and the solution is boiled to dissolve iron. The heating is continued until the solution volume is reduced to approximately 20 ml; than the sample is transferred to a 25-ml volumetric flask. Two milliliters of the reagent (1.5 g of 2,2′-dipyridyl, 200 ml of glacial acetic acid, 30 g of sodium acetate, and 50 g of hydroxylamine hydrochloride are dissolved in 500 ml of water) is added. The solution is brought to a 25-ml volume, mixed well, and allowed to stand for 0.5 hr. The absorbance is measured at 522 mμ using 1-cm cells against a reagent blank in the reference cell. A standard curve is prepared by adding known amounts of iron to solutions of dissolved triply distilled sodium and treating the solutions as described above for the actual sample.

(1) *Uranium.* If sodium or sodium–potassium alloy are to be used as a nuclear reactor primary coolant, it is usually desirable to establish the uranium impurity level so that one can be assured of a low initial level of fission-product activity in the system. The analysis may be accomplished by first separating the uranium via an extraction of the tetrapropylammonium uranyl trinitrate with methyl isobutyl ketone from an acid-deficient aluminum nitrate solution.[56] Uranium may be determined in the extract by fluorimetry [57] (see Chap. 1, Sec. 1–3.4). The sensitivity of the method is <0.01 ppm in sodium.

Only the separation procedure is given in detail below.

Procedure. A 1-g sample of sodium is dissolved in water and titrated with standard 6*N* nitric acid to the phenolphthalein end point. A slight excess of nitric acid is added, and the solution is boiled to ensure the dissolution of hydrated uranium oxide. The solution is evaporated to a point just prior to the salting out of sodium nitrate. The solution is transferred quantitatively to a 125-ml separatory funnel with two 25-ml washings of acid-deficient aluminum nitrate containing tetrapropylammonium hydroxide. (In the preparation of this reagent, sufficient water is added to 1050 g of aluminum nitrate hydrate to give a volume of 900 ml. After the salts are dissolved by warming, 67.5 ml of ammonium hydroxide is added, and the solution is stirred until the hydroxide precipitate dissolves. The solution is cooled to less than 50°C, 10 ml of 10 percent tetrapropylammonium hydroxide reagent is added, and the solution is stirred until dissolution is complete. The solution is diluted to 1 liter with water. The reagent is purified by extracting with methyl

isobutyl ketone, and an additional 10 ml of 10 percent tetrapropylammonium hydroxide reagent is added.) The first washing is heated slightly for a few minutes. The solution is extracted with 25 ml of distilled hexone for 10 min. The phases are allowed to separate. The lower, aqueous, phase is discarded, and the uranium in the hexone layer is determined fluorimetrically.

(m) *Other Elements.* Methods for other elements have appeared in the literature, including methods for nickel,[58] cobalt,[59] and calcium.[60]

10–3.4 Spectrographic Determination of Metallic Impurities in Sodium

Unless high accuracy is required, the method of choice for the determination of impurities in sodium would be a spectrographic technique. It is possible to estimate the concentration of many impurities in sodium utilizing only one or two samples instead of individual sample treatment. The time saved is thus an overriding factor when considering the analytical program to support a liquid-metal engineering facility.

Because the determination of a large number of metallic impurity elements is required, it is necessary to employ several different techniques for the complete spectrographic analysis of sodium. These separate spectrographic methods are discussed in (a), (b), (c), and (d) of this section.

Prior to spectrographic analysis, the sodium, when received in the metallic form, must be dissolved and converted to the appropriate salt. In all the methods the sample is dissolved by dropping small bits of the metal into 2 or 3 ml of water contained in a stainless-steel beaker. While the sodium is dissolving, a rapid stream of clean nitrogen is blown into the beaker to prevent ignition of the evolved hydrogen. As the solution becomes concentrated, the reaction rate decreases and may be controlled by small additions of water from time to time. Sodium–potassium alloy samples also are dissolved directly. However, this alloy is extremely reactive and must be dissolved in a mixture of dry ice and ethyl alcohol by a procedure similar to that described by Pepkowitz.[25] In this procedure the tube containing the sodium–potassium alloy is frozen in a dish setting on dry ice. The tube is then shattered. Small pieces of the frozen alloy are then carefully dropped into a slurry of ethyl alcohol and dry ice in an Erlenmeyer flask. The rate of the reaction is controlled by heating or cooling the flask.

When sodium is dissolved in this manner, there is always some contamination by iron, nickel, and chromium if a stainless-steel container is used. Therefore, if these elements are to be determined, the sodium sample must be dissolved in water in a polyethylene or Teflon beaker.

The procedure is identical to that described above, except that when using polyethylene more care must be taken to prevent overheating and damage to the beaker.

For the determination of most of the impurities [Sec. 10–3.4(a)], the dissolved samples are converted to sulfates by titration with $5N$ sulfuric acid. Avoidance of excess acid not only serves to measure the amount of sample taken but also facilitates the evaporation of the solution and drying of the sulfate salt. Similarly, for the determinations of barium and calcium [Sec. 10–3.4(b)] and for mercury [Sec. 10–3.4(c)], the sample solution is titrated with $5N$ hydrochloric acid as the first step in the preparation described below.

Standards are prepared for the determination of most of the impurity elements by the addition of oxides or sulfates of the elements to pure sodium sulfate powder. When standards that will include a large number of impurity elements are being prepared, it is advisable to separate the elements into three or four groups. These groups should be selected to avoid combinations of common groups of elements, such as alkalis and alkaline earths. Three or four high-impurity master standards are then prepared, each of which contains high concentrations of the impurities included in one of the preselected groups. Mixtures of these standards with each other are then made to obtain various concentrations of each of the impurity elements. The standards are mixed in such proportions that no final standard has an appreciably higher total impurity content than the others. When standards are prepared in this manner, there will be no general trend of concentration or composition, and interelement effects are minimized. A discussion of the effects of changing sample composition on element line intensities is given by Ahrens.[61]

No internal-standard element is added to these standards or to the sodium samples. Instead, at least one impurity standard is run in triplicate on each sample analysis plate. Revisions of sample estimates are made to conform to the apparent values for the impurities in this standard.

(a) *Determination of 27 Common Impurities.* The general method for the determination of most of the common metallic impurities in sodium begins with the conversion of the dissolved sample to the sulfate by titration with $5N$ sulfuric acid. The solution is then evaporated, and the dry salt is ground to a fine powder. A spectrograph with a dispersion of 5 to 7 A per millimeter is satisfactory. Normal photographic developing and processing procedures are employed. Other spectrographic conditions used for the analysis are listed in Table 10.7.

Table 10.7—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF GENERAL IMPURITIES IN SODIUM

Wave-length range	2200 to 3600 A
Photographic plate	Eastman spectrum analysis No. 1
Upper electrode	Cathode (3/16- by 1½-in. pure graphite, hemispherical tip)
Lower electrode	Anode (¼- by 1½-in. pure graphite, drilled with a 0.196-in.-diameter 0.120-in.-deep hole)
Sample charge	Salt sample (~75 mg) packed tightly into the anode crater
Excitation	15-amp d-c arc with 2-mm arc gap
Exposure	About 2 min (until the final disappearance of sodium color in the arc)

After the development of the plate, the line intensities of the 27 elements are observed and compared with the impurity lines on a plate of standard samples prepared in the same manner. The lines used and the approximate limits of detection are listed in Table 10.8. Since the method is semiquantitative, the comparison is accomplished by visual means using a projection comparator. Sample estimates are corrected by reference to the observed values for impurities in the standard sample. If these observed values are greater than 50 relative per cent different from the known values for the standard sample, the analysis plate is rejected and the samples are reanalyzed.

Table 10.8—ANALYSIS LINES FOR GENERAL IMPURITIES IN SODIUM

Element	Line, A	Limit of detection, ppm	Element	Line, A	Limit of detection, ppm
Al	3082. 2	4	Li	3232. 6	20
Sb	2598. 1	20	Mg	2795. 5	0. 2
As	2349. 8	50	Mn	2794. 8	1
Be	2348. 6	0. 2	Mo	3132. 6	2
Bi	3067. 7	1	Ni	3414. 8	1
B	2497. 7	2	Pd	3242. 7	2
Cd	2288. 0	1	Si	2881. 6	2
Cr	2835. 6	20	Ag	3280. 7	0. 1
Co	3453. 5	2	Tl	2767. 9	1
Cu	3247. 6	0. 2	Sn	2840. 0	10
Ge	3039. 1	5	Ti	3349. 0	5
In	3256. 1	1	V	3184. 0	2
Fe	3020. 6	1	Zn	3345. 0	20
Pb	2833. 1	1			

Table 10.9—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF BARIUM AND CALCIUM IN SODIUM

Wave-length range	3760 to 5120 A
Photographic plate	Eastman IV F spectroscopic plate
Upper electrode	Cathode (3/16- by 1½-in. pure graphite, hemispherical tip)
Lower electrode	Anode (¼- by 1½-in. pure graphite drilled with a 0.196-in.-diameter 0.100-in.-deep hole)
Sample charge	Salt sample (~60 mg) packed tightly into the anode crater
Excitation	15-amp d-c arc with 2-mm arc gap
Exposure	About 100 sec (until the final disappearance of the sodium color in the arc)

(b) *Determination of Barium and Calcium.* For this procedure the dissolved sample is neutralized with 5*N* hydrochloric acid. At this point a strontium chloride internal-standard solution is added to the sample in the ratio of 100 μg of strontium per gram of sodium dissolved. The sample is then evaporated and the residue is ground to a fine powder. A spectrograph with a dispersion of 5 to 7 A per millimeter is satisfactory. Normal photographic developing and processing procedures are employed. Other spectrographic conditions used are listed in Table 10.9.

Since this determination is an internal-standard method, the analysis line Sr: 4811.9 is measured, as well as the lines Ca: 4226.7 and Ba: 4554.0. Line intensities are read from a calibration curve prepared from two-step data by the preliminary-curve technique.[62] The standard curve is plotted as log I(analysis line)/log I(internal-standard line) vs. log concentration, and data for the curve are run in triplicate.

(c) *Determination of Mercury.* This determination is performed by a concentration technique in which a hydrochloric acid solution of the sample is stirred with copper powder. In a matter of a few minutes, all the mercury in any form in the solution is amalgamated with the copper. The copper powder is washed, dried, and arced in boiler cap electrodes for the detection of mercury at concentrations above 1.0 ppm in the sodium sample. The method has been described in detail by Landis and Pelrine [63] and appears to give a precision of approximately 20 relative per cent. Further work has extended the limit of detectability to as low as 0.1 ppm in sodium.

(d) *Determination of Some Rare-earth Elements.* The determination of the rare-earth elements is accomplished by a separation technique using yttrium as both a carrier and an internal standard. Forty milligrams of yttrium in a nitrate solution are added directly to the dissolved sodium sample. The solution is neutralized with HF, and

Table 10.10—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF RARE EARTHS IN SODIUM USING YTTRIUM CARRIER

Wave-length range	2350 to 4600 A
Photographic plate	Eastman Spectrum Analysis No. 1
Upper electrode	Cathode (3/16- by 1½-in. pure graphite, hemispherical tip)
Lower electrode	Anode (¼- by 1½-in. pure graphite, center-post type with an annular cavity of 0.190- and 0.080-in. diameters and a 0.060-in. depth, UCP type 5986)
Sample charge	~40 mg Y_2O_3 and graphite (1:1 mixture packed into annular cavity)
Excitation	12-amp d-c arc with 2.4-mm arc gap

an excess of 20 ml of concentrated acid is added to precipitate all rare-earth fluorides with the yttrium fluoride. The precipitate is washed thoroughly with 5 vol.% HF, filtered, and ignited to the oxide for spectrographic examination. A spectrograph with a dispersion of approximately 4 A per millimeter which is capable of covering the necessary wave-length range is satisfactory. Normal photographic developing and processing procedures are used. Other spectrographic conditions for the analysis are listed in Table 10.10.

After development of the spectrographic plate, the lines listed in Table 10.11 are read and converted to relative intensities. Intensity ratios of analysis lines to internal-standard lines as concentrations of the elements are read from the standard curves. The ranges of the individual standard curves are listed in Table 10.11. It should be noted that normally a 1-g sodium sample is taken, to which 40 mg of carrier is added. Therefore the concentration factor to be used is approximately 1/25 to convert percentages of rare earths from yttrium to sodium. The precision of this method varies from 10 to 20 relative per cent for the different elements determined.

Table 10.11—ANALYSIS LINES AND RANGES FOR RARE-EARTH ELEMENTS IN YTTRIUM CARRIER

Element line, A	Internal standard line for yttrium, A	Range, %
Ce 4012.39	4291. 03	0. 005–0. 5
Dy 3407.80	3450. 95	0. 005–1. 0
Eu 4435.60	4291. 03	0. 03 –1. 0
Gd 4327.10	4291. 03	0. 05 –1. 0
Sm 4334.14	4291. 03	0. 10 –2. 0

Table 10.12.—SUMMARY OF ANALYTICAL METHODS

Component or property	Method	Accuracy	Precision	Time required, hr
Biphenyl and *o*-, *m*-, and *p*-terphenyls.	Infrared spectroscopy*	$\sigma = \pm 0.5\%$ absolute	$\sigma = \pm 0.5$ wt. % absolute	3
	Gas chromatography†	$\sigma = \pm 0.5\%$ absolute	$\sigma = \pm 0.4$ wt. % absolute	4
Triphenylene	Ultraviolet spectroscopy‡	Variable	$\sigma = \pm 0.6\%$	4
Low boilers (benzene toluene, ethyl benzene, and others).	Gas chromotography	5 to 10 wt. % relative	5 to 10 wt. % relative	8
High-boiler components (group type analysis)	Mass spectroscopy (low voltage)¶			
High-boiler content	Microdistillation	?	$\sigma = \pm 0.6$ wt. % absolute	3
	Macrodistillation	?	$\sigma = \pm 0.23$ wt. % absolute	3
Molecular weight§	Signer method**	5 to 10%	5%	3
	Cryoscopic in benzene	5 to 10%	5%	2
	Cryoscopic in camphor	5 to 10%	5%	2
Carbon and hydrogen	Macrocombustion	%C ± 0.06% absolute		
		%H ± 0 03% absolute	Same	2
Olefin content	Ozone absorption	$\sigma = \pm 0.0303\%$ absolute 2 to 10% relative.	$\sigma = \pm 0.030\%$ absolute 2 to 10% relative.	4

*Applicable mainly to virgin coolants that absorb at designated wave lengths Radiolysis products or other components interfere

†Applicable to samples containing up to 40 per cent high boilers

‡Accuracy depends on composition, especially presence of other condensed-ring hydrocarbons and substituted triphenylenes Limit of detection is about 0 4 per cent as triphenylene

¶This method can be considered routine only when examining similar materials Time required depends mainly on difficulty of interpretation of data and is variable. Minimum time is about 8 hrs

§Accuracy and precision are estimates Duplicate determinations usually agree within 5 per cent, but differences between methods may be 10 per cent or more

**Two or three weeks may be required for equilibrium to be established

10.4 POLYPHENYL REACTOR COOLANTS

By C. J. Rodden

The use of organic materials for moderating and cooling reactors required that methods be developed for the determination of the organic coolants as well as their pyrolytic–radiolytic decomposition products.[64] The coolants are of the polyphenyl type and consist of biphenyl and ortho-, meta-, and para-terphenyls. Composition of the initial coolants is determined by gas chromatography or by an infrared absorption method.

The pyrolytic–radiolytic decomposition products of the polyphenyl coolants are grouped according to their boiling points. The low boilers have a higher boiling point than biphenyl and a lower one than terphenyl. High boilers have a higher boiling point than terphenyl. Because of the volatility of the low boilers, the total vapor pressure of the coolant mixture may depend to a considerable extent upon their presence. The low boilers are determined by gas chromatography.

Intermediate boilers may make up 6 to 10 per cent of the decomposition products, but their determination is not routine.

High boilers are usually determined by a mass-spectrometric procedure although triphenylene, a high-boiling decomposition product of terphenyl, is determined by a differential ultraviolet absorption method.

Other methods for the determination of individual compounds as well as for certain properties, such as high-boiler content of coolants, average molecular weight, carbon and hydrogen content, and olefin content, have been described in detail in Ref. 64. This report should be consulted for procedural details. The various methods used are summarized in Table 10.12.

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CHAPTER 11

TRACE ELEMENTS

By M. W. Lerner*

Impurities can have a profound effect on the nuclear, chemical, and physical properties of metals. Of primary importance in the metals used in nuclear technology is the parasitic capture of neutrons by these contaminants. This ability to absorb neutrons may be conveniently expressed as a danger coefficient, K, defined as the ratio of effective area presented to neutrons per gram of impurity to the effective area presented to neutrons per gram of reference material. The danger coefficient is calculated by

$$K=\frac{S_i}{S_s}=\frac{N\sigma_i/A_i}{N\sigma_s/A_s}=\frac{\sigma_i}{\sigma_s}\frac{A_s}{A_i}$$

where S is the effective area presented to neutrons per gram (cm^2/g); N is Avogadro's number (6.023×10^{23} atoms/mole); σ is the atomic cross section for absorption of thermal neutrons (cm^2/atom); A is the atomic weight (g/mole); and subscripts i and s refer to impurity and reference material, respectively.

The atomic cross section for thermal neutrons and the danger coefficient for each element with various materials as a reference are shown in Table 11.1.

The effect of each impurity on the neutron economy is the product of the concentration and K. The total effect of all the impurities, the total danger summation TDS, is thus the sum of all the products of concentration and K. If the neutron losses in a reactor are to be kept to an acceptable level, the TDS must not exceed a definite value. The determination of only traces of those impurities with large danger coefficients must, therefore, be made with some accuracy.

The increased knowledge of the effect of impurities on the corrosion resistance and metallurgical properties of metal reemphasizes the need for an accurate determination of the impurities. Consider, for example, the corrosion of zirconium. Although high-purity metal exhibits excellent corrosion resistance in water at elevated temperatures, as little as 40 ppm of nitrogen in the metal causes rapid disintegration under the same conditions.[3]

11–1 METHODS FOR OXYGEN, HYDROGEN, NITROGEN, AND CARBON

Contaminating elements of great importance because of their effect on metallurgical properties are the gases oxygen, hydrogen, and nitro-

*New Brunswick Laboratory, U.S. Atomic Energy Commission, New Brunswick, N.J.

Table 11.1—CROSS SECTIONS AND DANGER COEFFICIENTS FOR THERMAL NEUTRONS WITH RESPECT TO VARIOUS SUBSTANCES

Element	Cross section,* 10^{-24} cm²	Atomic weight†	Impurity danger coefficients (K)‡		
			K(U)	K(UO_2)	K(Be)
H	0. 33	1. 0080	10. 2	11. 6	290
Li	71. 0	6. 940	320. 5	364	9, 220
Be	0. 01	9. 013	0. 03	0. 04	1. 0
B	755	10. 82	2, 186	2, 480	62, 900
C	0. 0032	12. 011	0. 0083	0. 0095	0. 24
N	1. 88	14. 008	4. 20	4. 77	121
O	<0. 0002	16. 000	<0. 0004	<0. 0004	<0. 01
F	<0. 01	19. 00	<0. 02	<0. 02	<0. 5
Na	0. 505	22. 991	0. 688	0. 781	19. 80
Mg	0. 063	24. 32	0. 081	0. 092	2. 33
Al	0. 230	26. 98	0. 267	0. 303	7. 68
Si	0. 13	28. 09	0. 15	0. 16	4. 2
P	0. 19	30. 975	0. 19	0. 22	5. 5
S	0. 49	32. 066	0. 48	0. 54	13. 8
Cl	31. 6	35. 457	27. 9	31. 7	803
Ar	0. 62	39. 944	0. 49	0. 55	14. 0
K	1. 97	39. 100	1. 58	1. 79	45. 4
Ca	0. 43	40. 08	0. 34	0. 38	9. 6
Sc	24. 0	44. 96	16. 7	19. 0	481
Ti	5. 6	47. 90	3. 7	4. 2	105
V	5. 1	50. 95	3. 1	3. 6	90
Cr	2. 9	52. 01	1. 7	2. 0	50
Mn	13. 2	54. 94	7. 5	8. 5	217
Fe	2. 53	55. 85	1. 42	1. 61	40. 8
Co	37. 0	58. 94	19. 7	22. 3	566
Ni	4. 6	58. 71	2. 5	2. 8	71
Cu	3. 69	63. 54	1. 82	2. 06	52. 3
Zn	1. 06	65. 38	0. 507	0. 58	14. 6
Ga	2. 77	69. 72	1. 24	1. 41	35. 8
Ge	2. 35	72. 60	1. 014	1. 150	29. 2
As	4. 1	74. 91	1. 71	1. 94	49
Se	11. 8	78. 96	4. 68	5. 31	135
Br	6. 6	79. 916	2. 59	2. 94	74
Rb	0. 7	85. 48	0. 26	0. 29	7
Sr	1. 16	87. 63	0. 415	0. 471	11. 9
Y	1. 38	88. 92	0. 486	0. 552	14. 0
Zr	0. 180	91. 22	0. 0618	0. 0701	1. 78
Nb	1. 1	92. 91	0. 37	0. 42	11
Mo	2. 5	95. 95	0. 82	0. 93	24
Ru	2. 46	101. 1	0. 762	0. 865	21. 9
Rh	150	102. 91	46	52	1, 300
Pd	8. 0	106. 4	2. 35	2. 67	68

See footnotes at end of table.

Table 11.1—CROSS SECTIONS AND DANGER COEFFICIENTS FOR THERMAL NEUTRONS WITH RESPECT TO VARIOUS SUBSTANCES—Con.

Element	Cross section,* 10^{-24} cm²	Atomic weight†	Impurity danger coefficients (K)‡		
			K(U)	$K(UO_2)$	K(Be)
Ag	62	107. 880	18. 0	20. 4	520
Cd	3, 315	112. 41	923. 8	1, 048. 1	26, 580
In	190	114. 82	51. 9	58. 9	1, 490
Sn	0. 60	118. 70	0. 158	0. 179	4. 6
Sb	5. 5	121. 76	1. 42	1. 61	41
Te	4. 5	127. 61	1. 11	1. 25	32
I	6. 7	126. 91	1. 65	1. 88	48
Cs	29. 0	132. 91	6. 8	7. 75	197
Ba	1. 17	137. 36	0. 267	0. 303	7. 7
La	8. 9	138. 92	2. 01	2. 28	58
Ce	0. 70	140. 13	0. 157	0. 178	4. 5
Pr	11. 2	140. 92	2. 49	2. 83	72
Nd	46	144. 27	10. 0	11. 3	290
Sm	8, 250	150. 35	1, 719	1, 950	49, 500
Eu	4, 370	152. 0	900. 6	1, 021. 8	25, 900
Gd	39, 100	157. 26	7, 787	8, 835	224, 000
Tb	44	158. 93	8. 7	9. 8	250
Dy	1, 100	162. 51	210	240	6, 000
Ho	64	164. 94	12. 2	13. 8	350
Er	166	167. 27	31. 1	35. 3	890
Tm	118	168. 94	21. 9	24. 8	630
Yb	36	173. 04	6. 5	7. 4	190
Lu	108	174. 99	19. 3	21. 9	560
Hf	105	178. 50	18. 4	20. 9	530
Ta	21. 3	180. 95	3. 69	4. 18	106
W	19. 2	183. 86	3. 27	3. 71	94. 1
Re	84	186. 22	14. 1	16. 0	406
Os	14. 7	190. 2	2. 42	2. 75	69. 7
Ir	430	192. 2	70	80	2, 020
Pt	8. 1	195. 09	1. 30	1. 47	37. 4
Au	98. 0	197. 0	15. 58	17. 68	448. 4
Hg	361	200. 61	56. 4	64. 0	1, 622
Tl	3. 3	204. 39	0. 50	0. 57	14. 5
Pb	0. 170	207. 21	0. 0257	0. 0292	0. 739
Bi	0. 032	209. 00	0. 0048	0. 0054	0. 138
Th	7. 0	232. 05	0. 95	1. 07	27. 2
U	7. 60	238. 07	1. 000	1. 136	28. 81

*See Ref. 1.

†See Ref. 2.

‡For use with concentrations expressed in percent. When impurity concentrations are expressed in parts per million, danger coefficients must be multiplied by 10^{-4}.

Table 11.2—CURRENT METHODS FOR DETERMINATION OF OXYGEN HYDROGEN, NITROGEN, AND CARBON

Method	Elements determined			
	Oxygen	Hydrogen	Nitrogen	Carbon
Vacuum fusion	X	X	X	
Vacuum extraction		X		
Equilibrium pressure		X		
Inert-gas fusion	X			
Unreacted residue	X			
Combustion	X	X		X
Kjeldahl			X	
Bromination, chlorination	X			
Fluorination	X		X	
Isotope dilution	X	X	X	

gen, which are introduced during production and fabrication of the metal. These elements can be present as occlusions, in solid solution, or in such chemical combinations as precipitated oxides and nitrides. Carbon, free or combined, is another element frequently considered with the gases as a group.

Existing methods of determining oxygen, hydrogen, nitrogen, and carbon are numerous. Table 11.2 gives the commonly used names and the applications of the methods discussed in this chapter to the analysis of these elements.

11–1.1 Vacuum Fusion Method for Oxygen, Nitrogen, and Hydrogen

Conventional analytical techniques are generally not sufficiently refined for the determination of traces of gases in metals. However, the vacuum fusion technique, which has been used in the steel industry for many years, has been applied successfully to reactor metals, particularly to the determination of oxygen and hydrogen.

The vacuum fusion technique consists primarily in fusing the metal in a graphite crucible under high vacuum. The oxygen, hydrogen, and nitrogen in the sample are evolved, the oxygen chiefly as carbon monoxide with probable traces of carbon dioxide. Although the oxygen and hydrogen are quantitatively removed from the sample, the complete recovery of nitrogen as discussed in this section is often open to question. The evolved gases can be determined by conventional gas analysis or by the mass spectrometer after being isolated from the vacuum system, or, as in many current procedures, they can be analyzed directly in the evacuated system by low-pressure techniques involv-

ing chemical or physical methods of separation and manometric measurements.

The vacuum fusion technique thus measures simultaneously all the gases present in the sample which are evolved under the vacuum fusion treatment regardless of the forms in which they are present. Moreover, the vacuum fusion technique possesses the inherent advantage that gasometric methods have over gravimetric and volumetric methods, that of high sensitivity. For example, when the hydrogen is released from a 0.3-g sample containing 50 ppm of hydrogen and is confined to a volume of 1 liter, it exerts a pressure of 0.14 mm Hg. A McLeod gauge can readily measure pressures of 1×10^{-5} mm. It can easily be seen that the lower limit of determination is actually set by the magnitude of the blank values.[4]

In past years, all the vacuum fusion equipment was made in the individual laboratories carrying out the analyses and was, therefore, of variable design. Recently, commercial equipment has become available and one such apparatus is described in detail in Sec. 11–1.1(b)(1). Another recent innovation has been the development of simpler and faster microapparatus which is described in the same section.

However, despite the improvements that have led to fast and reliable determinations, the vacuum fusion method for oxygen may soon be supplanted by a much simpler procedure, devised by Smiley,[5] in which the fusion is carried out at near atmospheric pressure in a current of inert gas such as argon.

(a) *General Considerations.* (1) *Apparatus and Techniques.* The vacuum fusion apparatus consists of a furnace and heater, an evacuation system, and an analytical system. Many furnaces of macroapparatus now in use are identical to the design of Guldner and Beach.[6] A graphite melting crucible is packed in graphite powder inside a quartz crucible, the whole assembly being suspended inside a borosilicate furnace jacket. The glass jacket, which provides for full vision, is air cooled. Minor modifications of the basic design exist.[7-9]

The furnace is heated by high-frequency induction. The easily maintained spark-gap converter with its broad frequency band and the more complicated electronic type with a sharp peak are both satisfactory.[10] A helical copper coil around the furnace carries the high-frequency current. A 5- to 10-kw output is ordinarily sufficient; often heaters with 2- to 5-kw outputs are used.

The furnace and gas-analyzing system are evacuated, generally, by an oil diffusion pump backed by a mechanical pump. A fast two- or four-stage mercury pump coupled near the furnace removes the gases from the furnace area as rapidly as possible. Mercury cutoff valves appear to be more popular than stopcocks.

690–457 O—64——47

A major problem in vacuum fusion procedures is the loss of the evolved gases by absorption or by combination on a film of metal vaporized during the sample fusion, a phenomenon known technically as gettering. Titanium, zirconium, manganese, and certain impurities in uranium are efficient getters. Gas losses by gettering can be suspected if the results obtained with successive analyses of the same sample are progressively lower. Gettering can be practically eliminated in most cases by pumping the evolved gases away from the furnace area as rapidly as possible and by diluting the sample with a metal such as iron or platinum to reduce its volatility.[11] The metal bath has two other functions. First, it forms eutectic alloys with the metal sample, and thus permits the analysis to be performed at a considerably lower temperature than the melting point of the metal. Second, carbon is soluble to some extent in the metal bath, and thus more intimate contact of the sample with carbon is made.

A difficulty associated with the use of an iron bath is the increase is viscosity of the melt with time at 1800°C or higher. This gradual solidification, which may be caused by the accumulation of graphite flakes from the bath at the surface of the molten iron,[12] has been found to be a serious source of error in the iron-bath technique.[13] This difficulty can be overcome to some extent by the addition of more iron with each sample, or, as in recent procedures, by the use of platinum or a combination of platinum and iron for the bath. Not only does the use of a platinum bath eliminate the problem of bath solidification, but also it offers other advantages, e.g., low volatility, negligible attack on the graphite crucible, shorter outgassing time, and improved reproducibility and accuracy in the analysis of certain refractory metals. More than 80 per cent of the platinum is recoverable, and therefore the cost is not excessive. The use of tin, added either alone or with iron or platinum, is often used. The beneficial effect of the tin may be a result of the formation of a coating of tin on the furnace tube walls, covering up any reactive metal film.[4, 13] Other investigators suggest that tin enhances the fluidity of the bath and therefore promotes better contact [14] of the sample with carbon or that the tin, in boiling, helps to sweep out the carbon monoxide evolved from the bath.[13, 15] The different metal baths used are described under the discussions of the individual metals.

Once the system has been outgassed and a satisfactory blank has been obtained, a sample is introduced into the furnace, and the gases are collected. Early investigators transferred the gases to an external gas-analysis apparatus for conventional separation and measurement at atmospheric pressure. Large quantities of gas were necessary, and losses in transfer frequently resulted.

These procedures have been superseded for the most part by low-pressure methods in which the analyses are carried out directly in the evacuated system. Many different analytical arrangements are used. Mercury diffusion and Toepler pumps circulate the gases through the system, and measurements are made with McLeod or Pirani gauges, the former being used more often. Frequently the carbon monoxide and hydrogen are oxidized to carbon dioxide and water. The carbon dioxide, water, and nitrogen are then separated chemically or physically and measured.

Oxidation of the carbon monoxide and hydrogen is conveniently carried out by passing the gas through cupric oxide at about 375°C or through a mixture of kaolin, Misch Metal, and cupric oxide.[9] Other methods [16, 17] employ oxygen and a platinum filament at 500°C. This latter technique is generally unsatisfactory in that some oxygen is adsorbed by the platinum and must be determined by hydrogen addition and combustion. The selective oxidant, Hopcalite, an activated manganese dioxide (Mine Safety Appliances Co.), has been used to oxidize carbon monoxide to carbon dioxide, leaving the hydrogen unchanged.[18-20] In the Hopcalite procedure, the carbon dioxide is frozen out by liquid nitrogen, and hydrogen is determined by measuring the drop in pressure when the gas mixture is brought into contact with a palladium tube at 350 to 400°C. The residual gas is nitrogen. If only oxygen need be determined, the carbon dioxide is absorbed by Ascarite.[8] Turovtseva and Litvinova [21] prefer separating the hydrogen by diffusion through a palladium tube before oxidizing the carbon monoxide with cupric oxide.

In the widely adopted procedure used with the commercial apparatus of the National Research Corporation, the oxidant is specially prepared copper oxide held at 325°C. The water is separated by absorption in magnesium perchlorate, the carbon dioxide is frozen out in a liquid-nitrogen trap, and the residual nitrogen is measured. The carbon dioxide is then released by removal of the liquid-nitrogen trap and is measured. The hydrogen is calculated by difference. The magnesium perchlorate is reactivated at 250°C *in vacuo*. Aware of the danger in heating magnesium perchlorate, some workers do not recommend its use and prefer to separate the water in a dry-ice trap.[22]

In another widely used procedure, both the carbon dioxide and water are separated by a liquid-nitrogen trap before the residual nitrogen is measured. The liquid nitrogen is then replaced by a dry ice–acetone or a dry ice–methanol slush, and the carbon dioxide is evaporated and measured.

When mass-spectrometric analysis of the gas is desired, the gases may be collected in a manifold and transferred into bulbs, which

are taken to the mass spectrometer.[4, 23] The vacuum fusion apparatus can be attached directly to the mass spectrometer.[24] A major disadvantage of this analytical method is the difficulty in differentiating between carbon monoxide and nitrogen, both of which have a mass of 28. If the mass-29 fraction, which is chiefly the $C^{13}O$, is determined and is multiplied by the C^{12}/C^{13} abundance ratio of 89.1, the total carbon monoxide of the mass-28 fraction can be found, but only at the cost of considerable loss in accuracy.[23]

(2) *Standard Samples.* Since in most cases adequate standards are not available to check the efficiency of a vacuum fusion procedure, it is often necessary to take recourse to the results of analyses by a different procedure. For example, in the determination of oxide in zirconium, comparison can be made with results obtained by the hydrogen chloride residue procedure of Read and Zopatti.[25] However, it must be remembered that in vacuum fusion all the gases are measured, whereas in unreacted residue techniques only combined gases are determined. The problem is further complicated by segregation in the sample.

These two difficulties can be alleviated somewhat, if oxide standards are desired, by arc-melting the metal *in vacuo* or in an inert atmosphere before sampling. Once the base oxygen level has been established, pure metal oxide can be added to the now homogeneous metal, and another arc-melting can be carried out to provide a sample on which the oxygen recovery can be determined. This technique has been followed for niobium,[26] titanium,[15, 27] and zirconium.[13]

The direct use of pure-metal oxide added along with the sample may not be satisfactory because of the violent reaction of the oxide when it is dropped into the crucible. However, this procedure has been followed successfully with the following compounds and the corresponding metals: U_3O_8 (Ref. 21), ThO_2 (Refs. 20 and 28), ZrO_2 (Refs. 17 and 20), TiO_2 (Refs. 8, 9, and 21), BeO (Ref. 17), Na_2O_2 (Ref. 21), NaOH (Ref. 21), and Nb_2O_5 (Ref. 21).

Many attempts have been made to prepare oxide, hydride, and nitride standards of particular metals by the manometric addition of the gases to metal samples or simply by noting the weight increase after reaction of the metal with an excess of gas. By these procedures the following standards have been prepared: uranium oxide [23, 29] and nitride;[29] zirconium oxide,[14] nitride,[20] and hydride;[4] titanium oxide,[9, 27, 28] nitride,[9] and hydride;[9, 30] and niobium oxide.[26] Special apparatus to perform these manometric additions has been designed.[9, 23] Certain attempts to prepare uranium nitride [23] and beryllium oxide [17] standards by similar procedures failed. Samples prepared in this manner contain the oxide chiefly in the surface layer and

consequently must be used in their entirety. More homogeneous samples can be obtained by arc-melting.

The proper functioning of the apparatus has been checked by using cupric oxide.[19] Also, the National Bureau of Standards has eight standard iron and steel samples that can be used for the same purpose.[13, 31] Frequently such standards are used after a series of analyses to determine the absence of gettering.

(3) *Precision and Accuracy of Oxygen and Hydrogen Determinations.* In spite of the many differences in vacuum fusion apparatus and techniques, skilled operators can obtain remarkably reproducible values for oxygen and hydrogen on the same sample. However, true precision is difficult to establish because of the effect of sample inhomogeneity, which, however slight, can cause large variations.

The accuracy also is difficult to define because of the lack of standard samples and the uncertainty in the preparation of samples of known gas content. Moreover, any study in which the vacuum fusion results are compared with results of a chemical method suffers from the unreliability of the chemical method.

The precisions and accuracies reported by various investigators are listed under the discussions of the individual metals. In general, it can be stated that the results found by experienced analysts are reproducible to within 10 per cent. The accuracy obtainable is also within 10 per cent of the true value.

(4) *Determination of Nitrogen.* Although a few investigators report fairly reproducible values for nitrogen in uranium by vacuum fusion [platinum bath [21] (1900°C) and no metal bath [23] (1800°C)], there is ample evidence that the nitrogen values by vacuum fusion are unreliable and generally low for most metals. Table 11.3 lists nitrogen values found by Griffith, Albrecht, and Mallett [29] using both vacuum fusion and the Kjeldahl procedure on six samples of uranium.

Table 11.3—COMPARISON OF VACUUM FUSION AND KJELDAHL METHODS, FOR NITROGEN DETERMINATION IN URANIUM*

Nitrogen by vacuum fusion method (Fe-Sn, 1750°C), ppm	Nitrogen by Kjeldahl method, ppm
24	50
4	20
5	50
15	50
6	70
61	50

* From Ref. 29.

Booth, Bryant, and Parker [20] also found the nitrogen results unsatisfactory in the anlysis of uranium, although the oxygen and hydrogen values were reliable. They obtained similar results in their analyses of thorium, zirconium, and titanium. The metals were all analyzed by the platinum-bath technique at 1820°C, 1850 to 1900°C, 1900 to 1950°C, and 1880°C, respectively.

Three possible reasons for the low nitrogen values that were obtained are (1) failure to decompose the nitride, (2) gettering of the nitrogen, and (3) inaccurate gas analysis. Booth, Bryant, and Parker [20] could find no evidence for reasons (2) and (3). Tests made with thorium nitride prepared at 1860°C showed complete recovery of the nitrogen, whereas nitrides prepared at lower temperatures gave erratic recoveries. Presumably, then, the low nitrogen values can be related in some way to the failure to decompose the nitride.

The low recoveries of nitrogen in titanium or zirconium obtained by Yeaton [10] (dry tin bath, 1200 to 1900°C), see Sec. 11–1.1(b)(1); Goto, Suzuki, and Onuma [32] (iron bath, 1850 to 1900°C); Davis and Gray [19] (iron bath, 1700 to 1750°C); and Taylor [4] (iron-tin bath, 1900°C) may also be ascribed to the high stability of the nitride as compared to the oxide, although gettering has been blamed.[19] Yeaton suggests that a stable carbonitride may be formed.

On the other hand, near quantitative recovery of nitrogen from zirconium-base materials has been reported by Heumann [33] (platinum bath, 1950°C). Satisfactory recoveries of nitrogen from niobium and molybdenum have been reported by Turovtseva and Litvinova [21] (iron-tin bath, 1650°C) and Harris [34] (platinum bath, 1950°C). In the latter case, the use of an iron bath at 1750°C led to recoveries of only traces of nitrogen. Whether the difference was due to the bath composition or to the higher temperature of the platinum bath was not determined.

The determination of nitrogen in plutonium apparently offers no difficulties. Taylor [4] reports that reliable values can be obtained with an iron-tin bath at 1900°C and ascribes the success of the procedure to the low stability of the nitride as compared with the oxide.

Despite the occasional success of the vacuum fusion technique for the determination of nitrogen, it is apparent that the procedure leaves much to be desired. The majority of investigators feel that the Kjeldahl method, Sec. 11–8, should be employed as the method of choice or at least as a means of checking the vacuum fusion values.

(b) *Analysis of Individual Metals.* (1) *Uranium.* The iron-bath (1800°C) technique of Sloman and Harvey, [28] who also analyzed thorium, zirconium, titanium, molybdenum, and vanadium, gave erratic results for oxygen and nitrogen in uranium when used by Griffith,

Albrecht, and Mallett.[29] The addition of tin to the iron bath (1750°C) in a macroapparatus [35] developed for the analysis of molybdenum improved the oxygen results, but the nitrogen values were still unsatisfactory.

Gregory, Mapper, and Woodward [23] have described a microapparatus with which they believe no metal bath is necessary for the analysis of uranium. With a crucible temperature of 1800°C, results for oxygen, hydrogen, and nitrogen were in fair agreement with those obtained by the method of Sloman and Harvey.[28] An improved apparatus has been reported.[16]

A reliable procedure appears to be the platinum-bath technique reported by Booth, Bryant, and Parker,[20] who successfully analyzed uranium, thorium, zirconium, and titanium for oxygen and hydrogen. The nitrogen values were unsatisfactory. Turovtseva and Litvinova [21] have described a similar microprocedure and have reported oxygen, hydrogen, and nitrogen values; no evidence of the reliability of the nitrogen values was presented. These authors also analyzed beryllium, yttrium, tantalum, and silicon by the same technique.

Determination of Oxygen and Hydrogen by Vacuum Fusion (Microapparatus).[20] The microapparatus used by Booth, Bryant, and Parker is shown in Fig. 11.1. The graphite crucible, heat shield, and silica furnace are similar to those used by Gregory, Mapper, and Woodward.[23] A crucible temperature of 2400°C is obtainable with an induction heater, rated at 15 kw, at an indicated output of 8 to 9 kw. The large generator is necessary because the small crucible is surrounded by only a small part of the induction coil and because no graphite powder insulation around the crucible is used.

Twelve samples can be accommodated in the loading tree. The samples are released by raising retaining plungers magnetically. (Swann and Williams [36] have recently modified this loading tree.) Samples are guided into the crucible by a silica funnel, which is lowered by moving its counterweight with a magnet. Material for the metal bath is stored in the four side arms of the furnace assembly and can be dropped by raising the retaining plungers.

Temperatures are measured by an optical pyrometer of the disappearing-filament type. Observations are made through a quartz window in the side arm of the furnace tube, and corrections for absorption by the prism and window are made.

Evolved gases are removed from the furnace tube by a two-stage mercury diffusion pump with a pumping capacity of 6 liters/sec, which is connected to the furnace-tube assembly by 35-mm tubing. This transfer pump has a critical backing pressure equivalent to 4 mm of mercury since the pressure in the collecting volume may at times build up to 1 to 2 mm.

The system is evacuated by a two-stage mercury diffusion pump backed by a mechanical pump. Provision is made for all parts of the apparatus

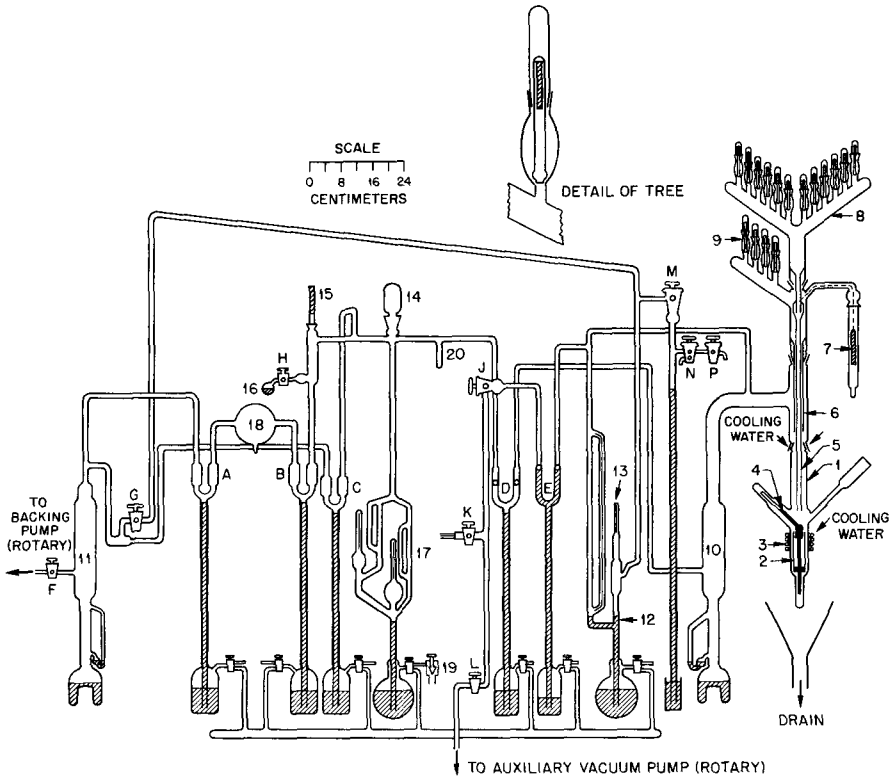


Fig. 11.1 Vacuum fusion microapparatus.

1. Silica furnace tube
2. Graphite crucible and heat shield
3. High-frequency heating coil
4. Graphite dolly attached to steel rod
5. Silica dropping funnel
6. Guide for dropping funnel
7. Counterweight for dropping funnel
8. Tree containing samples
9. Side arms for bath material
10. 2-stage mercury diffusion pump
11. 2-stage mercury diffusion pump
12. Gas buret
13. Precision-bore capillary tubing
14. Pirani-gauge head
15. Palladium tube
16. Bulb containing Hopcalite
17. McLeod gauge
18. 1-liter bulb
19. Needle valve
20. Cold finger

A, B, C, D, E—Mercury cutoffs. F, G, H, J, K, L, M, N, P—Stopcocks.

to be evacuated simultaneously to avoid mercury "fly-over." A second mechanical pump provides auxiliary services, such as lowering the mercury in the cutoffs, in the McLeod gauge, and in other components.

Pressure measurements are made with a double-scale McLeod gauge, 10^{-5} to 10^{-1} and 10^{-1} to 1 mm of mercury, or alternatively with a Pirani gauge. The Pirani gauge is invaluable in checking for completeness of gas evolution and in following the course of the gas analysis. The

calibration of the 800-ml collecting volume is carried out by measuring the pressure and volume of a suitable amount of dry oxygen confined in the precision-bore tubing of a gas buret and then transferring the gas into the collecting volume, measuring its pressure, and calculating the volume.

Hopcalite, an activated manganese dioxide, is used in the analytical system to oxidize carbon monoxide to carbon dioxide. The oxidation is accomplished in 2 to 3 min at room temperature. The carbon dioxide is frozen out in a liquid-nitrogen trap. Hydrogen is determined by measuring the drop in pressure when the gas mixture is brought into contact with a palladium tube heated to 350 to 400°C. The residual gas is assumed to be nitrogen. The complete analysis takes about 10 min.

Samples are prepared by cutting with a hacksaw and abrading with a file. After being degreased and weighed, the samples are stored in a desiccator. The samples and a suitable weight of platinum in the form of short lengths of wire are loaded into the tree and side arm, respectively. The furnace tube, fitted with a new crucible, and the tree are placed in position, and all joints are made secure with Picein wax. When the apparatus has been evacuated to about 10^{-3} mm, the induction heater is switched on, and the crucible is heated at 800 to 1000°C for a few minutes to remove loosely held moisture and air. Then the temperature is raised to about 2200°C until the blank run is acceptable, usually about 1½ to 2 hr. When outgassing of the crucible is complete, the crucible is allowed to cool to below 1000°C, and the platinum is added. The temperature is raised to 1860±20°C over a period of 2 to 3 min, and the platinum is outgassed for about 20 min. The temperature is then lowered to 1820±20°C, and the blank gas is collected for 10 min and then analyzed. The composition of the blank is typically 30 to 40 per cent carbon monoxide, 50 to 60 per cent hydrogen, and 10 per cent nitrogen.

The precise technique used for sample addition varies with the sample. With samples of thorium, titanium, and zirconium, the crucible can be maintained at the operating temperature throughout the run. With uranium, it is preferable to switch off the heater between samples if more than six to eight samples are to be analyzed; this is done to avoid metal evaporation. The evolution of gas is, in general, complete in less than 1 min, but a collection period of 2 to 3 min is given to allow a wide safety margin. After the collected gases have been isolated from the furnace tube by raising a mercury cutoff, the analysis is carried out, the residual gas is pumped away, and the next sample is added.

With 3 g of platinum in the bath at 1820±20°C and with 60- to 200-mg samples, the absolute standard deviation of the oxygen results obtained by Booth, Bryant, and Parker[20] on a sample of uranium was found to be 0.003 per cent at the level of 0.016 per cent oxygen. The hydrogen values were termed satisfactory. The uranium content of the bath should not exceed 30 per cent.

Determination of Oxygen and Hydrogen by Vacuum Fusion (Macroapparatus).[37] The New Brunswick Laboratory uses a commercial macroapparatus manufactured by the National Research Corporation for the routine analysis of uranium and thorium for oxygen and hydrogen.

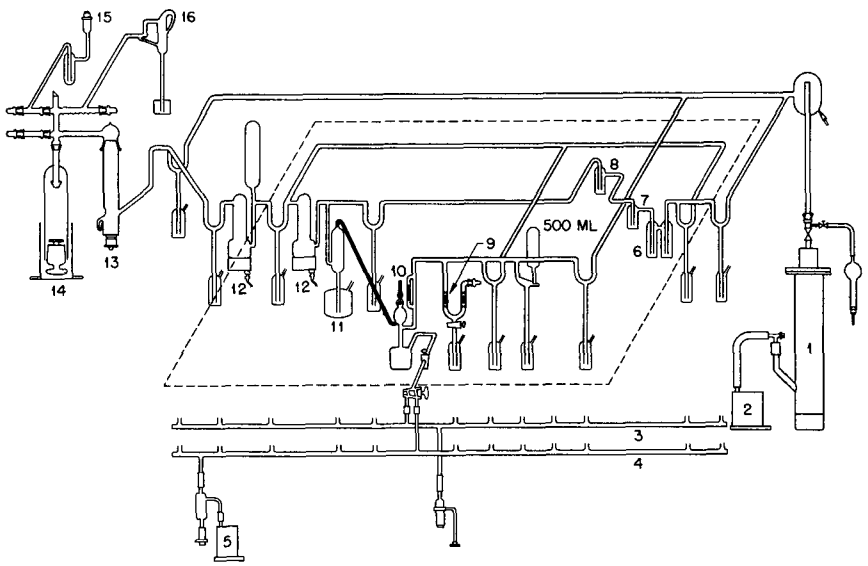


Fig. 11.2 Vacuum fusion macroapparatus (National Research Corporation).

1. Diffusion pump
2. Fore pump
3. Vacuum manifold
4. Air manifold
5. Manifold pump
6. Freezing trap
7. $Mg(ClO_4)_2$ trap
8. CuO trap
9. Mercury cutoff (stock) valve
10. 4-range McLeod gauge
11. Toepler pump
12. 3-stage diffusion pump
13. 2-stage transfer pump
14. Furnace
15. Ion gauge
16. Mercury lift

The apparatus, shown in Fig. 11.2, needs only a brief description since many points of its design have been discussed above. The entire system is evacuated by an oil diffusion pump and a mechanical forepump. A two-stage mercury diffusion pump removes the gases from the furnace, and a three-stage pump circulates the gases through the analytical system.

The sample loader ordinarily accommodates about 10 samples weighing from 1 to 2 g each. If one side arm is extended, about 24 samples can be inserted. Material for the crucible bath is held in the other loader arm. The samples and bath material are pushed along with an iron rod activated magnetically.

In the analytical system, the gases are collected by the Toepler pump and are transferred to the McLeod gauge, which measures the total gas volume. The gases are next pumped from the McLeod gauge through hot copper oxide. The water is removed by magnesium perchlorate, and the carbon dioxide is frozen out with liquid nitrogen. The remaining gas, nitrogen, is collected in the Toepler pump, transferred to the McLeod gauge, and measured. The liquid nitrogen is removed from the trap, thus releasing the carbon dioxide, which is collected by

the Toepler pump and is added to the nitrogen in the McLeod gauge. The combined volume is measured. The difference between this volume and the previously determined total volume is equal to the hydrogen volume.

A 2.5-kw electronic induction heater has been found satisfactory. Temperatures are measured by an optical pyrometer.

Samples of uranium of 1 to 2.5 g, previously pickled in hot nitric acid (1+1), washed with water and acetone, and air dried, are loaded into the loader arm. Samples to be analyzed primarily for hydrogen are best cleaned by abrading with a degreased file, suspending in the vapors of boiling carbon tetrachloride for 15 to 20 min, and air drying. The platinum for the bath, in 1- to 2-g pieces, is loaded into the other loader arm. The crucible is bedded with less than 250-mesh spectrographic-grade graphite in the quartz crucible holder, and the assembly is suspended in the furnace.

The joints of the furnace section are sealed with Apiezon wax, and the system is outgassed from 60 to 180 min at 2200 to 2400°C until a suitable initial reading of about 60 mm on the McLeod gauge for 20 min at 1920°C can be obtained. The temperature is lowered to 1700°C, and 30 to 40 g of platinum is dropped into the crucible. The temperature is then raised to 1920°C for 30 to 60 min.

The blank is determined by collecting the gas evolved at 1920±20°C for 20 min in the Toepler pump, transferring it to the McLeod gauge for volume measurement, and circulating it through the analytical system for analysis. A 40- to 60-mm blank is considered satisfactory.

The blank gas is pumped out, and a sample is introduced. The procedure given above is repeated. No more than 30 wt.% of sample can be added to the platinum bath.

The standard deviation of the oxygen values is within 10 ppm at the 100-ppm level. For hydrogen, the standard deviation is within 0.2 ppm in the 1- to 5-ppm range.

Simplified Procedures. Several simplified procedures have been described for the determination of hydrogen alone in uranium. Generally, the total volume is measured, the hydrogen is removed, and the remaining volume is measured and subtracted from the previous total. Iron bath [38, 39] (1650 and 1700°C), iron-tin bath [40] (1235°C), and dry graphite crucible techniques [41, 42] (1900°C) have been used with apparently no difficulty. Most procedures yield results precise to about 5 per cent or better in the 0.5- to 10-μg range with 1- to 10-g samples.

(2) *Plutonium.* Taylor [4] reports that the determination of oxygen, hydrogen, and nitrogen can be carried out either in an iron–tin bath or in a platinum bath at 1900°C. The loading tree and furnace assembly are held in a glove box.

(3) *Thorium.* Sloman and Harvey [28] report an iron-bath technique for the analysis of thorium for oxygen, hydrogen, and nitrogen. The micromethod of Booth, Bryant, and Parker [20] described under Sec. 11–1.1(b)(1) has been satisfactory. With 10- to 15-mg samples in a 3-g platinum bath at 1900±20°C, the absolute standard deviation for oxygen was found to be 0.03 per cent at the level of 0.36 per cent

oxygen. Again, the hydrogen values were satisfactory, and the nitrogen determinations were unsuccessful.

In the New Brunswick Laboratory procedure with the National Research Corporation apparatus, Sec. 11–1.1(b)(1), a platinum bath at 1970±20°C is used routinely. Again, no more sample than 30 wt.% of the platinum is used. The samples are first pickled in hot nitric acid (1+1) containing a few drops of 48 per cent hydrofluoric acid, washed in water and acetone, and then are air dried.

(4) *Beryllium.* Platinum-bath procedures have been described by Turovtseva and Litvinova [21] (2000°C) for oxygen, and by Gregory and Mapper [17] (1860°C) for oxygen and hydrogen. The latter investigators found no nitrogen in any of the samples analyzed. Booth, Bryant, and Parker [20] obtained only fair results for oxygen by this technique with powdered beryllium samples (the type of sample used by Gregory and Mapper [17]) and very erratic results with solid beryllium, concluding that further investigation was required for a satisfactory procedure. Bradshaw [43] compiled the oxygen results obtained by various methods, including vacuum fusion with platinum bath, and also recommended that, although the procedure was the only one experimentally capable of determining trace amounts of oxygen, further development was needed for routine work. Booth and Parker,[44] however, found that the addition of tin, both prior to the beryllium addition and together with each sample, spectacularly improved the procedure in that the solution of beryllium in the bath was more satisfactory and the evaporation of the beryllium was greatly suppressed. With the microapparatus [20] described above and with 8- to 14-mg samples in 3 g of platinum (1950°C) plus 60 to 70 mg of tin added with each sample, an absolute standard deviation of 0.09 per cent was obtained at the 0.85 per cent oxygen level. The results also agreed with those obtained by a copper sulfate–mercuric chloride dissolution (unreacted residue) method.[45]

(5) *Zirconium.* Although the iron–tin bath technique is apparently satisfactory for oxygen when certain precautions are observed, the more recently reported procedures favor the platinum bath. McDonald, Fagel, and Balis [13] recommend that additional iron and tin be added with each sample and that the outgassing time be minimized to circumvent bath solidification, a major source of error. Satisfactory results for oxygen in zirconium, titanium, and molybdenum were obtained by thus ensuring that the sample dissolves readily in the bath (1600 to 1800°C). Stanley, von Hoene, and Wiener's technique [14] of wrapping the sample in iron foil before dropping it into the bath (1900°C) may also serve this same purpose in addition to preventing the sample from wetting the crucible wall. These investigators use

the apparatus of McGeary, Stanley, and Yensen.[46] Oxygen results closely approximating the values found by chlorine volatilization[47] (unreacted residue) procedures were obtained.[4, 14] Otake[48] obtained good results with the iron–tin bath at 1850°C. The determination of hydrogen and nitrogen, as well as oxygen, by the iron–tin bath at 1860°C and also at 1900°C, has been reported.[4, 21] Apparently the zirconium content of the bath should not exceed 4 per cent.[21]

All these procedures are probably more reliable, at least for oxygen and hydrogen, than the iron-bath (1750°C) technique of Sloman and Harvey.[28] Goward[49] has reported the results of a comparative study of the determination of oxygen by the dry tin bath,[9] the iron–tin bath, and the platinum bath. The dry-bath technique was found to be inferior to the other two.

Essentially the same platinum bath (1850°C) procedure is used by Booth, Bryant, and Parker,[20] Gregory and Mapper,[17] and Horrigan.[50] The latter uses the National Research Corporation apparatus shown in Fig. 11.2. The zirconium content of the bath should not exceed 15 per cent. The results agree with those obtained by the hydrogen chloride (unreacted residue) volatilization procedure.[25] Booth, Bryant, and Parker[20] report an absolute standard deviation of 0.006 per cent at the 0.098 per cent oxygen level with 20- to 60-mg samples. Again the results for hydrogen were satisfactory, but the nitrogen results were not. The apparatus and procedure are described in Sec. 11–1.1(b)(1). Heumann[33] recommends the addition of 3 per cent iron to the platinum for the analysis of zirconium and Zircaloy to improve the reproducibility of the oxygen results and to bring the nitrogen recovery near 100 per cent. Heumann uses a modification of the apparatus of Horton and Brady.[51]

(6) *Titanium.* Four metal-bath techniques have been reported: iron with or without the addition of tin; platinum; platinum "flux"; and the so-called "dry" crucible containing only tin. Each procedure is apparently capable of yielding satisfactory results for oxygen and hydrogen.

Only minor variations exist in the iron-bath technique (Refs. 13, 19, 21, 28, and 52). McDonald, Fagel, and Balis[13] recommend the addition of more iron and tin (1600 to 1800°C) with each sample. A macro-evolution apparatus (1700 to 1750°C) combined with a micro-gas analytical system is used by Davis and Gray.[19] The titanium content of the bath (1750 to 1800°C) evidently should not exceed 4 per cent;[21] the oxygen results[20, 53] agree well with the chlorine volatilization (unreacted residue) procedure.[54] Zakharov[55] obtained satisfactory results with an iron bath with and without the addition of tin. Goto, Suzuki, and Onuma[56] use an iron bath at 1850 to 1900°C

for the determination of hydrogen and oxygen. Again, the oxygen results and the values obtained by chlorination agree.

The platinum bath procedures reported [8, 20, 31] are also similar. The temperature of the bath is 1850 to 1900°C. The titanium content of the bath should be less than 12 per cent.[8, 31] Bennett and Covington [8] also analyzed titanium alloys containing 5 per cent tin, aluminum, manganese, chromium, vanadium, nickel, iron, zinc, or molybdenum. Apparently, minor differences in individual technique, so evident in all vacuum fusion work, have important effects in the analysis of titanium. For example, the above investigators all find the precision of their oxygen results well within 10 relative per cent. Yet Gahler [57] reports that the Task Force on Oxygen of the Metallurgical Advisory Committee on Titanium in 1957 found the results of the platinum-bath procedure discouraging, particularly for manganese and aluminum alloys. The Committee at that time recommended the dry-crucible technique described below. In 1959, however, the platinum flux technique described below was recommended.

Hansen, Mallett, and Trzeciak [27] also report the platinum-bath procedure to be somewhat erratic for oxygen. They recommend either the dry-crucible procedure or a modified platinum-bath technique in which the platinum is added along with the sample (1850°C). The addition of platinum in a flux to sample ratio of 8 to 1 gave results, with 0.25-g samples, reproducible to within 10 relative per cent. There was at least 93 per cent recovery of oxygen from prepared standard samples.

The dry-crucible procedure, devised by Walter,[9] and widely used as an umpire method for oxygen in titanium,[58] involves the addition of the sample plus a quantity of tin to a crucible containing graphite powder, 20-mesh or small chips, at 1200 to 1900°C, to form titanium carbide and carbon monoxide. Albrecht and Mallett [15] have indicated the importance of using a crucible cover with this technique to avoid splattering and to minimize volatilization of titanium. Reproducibility with 0.2- to 0.5-g samples is claimed to be within 10 relative per cent and accuracy, within 6 relative per cent. A dry-crucible (graphite powder) procedure that uses no tin has also been reported for oxygen and hydrogen in titanium and for those gases and nitrogen in manganese.[21]

(7) *Niobium.* Harris [34] compared the iron-bath (1750°C) and the platinum-bath (1950°C) techniques. The standard deviation of the oxygen results with 60- to 400-mg samples was 15μg at the 0.1 per cent level with the platinum and 40 μg with the iron. Only a trace of nitrogen was obtained with the iron bath, whereas with the platinum the recovery was almost quantitative. On the other hand, Turovtseva and

Litvinova [21] and Mikhailova, Turovtseva, and Khalitov [59] reported quantitative recoveries of oxygen, hydrogen, and nitrogen with an iron bath (1650°C). The niobium content of the bath should not exceed 20 per cent.

Hansen and Mallett [26] report an interesting extraction procedure, which is described here since conventional vacuum fusion apparatus [35] is used. The sample is heated in a graphite crucible from 1200°C at the beginning to 2000°C. No metal bath is used. Apparently the oxygen diffuses to the sample surface, where it combines with carbon vapor from the crucible. Oxygen recovery from prepared standards is complete. The absolute standard deviation is 0.001 per cent at the 0.019 per cent oxygen level with 0.2- to 0.5-g samples.

(8) *Sodium and Sodium–Potassium.* Turovtseva and Litvinova [21] determined oxygen by heating the sample in a resistance furnace from 60°C at the beginning to 1200°C in a graphite crucible (for sodium) or in a molybdenum crucible containing graphite powder of 1-mm grain size (for sodium–potassium alloys). The metal is kept under an outgassed liquid hydrocarbon and is sampled just before charging the apparatus by means of a sampler punch. Prolonged storage under the hydrocarbon increased the oxygen content. The precision is about ±10 per cent; accuracy, ±15 per cent; and sensitivity, 0.001 to 0.005 per cent with 200- to 500-mg samples.

11–1.2 Vacuum Extraction Method for Hydrogen

(a) *Apparatus and Technique.* The technique of vacuum extraction involves heating the metal in a dry crucible, under vacuum, to a temperature sufficient to evolve hydrogen in a reasonably short time. In contrast to the vacuum fusion method, the temperature to which the metal is heated is generally below its melting point. In those cases where the melting point of the metal is exceeded, for example, in the analysis of the low-melting alkali metals, the sample is enclosed in an iron or steel capsule through which hydrogen can diffuse. Conventional vacuum fusion equipment or simpler apparatus, commercially available and specially designed (Fig. 11.3), often with resistance heating, is used. Molybdenum crucibles are often used because blanks are lower and outgassing time is decreased.

Vacuum extraction has many advantages over vacuum fusion for the determination of hydrogen. In the absence of temperatures near 2000°C and a metal bath, the initial preparation is simplified, lower blanks are obtained, and more samples can be accommodated. In addition, gettering is usually eliminated, samples can be recovered intact after analysis, and extraction crucibles can be reused several times. The gas analysis involved in vacuum extraction is simple compared to that in vacuum fusion because the gas evolved is assumed to be

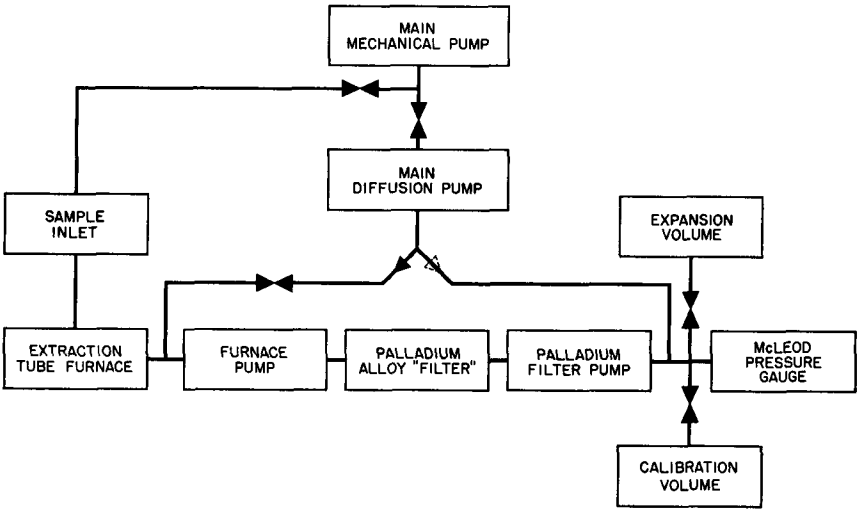


Fig. 11.3 Schematic diagram of Serfass hydrogen analyzer.

chiefly hydrogen. A single manometric measurement is frequently made based on that assumption which can be made firmer by the insertion of a palladium barrier to retain other gases.

(b) *Analysis of Individual Metals.* (1) *Uranium.* The evolution of hydrogen is slow at 500°C; complete extraction for 10-g samples [60] takes over 2 hr. Between 800 and 900°C complete evolution of the gas is obtained [61-64] within 10 to 20 min. The satisfactory procedure reported by Myers [61] is typical. Samples of 3 to 8 g are cut and cleaned with a degreased file before being weighed and transferred to a conventional vacuum fusion apparatus. The sample is heated by induction to 885°C in a graphite crucible. The hydrogen is collected for 20 min, and the gas pressure is measured. Since it has been established by repeated analyses that the gas is over 97 per cent hydrogen, only in random determinations is it necessary to oxidize the hydrogen to water with cupric oxide and take another pressure reading after removing the water. In the 0.5- to 6-ppm range, the standard deviation is within 0.1 ppm.

Tews and Miller,[65] before measuring the hydrogen, separate it from the gases evolved from uranium at 820°C by diffusion through a heated palladium tube. Seeking a more rapid method, Miller [66] measures only the total gas, the pressure of which is indicated by a vacuum gauge driving a strip-chart recorder.

(2) *Thorium.* Goldbeck [67] has analyzed thorium at 1000°C in the National Research Corporation vacuum fusion apparatus. Again, only the final pressure was measured since repeated analyses showed

over 95 per cent of the gas to be hydrogen. A procedure utilizing a molten–tin bath at 1150°C in a silica crucible has been described.[68] Hydrogen is separated from the evolved gases by the fractional freezing technique.

(3) *Zirconium.* Zirconium has been analyzed at 1200°C; the extraction is complete in 10 min. Samples were prepared by wet grinding followed by pickling in nitric acid–hydrofluoric acid–water solutions before analysis.[69] Other investigators prefer to use a temperature of 1050°C for the analysis of zirconium and Zircaloy.[33, 70] Elbling, Goward, and McGeary [70] use a National Research Corporation air-cooled furnace head instead of the water-cooled furnace described by McGeary.[69, 71] Taylor,[4] with his vacuum fusion apparatus modified by substitution of a quartz tube and resistance furnace for the original furnace assembly, recovered the hydrogen completely from prepared zirconium hydride standards by extraction at 950°C. Taylor analyzed intensely radioactive zirconium samples with no difficulty. Most of these investigators found the gas evolved to be from 95 to more than 99 per cent hydrogen by mass-spectrographic analysis. They also found that the vacuum extraction results agreed closely with the vacuum fusion values. With 0.1- to 1.0-g samples, the precision is indicated by a standard deviation of 1.0 ppm on a sample containing about 20 ppm.[69]

(4) *Titanium.* Titanium was analyzed by Young and Cleaves [72] at 920°C for 15 to 40 min with a McGeary apparatus [69] modified by the substitution of a Globar furnace and quartz tube for the original furnace assembly. Bulk samples are filed and degreased in benzene. Loose samples are wrapped in tin foil. Kroll sponge samples containing magnesium chloride are first vacuum dried at 300°C to remove any water of hydration. Typical results with 3-g samples of ingot drillings are 0.0120 per cent with an absolute standard deviation of 0.0010 per cent. An extraction temperature of 1200 to 1400°C with the National Research Corporation vacuum fusion apparatus has been reported.[73] Lakomskii,[74] on the other hand, recommends a temperature of 800°C. Rubinshtein and Mendlina [75] use a simple apparatus and a temperature of 600 to 700°C. Turovtseva and Khalitov [76] mix the sample with 10- to 20-mesh graphite, and heat the mixture in two stages: 1000°C for 5 min; 1850°C for 30 min. Only hydrogen appears in the first stage. The second stage yields carbon monoxide and hydrogen. The combined gases are analyzed to obtain the hydrogen and oxygen. McKinley [77] has published an excellent critical review of methods for the determination of hydrogen. Vacuum extraction at 1400°C and an equilibrium-pressure procedure described in Sec. 11–1.3(b)(3) are recommended over combustion procedures, Sec. 11–1.9(c)(6).

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(5) *Sodium.* The vacuum extraction of sodium has been reported by Pepkowitz and Proud.[78] The sample is sealed in a welded iron capsule held at 700°C; the hydrogen evolved diffuses through the capsule walls into a simple vacuum system. Holt,[79] however, could not obtain valid results on a sodium–potassium alloy with the identical procedure.

11–1.3 Equilibrium-pressure Method for Hydrogen

(a) *Apparatus and Technique.* If hydrogen dissolved in a metal behaved as an ideal liquid, a linear relation would exist between the logarithm of the equilibrium pressure and the logarithm of the hydrogen concentration in the metal under isothermal conditions. Hydrogen in many metals behaves in this manner, and it is generally the only gas evolved when the metal is heated to certain temperatures in a vacuum. Therefore, if the equilibrium pressure over the metal sample is determined in an apparatus of known volume and at a temperature for which the equilibrium pressure–concentration relation is known, data are obtained from which the hydrogen content can be calculated.[80, 81]

Although the apparatus is relatively simple, consisting primarily of a resistance furnace and a quartz or pyrex sample tube, a calibrated collecting volume, and a McLeod gauge or mercury manometer, the procedure is used infrequently because it requires gathering solubility data on metal closely similar to that being analyzed. Once the data are obtained, however, the determinations are convenient and reproducible.

(b) *Analysis of Individual Metals.* (1) *Uranium.* Davis[82, 83] found that equilibrium pressure is attained within 60 min at 600°C with 10-g samples. The precision is estimated to be from ±3 to ±10 per cent for samples containing 5 and 0.3 ppm, respectively. Massive samples, 200 to 400 g, with which a mercury manometer is used instead of a McLeod gauge, require [80] from 5 to 10 hr for equilibration at 570 to 600°C.

(2) *Zirconium.* Oak Ridge National Laboratory [84] uses the equilibrium pressure technique to determine hydrogen in Zircaloy–2. With 0.25- to 0.50-g samples, equilibrium is attained at 1200°C in 10 to 15 min. The hydrogen values agree with those obtained by vacuum fusion. The standard deviation is 5 per cent in the 30- to 70-ppm range. The quartz sample tube can be used about twenty times before replacement is required.

(3) *Titanium.* McKinley [81] describes a similar technique for the analysis of titanium. With 0.5-g samples of any form or shape and a temperature of 1000°C, equilibrium is attained within 10 min. A series of determinations on a sample containing 17 ppm showed a

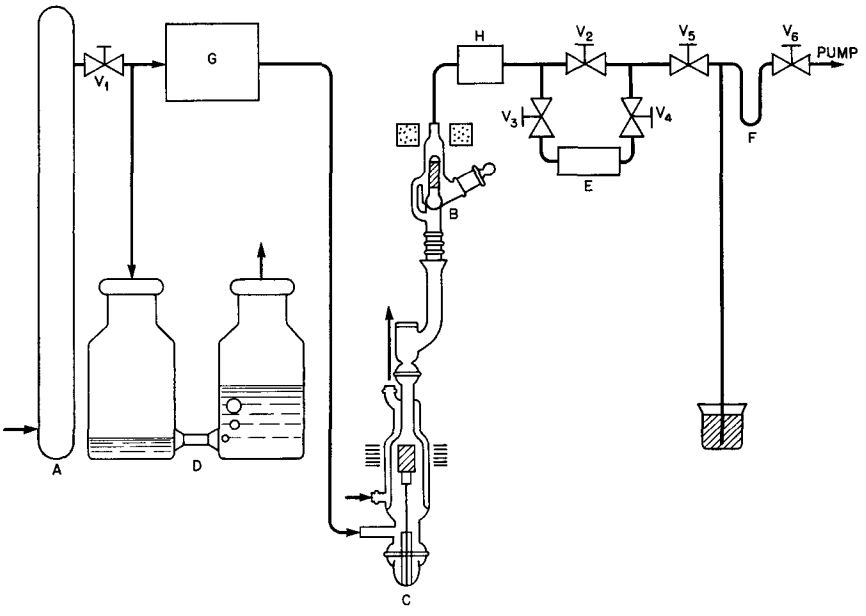


Fig. 11.4 Inert-gas fusion apparatus.

A. Ascarite and magnesium perchlorate
B. Sample holder
C. Induction furnace
D. Manostat
E. Modified Schütze's reagent
F. Capillary trap and manometer
G. Uranium furnace
H. Glass wool and magnesium perchlorate

V_1, V_2, V_3, V_4, V_5, and V_6. Brass bellows type valves.

standard deviation of 2 ppm. With higher hydrogen concentrations, the precision was correspondingly better. The results agreed with those obtained by vacuum fusion. In reviewing methods for the analysis of titanium for hydrogen, McKinley [77] recommends the vacuum extraction and equilibrium pressure techniques.

11–1.4 Inert-gas Fusion Method for Oxygen

(a) *Apparatus and Technique.* The use of high vacuum with its associated expense and trouble has been eliminated in the inert-gas fusion procedure developed by Smiley [5] (see Figs. 11.4 through 11.7). Since the fundamental reaction is the same as in vacuum fusion, the technique has the same wide applicability.

In addition to the relative simplicity of the apparatus, the inert-gas fusion procedure possesses other advantages over the vacuum fusion technique for oxygen. The collection of the carbon monoxide by a

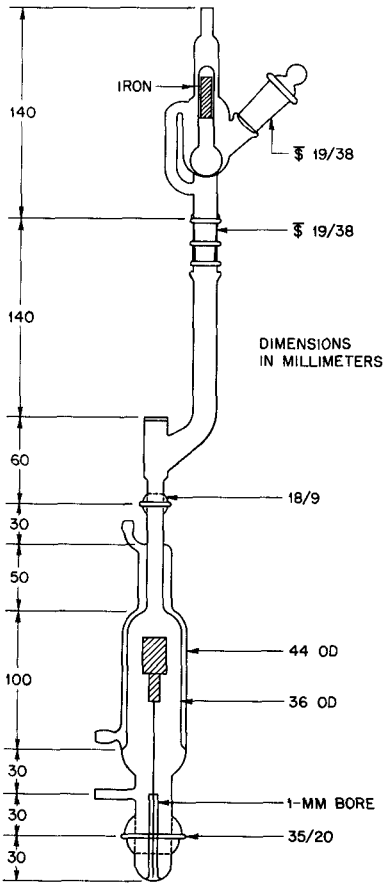


Fig. 11.5 Inert-gas fusion furnace and sample holder. The furnace is silica; other parts are borosilicate.

stream of gas is faster than can be accomplished by a diffusion pump. The blank reaches a stable value more quickly. The over-all procedure, then, is more rapid, only 12 min being required with most samples. Finally, only carbon monoxide is formed. In vacuum fusion there may be produced a small amount of carbon dioxide, and in accurate work this carbon dioxide should be measured separately since both atoms of oxygen come from the sample.

In Smiley's procedure [5] the sample is dropped into a bath of molten platinum in a graphite crucible held in an argon atmosphere. A stream of argon at atmospheric pressure removes the carbon monoxide, carrying it through Schütze's reagent, which oxidizes it to carbon dioxide. The carbon dioxide is condensed in a capillary trap held in liquid nitrogen and is measured after volatilization with a capillary

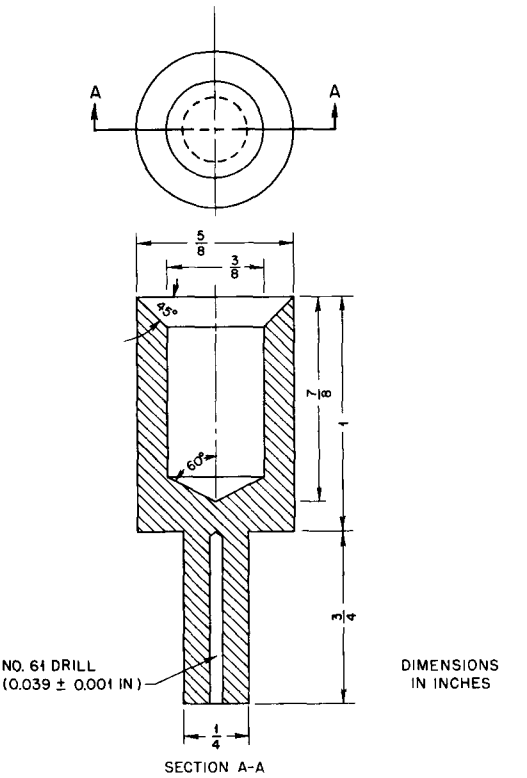


Fig. 11.6 Inert-gas fusion graphite crucible.

manometer. Thus the desired sensitivity is achieved by the use of a small volume rather than by measuring low pressures. Only a mechanical pump is used, and only the capillary trap is evacuated.

The crucible holds about 6 g of platinum and is heated to 1800°C. Sample weights are 100 to 200 mg. Complete oxygen evolution is obtained generally within 10 min. Both the accuracy and the precision of the results with standard cupric oxide are said to be as good or better than values shown by vacuum fusion. With the National Bureau of Standards cooperative steel sample No. 6, a value of 0.010 $\pm$0.0015 per cent was obtained. This value is somewhat higher than the range of cooperative values (from 0.003 to 0.0085 per cent) and indicates that no serious losses due to the presence of manganese (gettering) in the steel occurred.

The Laboratory Equipment Corporation (Leco) has developed an oxygen analyzer based upon the inert-gas fusion technique. The apparatus is shown in Fig. 11.8. Carbon dioxide, produced by the oxidation of the monoxide by iodine pentoxide, is absorbed in barium hydroxide and measured conductometrically in a conductivity cell

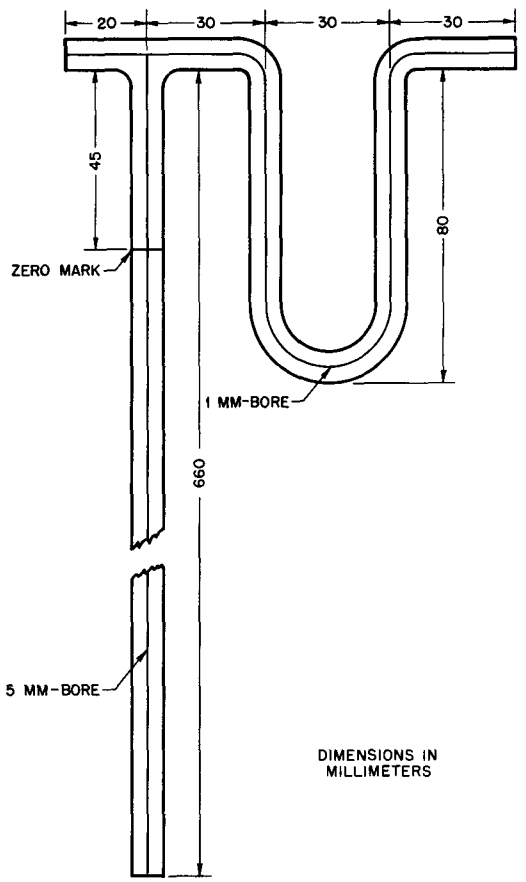


Fig. 11.7 Inert-gas fusion capillary trap and manometer, borosilicate glass.

identical to that used in the Leco carbon determination apparatus. The sensitivity of the apparatus can be varied markedly by changing the concentration of barium hydroxide. Calibration is carried out by analyzing either known amounts of silver oxide or a metal with known oxygen content. The apparatus is described as being capable of analyzing uranium, titanium, titanium alloys, zirconium, gadolinium, molybdenum, niobium, and other metals with results agreeing well with those obtained by vacuum fusion. A sample can be analyzed in 5 min.

(b) *Analysis of Individual Metals.* (1) *Uranium.* The analysis of uranium and uranium alloys is reported by Bane and Brody.[85] Uranium is prepared free of oxide coating by anodic electropolishing for 1 min at 8 volts in a bath of 46 per cent sulfuric acid and 6 per cent glycerol. A 20 per cent potassium carbonate solution is a more suitable

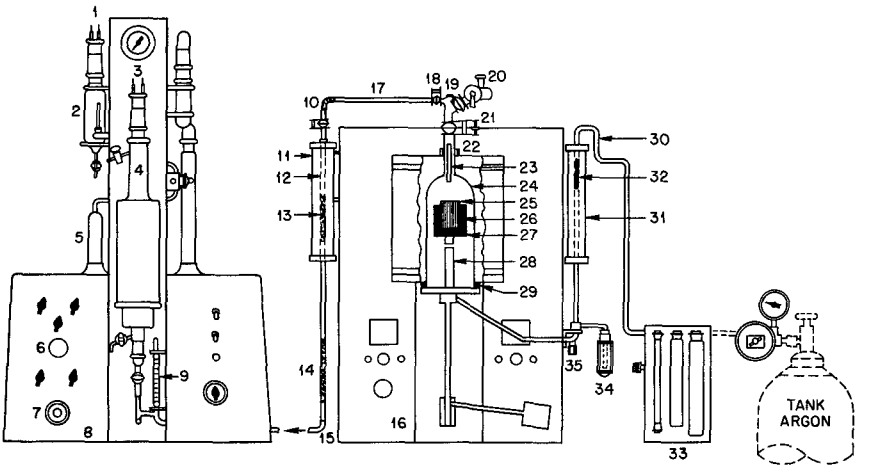


Fig. 11.8 Leco oxygen analyzer.

1. Standard-cell electrodes
2. Standard cell
3. Measuring-cell electrodes
4. Measuring cell
5. CO_2 trap for exhaust gas
6. Cathode-ray tube
7. Decade resistor
8. Conductometric analyzer
9. Input flowmeter
10. Ascarite
11. Catalyst heater
12. Glass tube
13. Special iodine pentoxide
14. Sodium thiosulfate
15. Right-angle bend
16. Induction furnace
17. Glass tube
18. Clamp
19. Crossarm
20. Loading stopcock
21. Clamp
22. Clip
23. Funnel
24. Reaction tube
25. Carbon crucible
26. Carbon black
27. Thimble
28. Pedestal
29. Ring seal
30. Glass tube
31. Catalyst heater
32. Titanium sponge
33. Purifying train
34. Pressure-relief valve
35. Quick disconnect

electrolytic bath for uranium–zirconium alloys. The sample, prepared as a smooth-surfaced cube, is held in a platinum basket that serves as the anode. After being electropolished, the sample is washed successively with water and acetone, and air-dried.

(2) *Plutonium.* Smiley analyzed plutonium.[86] The sample holder and furnace are enclosed in a dry box. Samples, 50 mg of turnings, are cleaned of any oxide coating by electrolytic action in 20 per cent potassium carbonate solution, followed by rinsing with water and then acetone. With manometrically prepared oxide standards, complete recovery of the added oxygen was obtained. Duplicate determinations on 15 metal samples containing from 50 to 150 ppm showed a standard

deviation of 7 ppm for the duplicates. This value, corresponding to 0.35 μg for a 50-mg sample, is about as good as the sensitivity of the manometer.

(3) *Thorium.* Smiley [5] analyzed thorium as well as iron, steel, and aluminum with satisfactory results. Holt [87] also analyzed thorium. Samples are cleaned in nitric acid (1+1) containing a trace of hydrofluoric acid.

(4) *Beryllium.* Beryllium has been analyzed by Kallmann [88] with the Leco apparatus. A nickel bath was used, and the sample of powder or chips was wrapped in copper foil before being added to the bath. This procedure has been used by Goldbeck,[89] who found that powdered beryllium could be analyzed satisfactorily. With beryllium chips, however, the results were unreliable.

(5) *Titanium.* Smiley [5] found that titanium caused some difficulty. Although the first sample appeared to give a reasonable result, succeeding samples gave progressively lower results, with dark spots occurring on the platinum surface. Apparently the flux was rapidly exhausted because of the low density of titanium carbide, which floated on the top of the platinum. It probably would be necessary to add more platinum with each sample. Attempts to use tin as a flux were unsuccessful.

11–1.5 Halogenation Methods for Oxygen and Nitrogen

Various halogenation techniques have been developed in the search for direct procedures for determining oxygen in metals without the use of expensive vacuum fusion equipment.

(a) *Bromine Trifluoride.* The use of bromine trifluoride to displace oxygen from oxides of metals which either form volatile fluorides or fluorides soluble in the reagent was first demonstrated by Emeléus and Woolf.[90] Hoekstra and Katz [91] developed this general reaction into a procedure for the determination of oxygen in oxides of uranium, thorium, and other metals. Typical reactions of the reagent can be represented as follows:

$$U + 2BrF_3 \rightarrow UF_6 + Br_2$$
$$UO_2 + 2BrF_3 \rightarrow UF_6 + Br_2 + O_2$$
$$2UH_3 + 6BrF_3 \rightarrow 2UF_6 + 3Br_2 + 6HF$$

If the oxygen is uncombined, as is frequently found in the case of titanium, it is simply evolved as molecular oxygen when the metal dissolves. Nitrogen, free or combined, in the sample is also liberated. In the determination of oxygen and nitrogen in metals, the total gas evolved is measured after the other reaction products have been condensed out with liquid nitrogen. The gas is then passed over hot copper to remove oxygen, and the residual gas is measured as nitrogen. The amount of oxygen is calculated.

(1) *Apparatus.* The apparatus [91, 92] consists simply of a reaction system and a gas-collection and -measurement system. The reaction system, a reaction tube and traps for condensable products, is fashioned from noncorrosive materials, for example, nickel and fluorothene for the tube and traps, respectively. The gas-collection and -measuring portion is standard glass high-vacuum equipment.

(2) *Analysis of Metals.* Total oxygen plus nitrogen in uranium and uranium hydride have been determined by this technique.[93] Although the results were not as satisfactory as those obtainable by vacuum fusion, the procedure is termed potentially useful, particularly for pyrophoric powders.[94]

In the application of this technique to titanium and titanium alloys by Dupraw and O'Neil,[92] the oxygen values agreed well with those obtained by vacuum fusion and were reproducible to within 5 relative per cent. With molybdenum alloys the oxygen results were somewhat low. With all alloys except those containing aluminum and iron, the nitrogen values agreed with the Kjeldahl results.

(b) *Bromine.* In the bromination–carbon reduction technique devised by Codell and Norwitz [95, 96] for the determination of oxygen in certain metals, the sample is mixed with graphite and treated with bromine at temperatures near 800°C. Argon or helium is used as a carrier gas. The former is preferred because of its slower diffusion rate through the Vycor reaction tube.

(1) *Apparatus and Technique.* Standard combustion-train components can be used for the most part. The oxygen in the sample is converted to carbon monoxide, which is oxidized to carbon dioxide by hot copper oxide. Metal bromides and excess bromine are frozen out of the carbon monoxide by dry ice–water and dry ice–ethyl alcohol traps. The carbon dioxide is either absorbed in Ascarite and weighed for macroamounts or determined conductometrically (Leco Carbon Determinator) for smaller amounts.[97]

(2) *Analysis of Metals.* Codell and Norwitz [95-97] analyzed titanium, titanium alloys, zirconium, chromium, vanadium, and steels by this procedure. The results agreed with the vacuum fusion values. With a standard titanium sample containing 0.038 per cent oxygen, a value of 0.040 per cent and an absolute standard deviation of 0.014 per cent were obtained. Otake [48] found that the bromination–carbon reduction procedure applied to zirconium gave results agreeing with those obtained with vacuum fusion. Takahashi, Kawane, and Mitsui,[98] using a slightly modified procedure, also obtained satisfactory results with titanium. Elwell and Peake [99] analyzed titanium and titanium alloys by a similar technique with chlorine and graphite. The analysis of zirconium gave some difficulty because of the plugging

of the train with zirconium tetrachloride. Hansen and Mallett,[100] in reviewing methods for oxygen in titanium, concluded that the bromination–carbon reduction procedure was as satisfactory as the vacuum fusion methods.

11–1.6 Isotope-Dilution Methods for Oxygen, Hydrogen, and Nitrogen

Kirshenbaum and Grosse [101] have developed a procedure, basically resembling the vacuum fusion technique, in which the sample is mixed with a known amount of O^{18}-containing "master alloy" and heated to the molten state in the presence of graphite. The O^{18} to O^{16} ratio in a portion of the carbon monoxide produced is determined by a mass spectrometer. Quantitative recovery of the carbon monoxide is unnecessary. Graphite, platinum, or molybdenum crucibles are used; heating is by induction.

Because of the similarity to the vacuum fusion technique, the difficulty in preparing the master alloy, and the need for a mass spectrometer, this isotope-dilution procedure has gained little acceptance. Kirshenbaum and Grosse [102] found that with titanium samples the oxygen results were 10 to 15 per cent higher than those obtained by vacuum fusion. Zirconium was also analyzed.[103]

An isotope-dilution technique for determining hydrogen in zirconium,[104] uranium, niobium, and tantalum [105] has been devised by Zaidel and Petrov. A metal sample is heated in a deuterium atmosphere, and the isotopic composition of the gas, after equilibrium has been reached, is determined spectrographically.

A similar procedure is used by Holt [106] for determining hydrogen in sodium and sodium-potassium alloys. The isotopic ratio is measured mass spectrometrically.

Staley and Svec [107] have proposed still another isotope-dilution technique for determining nitrogen in metals. The metal sample and ammonium sulfate of known N^{15} content different from normal are dissolved in acid. The solution is made basic, and ammonia is distilled into an acid solution, where it is oxidized to nitrogen by alkaline sodium hypobromite. The nitrogen is collected and analyzed for N^{15} by a mass spectrometer. Thorium, titanium, and other ferrous and nonferrous metals and alloys were analyzed.

11–1.7 Miscellaneous Methods for Oxygen and Carbonate

Silverman and Bradshaw [108] determined uncombined oxygen in zirconium by dissolving the metal in hydrofluoric acid and absorbing the molecular oxygen in alkaline manganous chloride–iodide solution. The liberated iodine is extracted with *o*-xylene and determined spectrophotometrically at 495 mμ.

Dean and Hornstein [109] estimated the oxide content of titanium by measuring the potential between an electrode of titanium of known

oxide content and a sample metal electrode immersed in a suitable molten electrolyte.

Carbonate in sodium metal is determined by dissolving the metal in water under nitrogen, decomposing the carbonate with dilute acid, absorbing the carbon dioxide in excess barium hydroxide, and back-titrating with standard acid.[110]

11–1.8 Kjeldahl Method for Nitrogen

As discussed in Sec. 11–1.1(a)(4), nitrogen values found for most metals by vacuum fusion are generally low compared to results obtained by the Kjeldahl method, in which an acid solution of the metal is made alkaline with an alkali hydroxide and the ammonia is distilled off and determined. The bromine trifluoride method appears to give reasonable results for nitrogen with the few metals studied; but the method is relatively complex, and the recoveries are unknown with most metals.

The classic Kjeldahl procedure can be applied satisfactorily to all the metals of interest. The Parnas–Wagner,[111] Beeghly,[112] or one-piece Kirk [113] apparatus, all obtained commercially, are generally used. The determination of the ammonia is usually volumetric but occasionally is colorimetric. In the latter technique, either Nessler's reagent or sodium phenate–hypochlorite are used. (Sodium phenate is an ethyl alcohol and acetone solution of phenol mixed with a sodium hydroxide solution.) The volumetric determination can be used over a wide range.

An important step in the Kjeldahl procedure is the dissolution of the metal. Complete dissolution is obviously desirable; yet satisfactory recovery of the nitrogen can be obtained sometimes when a residue remains undissolved, as in the case of uranium dissolved in hydrochloric acid.[114] The addition of strong oxidants to aid in the dissolution, however, frequently results in loss of nitrogen. Prolonged digestions with perchloric acid and sulfates in high concentrations, therefore, should be avoided.

The precision of the Kjeldahl procedure is generally good. A standard deviation of less than 5 per cent in the 20- to 70-ppm range can be obtained.

Typical procedures for uranium are described below. For most of the other metals discussed, identical procedures, except for sample preparation and dissolution, can be used. Modified procedures are applied to the analysis of lithium and plutonium.

(a) *Analysis of Uranium.* Prolonged fuming with perchloric acid has been shown to result in some loss of nitrogen.[115] Slightly greater sensitivity can be obtained by using sodium phenate–hyochlorite [116-118] instead of Nessler's reagent.

The use of perchloric acid or hydrogen peroxide in conjunction with the hydrochloric acid appears to be unnecessary for some uranium metal samples.[114] Certain metals, however, contain nitrides resistant to hydrochloric acid alone.[119, 120] The judicious use of either the peroxide or perchloric acid to aid in the sample dissolution is therefore recommended for all uranium samples.

Volumetric Procedure.[121] A sample weighing about 2 g is cleaned by immersion in boiling 15 per cent sodium carbonate, rinsing in cold water, immersion in hot hydrochloric acid (1+19), and a second rinsing in water and acetone. The sample is weighed immediately. To the cleaned and weighed sample in a micro-Kjeldahl digestion flask is added 10 ml of hydrochloric acid (1+1). When the reaction stops, 0.2 ml of hydrogen peroxide is added, and the solution is warmed gently until a clear solution is obtained. While the sample is dissolving, a commercial Parnas–Wagner microapparatus is steamed for 15 to 30 min. When the apparatus has cooled somewhat from the steaming process, 10 ml of sodium hydroxide solution (50 g of sodium hydroxide per 100 ml of solution) is added to the distillation flask. A receiving flask containing 5 ml of 2 per cent (w/v) boric acid and 5 drops of mixed indicator (5 parts of 1 per cent alcoholic bromocresol green plus 1 part of 1 per cent alcoholic methyl red) is placed under the condenser tip. The sample solution is added, and the distillation is started. When about 10 to 20 ml of distillate has been collected, the flask is removed, and the solution is titrated with 0.01*N* hydrochloric acid. A reagent blank is carried through the same procedure before the sample is run. The blank should be less than 0.1 ml of the standard acid, and it should be constant.

Colorimetric Procedure.[122] Nessler's reagent is prepared by dissolving 50 g of potassium iodide in 35 ml of water. A saturated solution of mercuric chloride is added slowly and with stirring to the iodide solution until a slight precipitate of red mercuric iodide persists. Then 400 ml of 9*M* sodium hydoxide is added, and the mixture is stirred vigorously. After the mixture has been allowed to stand 48 hr, the clear supernatant liquid is siphoned off and stored in a dark-glass bottle. Each batch of reagent should be standardized with a standard nitrogen solution prepared from ammonium chloride. The standard curve is linear from 0 to 200 μg.

The cleaned uranium sample is dissolved in 50 ml of warm dilute hydrochloric acid containing 2 ml of hydrochloric acid (1+1) per gram of sample. The black residue remaining in the solution is dissolved by adding 1.3 ml of 70 per cent perchloric acid per gram of sample and evaporating the solution until it is clear. The solution is then heated to fumes, fumed *only* for 2 to 3 min, cooled, and diluted to a definite volume. [An alternative dissolution method is recommended by Battelle Memorial Institute[123] to avoid the possibility of nitrogen loss by the fuming operation. A 5-g sample is added to 25 ml of hydrochloric acid (1+1), and the mixture is warmed until the reaction stops. Then 5 drops of 30 per cent hydrofluosilicic acid and 5 drops of 30 per cent hydrogen peroxide are added, and the mixture is warmed until the black precipitate is dissolved and the peroxide is decomposed.] The distilling apparatus is steamed until the distillate on treatment with

1 ml of Nessler's reagent gives a constant absorbance after standing 10 min. A suitable aliquot of the sample solution is then placed in the distilling flask of the apparatus and made alkaline with 25 ml of 20 per cent sodium hydroxide solution (20 g of sodium hydroxide per 100 ml of solution). To the receiving graduated cylinder 5 ml of 0.1*N* hydrochloric acid is added. About 45 ml of distillate is collected. Then 1 ml of Nessler's reagent is added, and the solution is made up to volume and allowed to stand for 10 min. The absorbance is measured at 430 mμ in 1-cm cells against a reagent blank.

(b) *Analysis of Other Metals.* (1) *Plutonium.* Plutonium samples can be dissolved in dilute hydrochloric acid.[85] All operations should, of course, be carried out in a glove box or fume hood with a high airflow system. Another technique, resembling the Kjeldahl procedure, has also been used for small samples of plutonium.[124] A solution of the metal is placed in the outer chamber of a Conway diffusion cell. The cell is sealed with a suitable liquid or grease previously tested to assure minimal gas absorbance. Dilute sulfuric acid containing methyl red is placed in the inner chamber. The sample solution is made alkaline with sodium hydroxide, and, after diffusion of the ammonia has occurred, the excess acid is titrated with 0.01*N* sodium hydroxide in a micrometer microburet.

(2) *Thorium.* Thorium samples are dissolved in dilute hydrochloric acid containing a trace of fluoride ion.[68, 125] Samples can be cleaned before weighing by pickling until bright in nitric or hydrochloric acid (1+1) containing a trace of fluoride ion.

(3) *Beryllium.* Beryllium samples are dissolved in dilute hydrochloric acid [126, 127] or sulfuric acid.[128] The toxicity of beryllium and its compounds should be kept in mind during all operations.

(4) *Zirconium.* Zirconium and zirconium alloys are dissolved in either dilute hydrochloric [129, 130] or sulfuric acid [131, 132] containing small amounts of hydrofluoric acid, or in dilute hydrofluoric acid alone.[130] Small amounts of hydrogen peroxide are frequently added to the acids, especially in the analyses of uranium alloys,[131] to aid in the dissolution. Samples can be freed of surface contamination by etching in dilute nitric acid and hydrofluoric acid prior to weighing.

(5) *Titanium.* Sponge titanium is dissolved in dilute sulfuric acid. Cast or wrought samples require the addition of hydrogen peroxide to the acid.[133] Hydrogen peroxide is also used frequently to oxidize Ti(III) after sample dissolution. Dilute hydrochloric acid containing hydrofluoric acid dissolves many samples, but any insoluble portion should be filtered off and treated with pyrosulfate and sulfuric acid in the presence of selenium for dissolution.[134] Many titanium alloys are dissolved easily in dilute sulfuric acid containing hydrofluoric acid.[135] Dilute hydrochloric acid alone also can be used, any insoluble

residue being dissolved in sulfuric acid plus hydrogen peroxide.[136] Copper–titanium alloys are dissolved by heating 1-g samples with 5 ml of 70 per cent perchloric acid plus 2 ml of water to light fumes. When sulfuric acid–potassium sulfate mixtures are used for dissolution, losses of nitrogen occur if the composition of the mixture approaches an equimolar ratio.[137] Drilling or milling titanium or alloy samples may result in nitrogen contamination.[138] A compact Kjeldahl apparatus with ball joints, developed for the analysis of titanium metal, is described by Somiya, Momoki, and Kawashima.[139] Direct Nesslerization without distillation has also been used to analyze titanium metal.[140]

(6) *Niobium.* Niobium is dissolved in a mixture of hot concentrated sulfuric acid containing potassium sulfate and a small amount of copper sulfate. Without the latter two substances, the dissolution is slow.[141] Goward and Tretow [142] recommend a mixture of hydrofluoric acid and hydrogen peroxide to dissolve niobium.

11–1.9 Combustion Methods for Carbon, Hydrogen, Oxygen, and Nitrogen

The determination of carbon is carried out mainly by dry combustion. Hydrogen and carbon are sometimes determined simultaneously. There are two general techniques available, combustion at atmospheric pressure and low-pressure combustion. The former technique is used nearly exclusively at the present time because of the need for high-vacuum equipment with the low-pressure method and because of the development of refinements which increase the sensitivity and precision of this technique over that of previous conventional atmospheric combustion methods.

Wet combustion procedures are sometimes used for the analysis of certain metals.

(a) *Atmospheric-pressure Combustion.* (1) *Apparatus and Technique.* The general apparatus and procedure for atmospheric-pressure combustion are derived directly from microchemical techniques used for determining carbon and hydrogen in organic materials. The metal samples are burned in oxygen, and the carbon and hydrogen are oxidized to carbon dioxide and water, respectively.

Many variations are found in the components of the combustion trains. Vycor, quartz, aluminum, or zirconium silicate-base refractory (McDanel) combustion tubes are used. Samples are held in quartz, Alundum, zirconia, zirconium silicate, porcelain, or fire-clay boats. Gas burners, resistance heaters, or induction heaters are used to ignite the sample. Fluxes such as tin, lead, iron, or copper, combinations of these metals, or oxides such as chromic oxide can be used to accelerate the ignition of certain metals.

Purification of the oxygen used for combustion is usually carried out by passage of the gas through hot cupric oxide, anhydrous magnesium perchlorate (Anhydrone), and sodium hydroxide–asbestos (Ascarite). Platinum or palladium catalyst oxidizers are useful. The carbon dioxide produced in combustion is purified by adding components to the train directly after the combustion tube: manganese dioxide or sulfuric acid–chromic acid to remove sulfur combustion products; magnesium perchlorate; silver wool to remove chlorides; and copper sulfate to remove chlorine. Any carbon monoxide or hydrogen in the exit gases can be oxidized by a platinum or palladium catalyst oxidizer or hot cupric oxide. Frequently, many of these components designed to purify the exit gases are omitted.

(2) *Measurement of Carbon Dioxide and Water.* The major differences in the procedures are found in the measurement of the carbon dioxide. In the classic gravimetric technique,[143] the carbon dioxide is absorbed in Ascarite. Hydrogen and carbon dioxide can be determined simultaneously by absorbing the water in magnesium perchlorate. Generally, however, only carbon is determined by the gravimetric procedure since the amount of water obtained from the traces of hydrogen present in most metals is too small to be weighed accurately unless large samples are taken. The development of vacuum extraction and similar methods for hydrogen discussed previously, together with the development of the sensitive gasometric measurement techniques described below, have further discouraged the determination of hydrogen by the combustion-gravimetric procedure.

Frequently the carbon dioxide is absorbed in a solution of barium hydroxide and determined by titration of the excess base with standard hydrochloric acid using thymolphthalein as the indicator.[144] Details of this procedure applied to the analysis of uranium are given in the following paragraphs. Potentiometric titrations also have been described.[145, 146]

Combustion-Titration Procedure.[144] The apparatus for the combustion-titration procedure is shown in Fig. 11.9. The buret is filled with 0.05*N* hydrochloric acid. With the preheater turned on, oxygen is passed through the combustion tube, the receiving flask, and the absorption tube at a rate of about 50 ml/min. (This flow rate will be approximated if 3 to 4 bubbles per second form in the bubble counter.) The apparatus is swept out for 5 min.

Ten milliliters of 0.04*N* barium hydroxide, which is 1.0*M* in barium chloride, plus 4 drops of 0.5 per cent thymolphthalein in 95 per cent ethanol are added to the absorption tube. The burner is ignited and placed under the combustion tube. Oxygen is passed through the combustion tube for 20 min. If the bubbles entering the absorption tube are not discrete, the flow rate is reduced slightly.

The barium hydroxide solution is drained into the receiving flask, and the absorption column is rinsed twice with freshly boiled water.

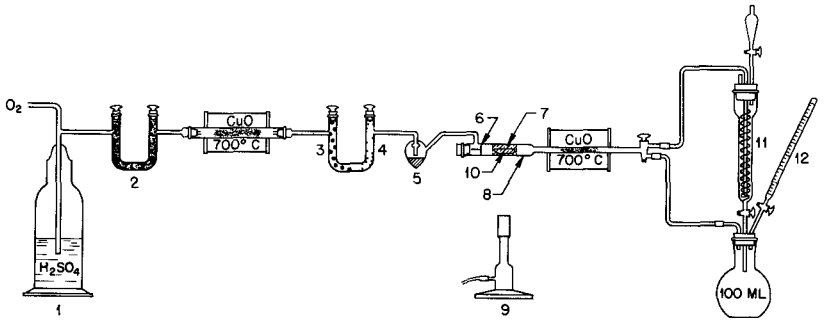


Fig. 11.9 Combustion-titration apparatus.

1. Pressure regulator
2. Drierite
3. Ascarite
4. $Mg(ClO_4)_2$
5. Bubble counter, H_2SO_4
6. Platinum baffle
7. Wire-mesh sleeve
8. Quartz combustion tube
9. Meker burner
10. Carbon-free ceramic boat
11. Zackerl–Krainick absorption column
12. 10-ml buret

The solution is titrated slowly with swirling to the disappearance of the blue color. With experience, the end point can be determined within 0.02 ml despite the haze of precipitated carbonate. The blank determination is repeated until a constant value is obtained. This constant value is then used throughout the day.

A 2.5-g sample of uranium, chips or other solid pieces, is cleaned by immersing it in concentrated nitric acid for a moment. It is then rinsed with water, alcohol, and ether; air dried; and weighed into a porcelain boat (Coors No. 2) fitted with a quartz cover. Possible loss of uranium carbide from samples with high surface to volume ratios is avoided by simply flushing acid and alcohol over the sample.[147] With a clean absorption tube and receiving flask in place and the buret again filled with standard acid, the boat is placed quickly in the combustion tube. The receiving flask is swept out for 5 min. The oxygen flow is switched to the absorption tube. Then 10.0 ml of the barium hydroxide solution is added to the absorption tube.

The burner is placed under the sample in the combustion tube. When the metal ignites, the stopcock to the absorption tube is closed, and the oxygen flow is increased slightly to keep the pressure regulator full. When bubbles stop appearing at the bubble counter, usually in 5 to 10 min, the stopcock to the absorption tube is opened, and oxygen is allowed to pass at the former rate of 3 to 4 bubbles per second for 20 min. The barium hydroxide solution is then drained and titrated as before. The difference between the volume of acid used in the blank run and in the sample run is equivalent to the amount of carbon dioxide.

(3) *Other Carbon Dioxide, Water, and Nitrogen Measurements.* Measurement of carbon dioxide by conductivity after absorption in either sodium or barium hydroxide is sometimes used.[148-150] The Leco

Conductometric Carbon Determinator is a commercially available apparatus based on this principle. This instrument is shown incorporated in the Leco Oxygen Analyzer in Fig. 11.8 Still, Dauncey and Chirnside [151] describe a conductivity cell, bridge, and vibration galvanometer unit for improved precision with this technique.

Another procedure available is the measurement of the volume of the carbon dioxide and excess oxygen before and after absorption of the carbon dioxide by a potassium hydroxide solution.[68, 152, 153] The Lindberg Volumetric Carbon Determinator and the Leco Gasometric Carbon Determinator are commercial instruments based on this technique.

A combustion–mass spectrographic procedure is described for the determination of carbon and nitrogen.[154]

Other procedures isolate the carbon dioxide by cold traps and measure it either by a McLeod gauge [155] or by a capillary monometer.[156–158] In the method described by Pepkowitz and Moak,[155] a high-frequency combustion apparatus is used to ignite the sample. The combustion products are frozen out at liquid-nitrogen temperature, and the carbon dioxide is allowed to sublime off at −102°C, the temperature of a methanol–nitrogen slush, into a McLeod gauge. At this temperature only the carbon dioxide sublimes; the water, sulfur trioxide, oil vapor, etc., remain frozen in the trap.[51] As in the capillary manometer procedure, described below, high vacuum is unnecessary. Only a mechanical pump is used, and only the measuring unit is evacuated.

The combustion-manometric procedure for carbon determination is an adaptation of the capillary trap method of Smiley [5] to the standard combustion method. The sample is burned in a stream of oxygen. The uranium metal, which normally burns violently in oxygen, is kept in an argon atmosphere prior to combustion. If the gas mixture becomes increasingly rich in oxygen as the ignition proceeds, the uranium will burn mildly and evenly.[158] The water and carbon dioxide are selectively frozen out and measured in sensitive capillary manometers. The water vapor is heated to 100°C before measurement.

Combustion-Manometric Procedure.[158] The apparatus is shown in Figs. 11.10 and 11.11. Only a few details need to be described. Two combustion tubes are shown. The horizontal tube is convenient for finely divided samples; when it is used, that portion of the tube containing the sample in a quartz boat is wrapped in platinum foil and is heated with a Fisher burner to 1000°C. Copper oxide maintained at 900°C is held near the exit end by platinum gauze. Beyond the copper oxide is placed a small tuft of silver wool for chloride removal. Chunk samples are analyzed with the vertical tube, which contains a quartz liner partially filled with Alundum chips, copper oxide, and silver wool. The sample is placed in the tube by an electromagnetic sample dumper.

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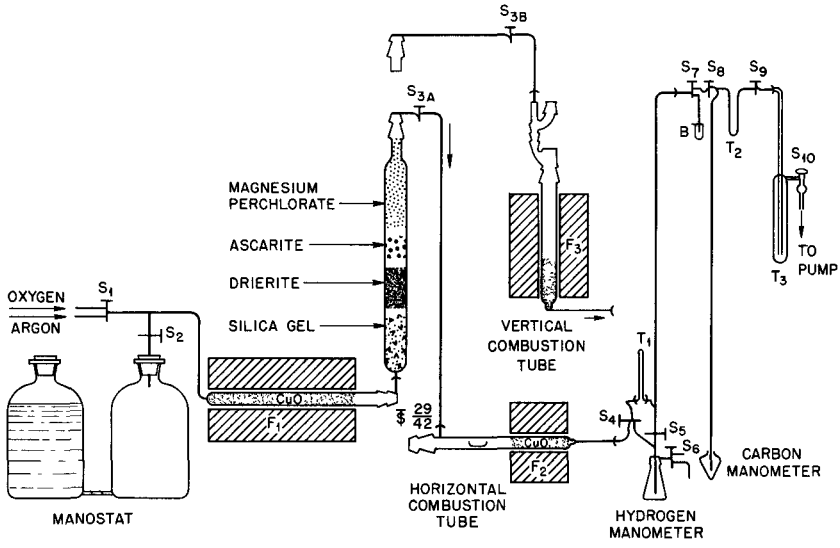


Fig. 11.10 Combustion-manometric apparatus.

Blanks for hydrogen with the vertical-tube arrangement are smaller than those with the horizontal tube. The span of tubing between the furnace F_2 or F_3 and stopcock S_4 is heated to 100°C by heater tape to prevent condensation of water.

The swivel-jointed constant-volume manometer for the water measurement is shown in Fig. 11.11. The capillary U tube serves as a cold trap for water collection and also as a fixed-volume manometer leg; it is heated to 100°C for the pressure measurement. This dual role is made possible by the swivel arrangement. The glass-wool plug in the U tube retains ice crystals.

An electric heat fan with a turbo blower is used to raise the temperature of the U tube quickly to 100±1°C. The equilibrium temperature at full heat is regulated by the air intake. Furnaces F_1 and F_2 are operated at 900°C; furnace F_3 is operated at 1000°C.

Water vapor is condensed out in T_1 by dry ice–acetone, and carbon dioxide is condensed by liquid nitrogen in T_2. A grooved stopcock, S_8, controls the flow rate of the gas mixture at about 125 ml/min. The pressure in T_1 is slightly above atmospheric, whereas the pressure in T_2 is held at about 50 mm of mercury.

At the end of a 10-min combustion period, S_4 is closed and S_8 is opened to evacuate both manometers. When the pressure reading is zero on the carbon manometer, stopcocks S_4 and S_5 are turned to connect the hydrogen manometer to the mercury reservoir. When air is admitted to the partially evacuated reservoir through S_8, mercury is driven upward into the three legs, entrapping any water frozen in the U tube. The U tube is then swiveled upward, and the mercury is driven farther up past the joints to a level in the zone to be heated. A glass T joint, serving as a hot-air flue and a coupling to the heat fan, is now placed over the U tube, and heat is applied for 3 min to bring the U tube to 100±1°C.

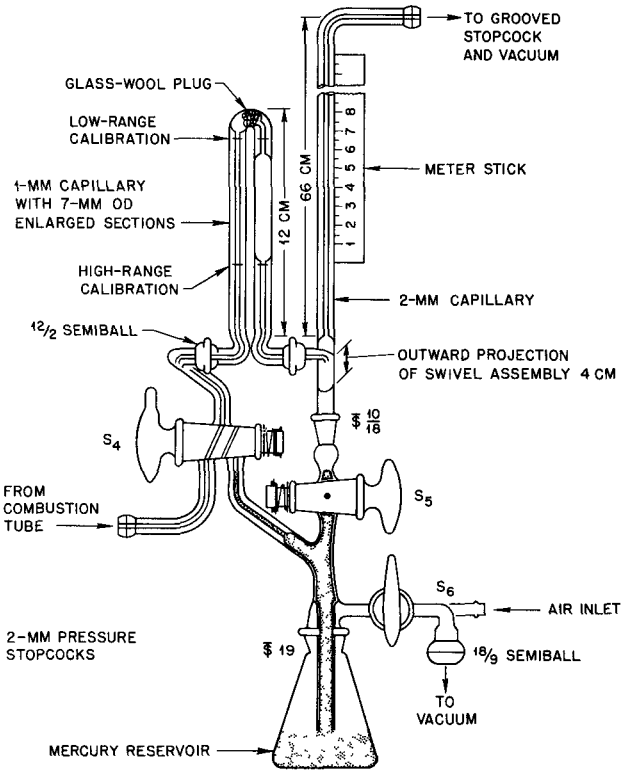


Fig. 11.11 Swivel-joint manometer.

During the 3-min heating period, the carbon dioxide measurement is made. Stopcocks S_8 and S_9 are closed, and the liquid nitrogen is removed from T_2. When T_2 is at room temperature, the depression of the mercury manometer is observed. A calibration curve of depression vs. micrograms of carbon gives the carbon content. Stopcocks S_8 and S_9 are then reopened.

At the end of the 3-min heating period, air is again admitted to the mercury reservoir to drive the mercury to the top calibration mark of the U tube. Because of the confinement of the water vapor to the small fixed volume, the mercury in the other leg of the manometer is driven up above the reference level to a height proportional to the amount of steam confined. If the amount of steam is so great that the mercury cannot be driven up to the upper calibration mark, the mercury is lowered to the high-range mark for the measurement. With low- and high-range fixed volumes of 0.225 and 1.67 ml, from 0.00 to 7.00 μg and from 0.0 to 60 μg of hydrogen, respectively, can be measured.

After the measurement has been taken, the heating element of the fan is cut off, and unheated air is blown through the fan for 1 min to cool the U tube. As the water vapor recondenses, the mercury in the measuring column is lowered. When the U tube is approximately at room temperature, the fan is removed, and the pressure is reduced by

painting the bend with dry ice–acetone slush. The mercury is now lowered to the original position, and S_4 and S_5 are closed.

The apparatus is voided completely when stopcock S_4 to the combustion tube is opened slightly until the gas flow in the line depresses the mercury in the carbon manometer by about 10 cm. The U tube is flamed to ensure degassing of the glass-wool plug. After 2 min of flushing, S_3 is closed, and S_5 is opened completely to the combustion tube. The tube is now ready for another run or for closing down.

With the vertical combustion tube, the violent combustion reaction of uranium is not too objectionable. Argon, therefore, may be eliminated if small samples are used.

The hydrogen manometer is calibrated by measuring the pressure of the water vapor produced when known quantities of hydrogen are burned in the combustion tube. The hydrogen is added by a dosing stopcock inserted into the line between the purification tube and the combustion tube.

(b) *Low-pressure Combustion.* The low-pressure method for determining microgram amounts of carbon involves combustion of the metal in an atmosphere of oxygen at reduced pressure, adsorption of the carbon dioxide in a cold trap, and subsequent release of the carbon dioxide, after removal of the excess oxygen, into a McLeod gauge. The sample is held in a platinum crucible and induction heating is used. The development of the procedure and apparatus has been discussed by Templeton and Watters.[159] Improved apparatus has been described by Barnett, Gregory, and Mapper [160] and by Edgerton and Davis.[161]

The low-pressure combustion method is reliable and possesses advantages in accuracy and precision over most conventional microcombustion procedures. Apparatus blanks are small and stable. Small samples can be used, and the gasometric measurement of the carbon dioxide makes the procedure very sensitive.

However, despite these advantages, few procedures have been reported for the analysis of the metals of interest in reactor technology. The need for expensive high-vacuum equipment and the difficulties associated with high-vacuum techniques have discouraged the use of the low-pressure method for determining carbon. The development of other methods, such as the atmospheric-pressure combustion-manometric procedure, possessing many of the favorable characteristics of the low-pressure technique also has made it less attractive.

(c) *Analysis of Individual Materials.* (1) *Uranium.* The uranium metal can be cleaned by degreasing in acetone followed by pickling in nitric acid (1+1) until it is silvery white. It is then washed with water and with acetone and is air dried. Frequently, the surface of a single-piece sample is removed, after pickling, with a degreased file. Samples can also be cleaned by anodic electropolishing at 8 volts for 1 min in a bath of sulfuric acid (1+1) containing 6 per cent glycerol.[158]

The combustion-gravimetric procedure is frequently used for uranium analysis.[143] The apparatus is similar to that shown in Fig. 11.9 except that two Friedrich, or similar, absorption tubes replace the Zackerl–Krainick tube. The water-absorption tube is filled with Anhydrone held in place by a small glass-wool plug in the bottom of the outer tube. The carbon dioxide absorption tube contains Ascarite for two-thirds of the length of the inside tube and Anhydrone in the remaining space, also held in place by glass-wool plugs. Beyond the two absorption tubes is a U tube containing glass beads in the curved portion of the tube and sufficient concentrated sulfuric acid to cover the beads. An accurate initial weight of the tube depends on previously flushing it with the gas to be used in the train. After removal from the train, the absorption tubes are wiped with a damp flannel cloth and then with chamois. They are set on a rack outside the balance case for 10 min. The tubes are then placed in the balance case for 5 min and weighed against a counterpoise absorption tube previously adjusted with enough lead shot to weigh about 5 mg less than the corresponding absorption tube. The carbon dioxide blank with a quartz combustion tube and quartz boat should not exceed 0.05 mg. Samples weighing from 2 to 3 g are generally taken.

If it is desired to determine hydrogen along with the carbon, the hydrogen blank should not exceed 0.08 mg. The quartz boat must be replaced when it becomes pitted since an etched boat rapidly absorbs moisture upon exposure to air for even a brief period. Alundum boats are quite useless for hydrogen for the same reason. Porcelain boats give small hydrogen blanks, but they can be used for only one or two runs.

With a macrocombustion apparatus as commonly used in the iron and steel industry, samples up to 8 g can be burned without danger, although the reaction is quite violent. With these large samples it is convenient to use a mixture of oxygen and nitrogen corresponding to air to control the combustion.[162] By this procedure, 10-g samples can be analyzed with a standard deviation of less than 5 per cent in the range of 600 to 700 ppm of carbon.

Hydrogen has been determined by Gregg, Wartel, and Kopelman [163] by igniting 15- to 20-g samples at 500°C for 120 min. Here again the combustion is controlled by using air instead of oxygen. The air is purified by a drying tower only.

The combustion-titration procedure [144] already described in detail is convenient for routine analyses for carbon since it is rapid and eliminates the use of a microbalance. With an induction heater the ignition and sweep-out time is reduced to 15 min.[164]

A combustion-conductometric procedure for uranium analysis has been reported.[148] The mechanical difficulties associated with the use

of the fine capillary tube to bubble the combustion gases through the small volume of alkali solution would no doubt be alleviated by the use of absorption and conductivity cells as in the Leco Carbon Determinator.

Smiley has analyzed uranium and plutonium by the combustion-manometric technique.[156] The apparatus used is similar to that shown in Fig. 11.10, except that no argon is used and the hydrogen manometer is omitted. Other differences are: (1) the gases from the vertical combustion tube are passed through amalgamated copper turnings to remove a trace of some unknown material that attacks mercury and makes frequent cleaning of the manometer necessary if it is not removed, and (2) the gases are then passed through magnesium perchlorate to remove the last traces of moisture. The McDanel combustion tube is heated to 1000°C by a resistance furnace, and the ignition and sweep-out are completed in 10 min. With the use of a preheater containing quartz chips at 900°C, the blank is lowered to less than 0.5 μg and can ordinarily be neglected. No crucible is necessary since the sample is held in the combustion tube on a packing of loose quartz chips covered with a layer of copper oxide wire 2- to 3-cm deep. The copper oxide serves to prevent large masses of sample oxide from fusing together and enclosing grains of carbide during the combustion. The combustion tube, furnace, and sample dumper are mounted in a dry box. Freshly cleaned samples of uranium gave lower carbon values than samples cleaned and stored for some weeks.

Smiley [156] also analyzed uranium and plutonium for carbon by a low-pressure combustion procedure. The apparatus was similar to that described by Naughton and Uhlig.[165] About 30 min. was required for each sample. Although the precision of the method was good, platinum crucible failures, limitations imposed upon the sample size and form by the sample dumper, and the usual high-vacuum difficulties left much to be desired.

The combustion-manometric procedure of Holt [158] for the determination of carbon and hydrogen in uranium is described in detail in Sec. 11–1.9(a)(3). Hydrogen blanks with the vertical quartz combustion tube ranged from 0.02 to 0.18 μg; with the horizontal quartz combustion tube, they ranged from 0.04 to 0.60 μg. With a vertical sillimanite McDanel tube, they ranged from 0.25 to 1.56 μg. Typical results for high-purity uranium containing 0.92 ppm of hydrogen with the vertical quartz combustion tube showed a standard deviation of 0.13 ppm.

(2) *Plutonium.* Smiley [156] analyzed plutonium for carbon by a low-pressure combustion procedure and also by the combustion-manometric procedure. The latter procedure was found to be definitely superior with respect to speed, accuracy, and convenience. With 100-

to 150-mg samples the standard deviation was found to be about 4 ppm at the 200-ppm level with the combustion-manometric technique. In contrast to uranium, plutonium metal apparently does not pick up carbon dioxide from the air since the electropolishing of samples covered with oxide scale had no effect on the carbon values.

Carbon in plutonium has also been determined by a combustion-titration procedure.[166] The sample is held in a quartz boat in a quartz combustion tube at 1000°C. Ignition and sweep-out time is 30 min. The entire apparatus is held in a dry box. With 0.5-g samples the standard deviation is about 13 per cent at the 50-ppm level.

(3) *Thorium.* It is generally necessary to use powder, filings, or turnings to obtain complete combustion of thorium metal.[143] Samples are simply degreased before combustion.

The conventional combustion-gravimetric procedure is satisfactory for determining carbon in thorium.[143] Induction heating to 3000°C, with or without low-carbon steel as a flux, has been used.[68] At this temperature the combustion and sweep-out time is about 8 min. If a resistance furnace is used, the combustion [68] is carried out at 1200 to 1300°C. Nearly 30 min is required to complete the combustion and sweep-out at this temperature. The sample is frequently placed on a bed of Alundum or zirconia powder to conserve the Alundum or Zircofrax boats that are generally used. The combustion-titration procedure is often used.[68, 167]

The use of a mixture of iron and copper as an accelerator for the combustion at 1430°C has been reported.[68] In this method the carbon dioxide is absorbed in a caustic pipet in the manner mentioned previously.[152] This procedure was used with samples having a carbon content greater than 0.01 per cent. For lower concentrations a conductometric measurement was made.

(4) *Beryllium.* The combustion-titration procedure for the determination of carbon in beryllium is described in detail in Chap. 4; the separate determination of carbide and graphitic carbon is also discussed.

(5) *Zirconium.* In the combustion-gravimetric procedure, chips of zirconium or Zircaloy [168] on a bed of 60-mesh Alundum in an Alundum boat are ignited at 1150°C in oxygen for 30 min. With induction heating to much higher temperatures, it may be necessary to add either tin,[169] iron,[169] or a mixture of iron and copper oxide [152] as a flux to obtain complete combustion. In the procedure described by Pepkowitz and Chebiniak,[152] combustion of zirconium metal with the iron and copper oxide flux is followed by absorption and measurement of the carbon dioxide by means of a caustic absorption pipet.

The combustion-titration procedure has been applied to the analysis of zirconium and Zircaloy.[168] A conductometric procedure has been

described by Morrow and Tretow.[170] Sulfur compounds and halides, both of which interfere in this procedure, are removed by a trap containing silver wire and manganese dioxide placed before the absorption cell.

In the method of Elwell and Wood,[171] combustion of large samples is controlled by filling the combustion tube first with argon. No flux is used. Wood and Williams,[172] however, recommend a flux of iron and bismuth together with the use of argon to moderate the combustion at 1150°C. Gregg, Wartel, and Kopelman [163] ignite the sample in air purified by a drying tower to control the reaction in the determination of hydrogen. Ignition in pure oxygen is also reported by these authors. At 1250°C the combustion and sweep-out time is 15 min for 5- to 10-g samples.

(6) *Titanium.* The sample for titanium analysis preferably should be coarse drillings or chips that have been degreased in carbon tetrachloride before analysis.

Several combustion-gravimetric procedures are available. Induction heating to temperatures over 1800°C in the absence of a flux has been reported.[136] Nunemaker and Shrader [173] have determined carbon and hydrogen by igniting the metal and its alloys at 1200°C in the presence of a flux of iron, tin, and copper. The quartz combustion tube is protected by an Alundum shield. Codell, Norwitz, and Schneider [174] report that an initial temperature of 900°C should be used, with granulated lead as a flux, for the determination of carbon in titanium and its alloys. A manganese dioxide–copper sulfate on asbestos trap removes sulfur dioxide and chlorine. Codell and Norwitz [175] have determined hydrogen in titanium and various titanium alloys under the same conditions. Again the reaction tube is protected from the large amount of heat generated by the ignition, either by resting the covered sample boat on an empty boat or by placing the sample in an inner Vycor tube resting on clay supports. Oda and Norishima [176] have reported the use of a temperature of 1250°C, tin as a flux, and a double porcelain boat to hold the sample. The use of a heated silver gauze to eliminate chlorides did not interfere with the hydrogen determination. Wood and Williams [172] studied the combustion of titanium at 1150°C with lead, tin, or copper as the flux and concluded that only lead was an effective flux for titanium.

A copper oxide flux is recommended by Pepkowitz and Chebiniak,[152] who measured the carbon dioxide by means of a caustic absorption pipet.

Fischer and Schmidt [177] have applied a combustion-potentiometric titration procedure for the determination of carbon in titanium and its alloys. In their method the sample is burned in moist oxygen at

1150°C with a copper, lead, and tin flux. After the carbon dioxide has been absorbed, the barium hydroxide is titrated with dilute hydrochloric or oxalic acid using a platinum–manganese dioxide electrode couple.[146] A titration technique in which the residue that remains after the sample has been brominated to determine oxide is ignited has been described by Millner, Hegedus, and Dvorszky.[178] In their method the carbon dioxide is absorbed in silica gel, which is cooled by a dry ice–ethanol freezing mixture, and then is expelled and absorbed in a barium hydroxide solution, which is titrated in the conventional manner.

Low concentrations of carbon are conveniently and accurately determined in titanium as well as in iron, steel, manganese, molybdenum, copper, lead, and tin by the procedure of Pepkowitz and Moak[155] described in Sec. 11–1.9(a)(3). By induction-heating combustion at over 1700°C in the presence of a manganese flux, freezing out the carbon dioxide in a liquid nitrogen trap, and then subliming off the carbon dioxide from a methanol-nitrogen slush into a McLeod gauge, carbon can be determined with an absolute standard deviation of about 0.0004 per cent in the 0.0100 to 0.0200 per cent concentration range with 300-mg samples.

Other combustion procedures that have been reported measure the carbon dioxide conductometrically.[151, 179] Still, Dauncey, and Chirnside[151] found that low and variable results were obtained for carbon in titanium by conditions allowing vigorous combustion; carbon remained in the slag and was only slowly given up. Reproducible results were obtained if the sample was introduced when the reaction tube was at 1100°C and the temperature was then raised to 1300°C. No flux was necessary under these conditions. Samples were held in double boats to protect the combustion tube. Sodium hydroxide solution was preferred for the conductivity cell for both high and low concentrations of carbon. Barium hydroxide solution was recommended for the low concentrations only when the highest precision was desired.

Tsuchiya[154] has described a combustion procedure in which titanium is ignited at 1100°C and the combustion gases are analyzed by mass spectrometry. Carbon and nitrogen are determined in this procedure.

Elwell and Wood[171] have controlled the combustion of large samples by filling the combustion tube first with argon. A lead flux is recommended for titanium and its alloys.

A spectrophotometric method of determining carbon in titanium by oxidation has been described by Codell, Norwitz, and Simmons.[180] The metal is dissolved in hot sulfuric and fluoboric acid. Nitric acid is then added, and the solution is heated to boiling to give a yellow

color, the absorbance of which is measured at a wave length of 450 mμ against a reagent blank. Iron and chromium interfere seriously, and the procedure is not applicable to titanium containing less than 0.03 per cent carbon. The chemistry of the yellow color is obscure.

(7) *Sodium and Sodium–Potassium.* A wet combustion procedure for the analysis of sodium for elemental carbon has been reported by Pepkowitz and Porter.[181] The sample is dissolved in water, acidified with sulfuric acid, and evaporated nearly to dryness. The carbon is oxidized with oxygen and Van Slyke oxidizing solution (fuming sulfuric acid, orthophosphoric, and chromic acid mixture). The carbon dioxide is swept out of the solution with oxygen and is frozen out and measured by the manometric technique recommended by Pepkowitz and Moak[155] described previously, Sec 11–1.9(a)(3). A similar procedure has been applied to the analysis of sodium–potassium alloys.[182]

Both the sampling of a hot dynamic sodium–potassium alloy system and a combustion-gravimetric procedure for determining carbon in the sample have been described by Stoffer and Phillips.[183] The alloy is ignited at 950°C in a quartz boat. The quartz combustion tube is protected from the fluxing action of the hot alkali by a quartz sleeve.

Hydrogen in sodium–potassium alloys can be determined by oxidizing the sample with oxygen and introducing deuterium oxide of known concentration. The hydrogen present in the alloy can be calculated by distilling the excess water and determining the deuterium-to-hydrogen ratio in the distillate with a mass spectrometer.[184]

(8) *Carbon.* Guldner and Beach[185] have determined hydrogen in carbon by a low-pressure combustion process. The granular samples are held in a platinum-mesh bag and are ignited by an induction furnace at 1000°C. The water produced is separated from the excess oxygen and carbon dioxide by a dry ice–Cellusolve acetate trap and is measured in a calibrated closed-end manometer. The precision in the range of 0.004 to 0.01 per cent hydrogen is about 7 per cent of the hydrogen present.

Oxygen in carbon can also be determined by combustion. In the procedure of Blanzat and Barbe,[186] the sample is heated to a high temperature in a stream of nitrogen. Iodine pentoxide is used to convert the carbon monoxide produced to carbon dioxide for measurement.

11–1.10 Unreacted-residue Methods for Oxygen

Unreacted-residue methods are those in which the metal is separated from the oxide by chemical or physical means. Selective dissolution of the metal; formation and removal of a volatile halide of the metal by hydrogen chloride, chlorine, or bromine; and amalgama-

tion or distillation of the metal, all may leave an unreacted residue that is chiefly oxide. Another example is one of the methods devised for sodium or sodium-potassium alloys in which the metal is made to react with *n*-butyl bromide to yield the hydrocarbon octane and metal halide. Again, the oxide is unreactive.

In many of these procedures, the oxide can be collected and simply weighed. If the residue is small and heavy contamination with impurity elements is expected, the residue is frequently dissolved and analyzed spectrophotometrically for the particular metal. The oxygen content is then calculated, assuming that the metal is present only as oxide.

The possibility of errors in all these procedures is obviously great. For example, the residue might be contaminated with unreacted carbides or silicates, or oxides of other elements might be present. However, despite these errors and others associated with the sample manipulation, the unreacted-residue procedures are frequently used. The apparatus is relatively simple, and the procedures in some cases are fairly rapid. With large samples of metal containing significant amounts of oxide, the results are often sufficiently accurate for oxygen.

(a) *Analysis of Uranium.* The application of unreacted-residue techniques to uranium apparently has been limited to the analysis of powdered samples in powder metallurgy. Two procedures have been found to be applicable to samples prepared by the calcium reduction of uranium dioxide. One is a chlorine volatilization procedure [187] of the type described in Sec. 11–1.10(c)(1) in which the oxides are retained as uranyl chloride upon chlorination at 700°C. As with zirconium, any carbon present escapes as carbon monoxide, and a correction must be applied for this loss of oxygen.

The other procedure [187] involves a thermite type reaction in which the powdered sample is mixed with aluminum powder and the mixture, in a stainless-steel or Inconel boat, is heated in a stream of argon at 1000°C. The refractory alumina thus produced by the reduction of uranium oxide is insoluble in an acid mixture $5M$ in hydrochloric acid and $1M$ in nitric acid, which dissolves all other reaction products. Carbon in the sample does not interfere, but any calcium over 0.05 per cent gives low results. Although this procedure is simple and fairly accurate, the high blank resulting from the oxygen in the aluminum powder gives poor precision for oxygen levels below 0.1 per cent.

(b) *Analysis of Thorium.* Selective dissolution of thorium in hydrochloric acid,[188] hydrochloric acid plus a trace of hydrofluoric acid,[68] or mixed acids [68, 189] (hydrochloric, nitric, and perchloric acid) is used to obtain the acid insolubles as an indication of the combined oxygen.

Determination of Oxide by Selective Dissolution in Hydrochloric Acid. Procedure.[188] Nitrogen is bubbled through 300 ml of hydrochloric acid (1+1) in a covered 800-ml beaker for 5 to 10 min. A 1- to 1.5-g sample, previously cleaned by treatment with dilute nitric acid containing a trace of fluoride ion, is added, and the acid is boiled gently on a hot plate for 4 hr. The volume is maintained during the boiling period by periodic addition of acid (1+1) free of oxygen. At the end of 4 hr, if the solution is yellow, boiling is continued until the yellow color disappears. The solution is cooled and filtered through Whatman No. 42 filter paper. The paper is washed with five 100-ml portions of hydrochloric acid (1+1) and is ignited in a platinum crucible at 1000°C for 1 hr. The residue is weighed as thorium oxide.

(c) *Analysis of Beryllium.* Unreacted-residue techniques based on selective dissolution in hydrochloric acid,[190] copper sulfate solution,[45, 191] and bromine in methanol [192] have been used for the determination of oxygen in beryllium. Volatilization procedures with chlorine,[193] bromine,[194] and hydrogen chloride [195] have also been applied. Evaluations of these procedures and other techniques for determining oxygen were made by Bradshaw,[43] and Beard, Johnson, and Bradshaw.[196] These procedures are discussed in some detail in Chap. 4.

(d) *Analysis of Zirconium.* The hydrogen chloride volatilization procedure described by Read and Zopatti [25] is commonly used for determination of oxygen in zirconium. Dry hydrogen chloride is passed over the metal held at 550°C in a Vycor or quartz tube. Conditions are carefully controlled to prevent both oxygen pickup during the volatilization of the metal chloride and oxygen loss from reaction with any carbon in the sample. The residue is either weighed as zirconium oxide, or is analyzed for zirconium and the oxygen calculated on the assumption it is all present as zirconium oxide. The procedure is described in detail in the following paragraphs.

Determination of Oxide by Hydrogen Chloride Volatilization. Apparatus and Procedure.[25] The apparatus is shown in Fig. 11.12. A solid sample of zirconium metal weighing about 1 g is cleaned in 50 ml of nitric acid (1+1) containing 5 to 10 drops of 48 per cent hydrofluoric acid by boiling the acid until the appearance of brown fumes. The sample is then rinsed thoroughly with water. Three samples can be cleaned and carried through the volatilization procedure at the same time.

The weighed sample is placed in a small platinum or quartz boat (1½ by ½ by ⅞ in.) held in a large quartz boat (6 by ⅝ by ⅞ in.), which is transferred to the cold end of the combustion tube. About 300 g of sodium chloride crystals, previously dried at 130°C, is added to the hydrogen chloride generator.

With the preheater at 400°C and the volatilization furnace at 650°C, the air in the generator is replaced with argon in the following manner: Clamps A_1, A_2, A_3, and C are opened, and stopcocks D and E are closed. Stopcock B is opened to allow argon to flow through the generator and out at clamp C at about 100 to 150 ml/min. After 20 min stopcocks E

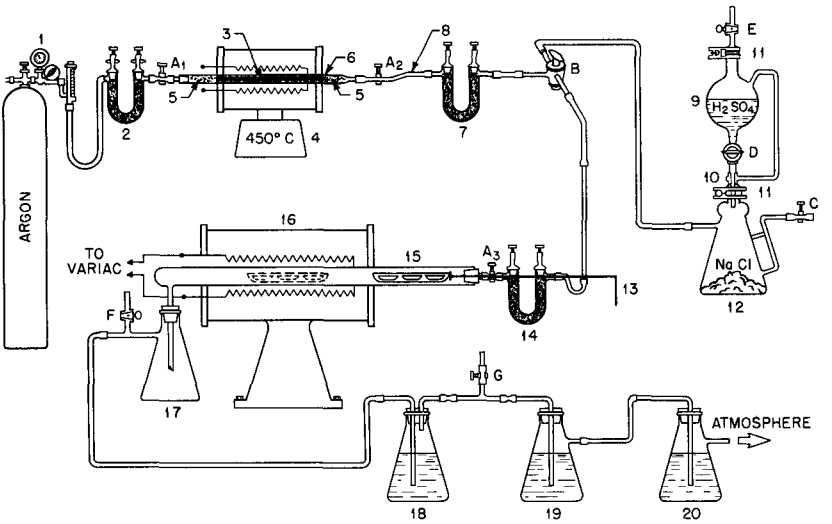


Fig. 11.12 Hydrogen chloride volatilization apparatus.

1. Regulator
2. U tube containing Drierite
3. Cu chips
4. Fisher micro-combustion furnace
5. Glass wool
6. 19-mm diameter Vycor tube
7. U tube containing Drierite
8. Rubber tubing connections
9. 500-ml bulb
10. Ring seal
11. Ball-and-socket joint
12. HCl generator (1 liter)
13. Stainless-steel push rod
14. U tube containing Drierite
15. 30-mm diameter Vycor tube
16. "Hevi-Duty" furnace
17. Primary trap (500 ml)
18. H_2SO_4 trap (500 ml)
19. H_2O trap (500 ml)
20. 10%NaOH trap (500 ml)

A_1, A_2, A_3, C, G—Clamps. B, D, E, F—Stopcocks.

and D are opened, and clamp C is closed. After 15 min stopcock D is closed. The ball-and-socket joint under stopcock E is opened, and 250 to 300 ml of concentrated sulfuric acid is added to the acid reservoir. The ball-and-socket joint is then closed and clamped; the argon is allowed to flow out of stopcock E for 10 more minutes. Stopcock F and clamp G are then closed, and stopcock B is adjusted to allow the argon to enter the combustion tube at A_3. Stopcock E is closed *immediately*. The argon is passed through the combustion tube for 1 hr. Stopcock F is opened for a few seconds during this time and closed again.

The argon tank valve is closed, and stopcock B is turned to permit hydrogen chloride to flow from the generator through the combustion tube. The sulfuric acid is then allowed to drip so as to maintain a steady flow of hydrogen chloride of about 150 ml/min. The large boat is placed in the hot zone of the combustion tube by means of the stainless-steel push rod. The push rod is pulled back immediately.

The primary trap will be filled with a white cloud of zirconium tetrachloride soon after initiating the generation of the hydrogen

chloride but will clear after the sample has been completely volatilized. The flow of hydrogen chloride is continued for 15 min after the disappearance of white fumes in the primary trap, then stopcock D is closed. When the flow of hydrogen chloride has almost stopped, stopcock B is turned to allow argon to flow through the combustion tube, and stopcock E is opened *immediately*. With the argon flowing at the rate of 100 to 150 ml/min, the furnace is allowed to cool for about 30 min. The argon tank valve is closed, and the boat is removed and cooled.

The residue in the boat is transferred to a platinum crucible. The crucible is ignited over a Meker burner, cooled in a desiccator, and weighed. The residue is zirconium oxide generally contaminated with iron, nickel, chromium, and other impurities.

About 1 g of fusion mixture (1 part sodium carbonate to 4 parts sodium tetraborate) is added to the crucible and mixed with the residue. The mixture is fused over a blast furnace to a clear melt. When cooled, the crucible is added to 50 ml of water and 5 ml of conconcentrated hydrochloric acid in a 150-ml beaker, and the melt is dissolved by heating. After the crucible has been washed with water, the solution is diluted to 250 ml in a volumetric flask.

An aliquot containing 0.05 to 0.3 mg of zirconium is pipetted into a 100-ml volumetric flask and diluted to about 75 ml with hydrochloric acid of pH 1.0. Then 5.0 ml of 0.05 per cent Alizarin Red *S* is added, the flask is filled to the mark with hydrochloric acid of pH 1.0, and the solution is mixed well. After 1 hr the absorbance is measured in 5-cm cells at 510 mμ using water as a reference. The absorbance is corrected for a reagent blank prepared by treating 1 g of fusion mixture in the same manner as the sample melt. A standard curve is prepared by determining the absorbance against water of samples containing 0.50, 100, 150, 200, and 300 μg of zirconium treated in the same manner as the sample aliquot.

Tighe, Gerds, Center, and Mallett [197] have described a modification of the preceding method in which the operation is somewhat facilitated.

Chlorine has been used by Lilliendahl, Wroughton, and Gregory [47] to volatilize the metal. In their procedure some oxygen is lost by reaction with carbon in the sample, and correction must be made by determining carbon in the original metal and the oxide residue. The oxygen lost is calculated, assuming the formation of carbon monoxide.

(e) *Analysis of Titanium.* A bromine,[178] a chlorine, [198] and a hydrogen chloride [199] volatilization technique have been applied to titanium for oxygen determination. In the chlorine procedure, low results for oxygen may be obtained, presumably because of impurities in the chlorine.[198] However, Corbett [54] has found that the chlorine procedure can be applied successfully provided that (1) the chlorine is of high purity and (2) a correction is made for the loss of oxygen by carbon monoxide formation. As in the zirconium analysis, the

oxygen loss, as a result of the following reaction, was calculated by determining the carbon content of the metal and the residue:

$$TiO_2+2TiC+6Cl_2\rightarrow 3TiCl_4+2CO$$

The basic procedure is similar to that described for the hydrogen chloride volatilization of zirconium. Freshly cut samples of 1 to 2 g are volatilized in 2½ hr at 300 to 400°C. If tank chlorine is used, the first fraction of gas is removed and discarded. The gas is dried by passage through concentrated sulfuric acid, calcium chloride, and phosphorus pentoxide.

The carbon in the metal and in the residue is determined by the combustion-titration procedure; the metal is burned at 1100°C, and the residue, at 1000°C. After the residue has been analyzed for carbon, it is fused with potassium bisulfate, and the melt is leached with sulfuric acid (1+9). Titanium is precipitated with cupferron. The precipitate is ignited and weighed as titanium dioxide. To the oxide weight is added an amount equivalent to the difference between the carbon content of the metal and the carbon left after chlorination.

With these chlorination procedures the presence of tungsten and molybdenum can lead to low results owing to the formation of volatile oxychlorides.[140]

(f) *Analysis of Sodium and Sodium–Potassium.* The metal is separated from the oxide and other impurities by distillation, amalgamation, or reaction with *n*-butyl bromide. The isolated oxide is then dissolved in water and titrated with standard acid.

In the distillation procedure reported by White,[200] the stainless-steel sampling and distillation apparatus can be connected to either a dynamic or a static system for sampling sodium or sodium-potassium alloys at operating temperatures. A fixed volume of the sample is retained in a removable hemispherical cup. The metal is distilled at a temperature of 427°C and a pressure of less than 5×10^{-3} torr. The cup is then removed from the sampler, and the oxide is dissolved in water. The resulting solution is titrated to a methyl orange end point with standard hydrochloric acid.

The procedure of Pepkowitz and Judd [201] for oxygen determination depends on the mercury extraction of sodium and potassium. Practice and particular care are essential. Samples are taken by drawing molten metal into 0.25-in.-ID borosilicate tubing. When the metal has solidified, the tubing is cut into suitable lengths, generally 3 in., and the ends are sealed with de Khotinsky cement. Each length of tubing is then deeply scored near each end so that the final middle portion, after separation, contains the approximate sample weight desired.

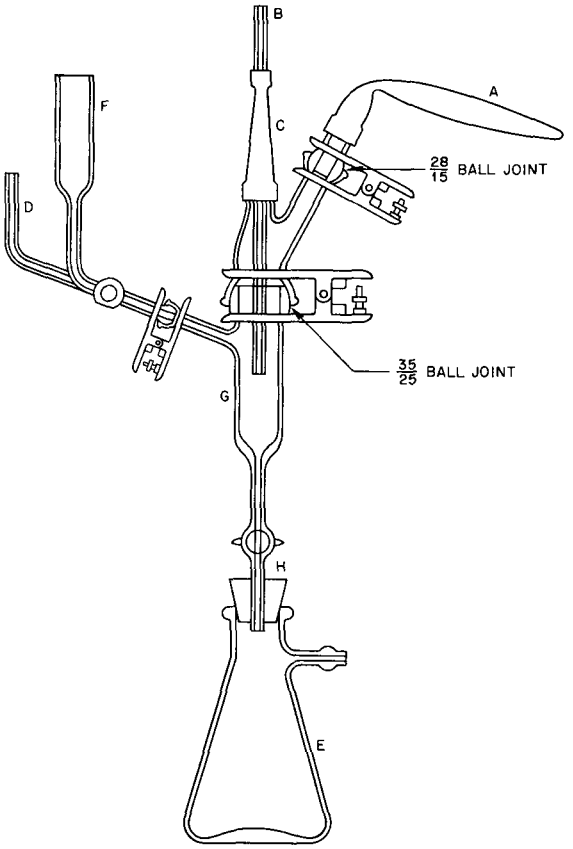


Fig. 11.13 Amalgamation apparatus.

A. Gooch rubber sample tube
B. Stirring rod
C. Rubber sleeve
D. Gas inlet
E. Vacuum receiving flask
F. Mercury inlet
G. Extraction flask
H. 2-mm capillary

Determination of Oxide by Amalgamation.[201] The apparatus is shown in Fig. 11–13. The sampling tube A is a length of Gooch rubber tubing, sealed on one end and cemented to a ball joint on the other. Stirring rod B is connected to the extraction chamber G through a gas-tight flexible rubber sleeve C. Nitrogen is introduced through D after passage through Anhydrone, copper turnings at 400°C, Anhydrone, and a gas manifold, in the order given. Vacuum flask E receives the amalgam; it is replaced by a similar flask during the dissolution of the oxide. Mercury is introduced through funnel F, which is mounted on the gas-inlet tube. H is a 2-mm capillary tube.

The extractor is cleaned, dried, and attached to the gas manifold at D. The length of sample tubing is wiped dry, flamed lightly, and placed in the sampling tube at A through the ball joint. The entire

apparatus is dried by alternate flushing with nitrogen and evacuation plus occasional flaming. Triply distilled mercury is then placed in tube F, and about 20 ml is run into the extractor. The ends of the sample tube are broken off inside tube A, and the middle portion is dropped into the extractor.

A positive gas pressure distending the rubber tubing is maintained during the extraction. The sample tube is pushed down and thoroughly broken up with the stirring rod. The amalgamation reaction is vigorous, and considerable heat is evolved. The extractor is cooled by an air stream while the amalgam is being stirred rapidly.

When cool the amalgam is drawn into the receiving flask by applying a slight suction. About 2 ml of amalgam is left in the extractor to retain the oxide. The extractions are repeated until the extractor rod and glass fragments are free from any metallic luster. About 10 cycles are necessary. When the last mercury extract is dropped into a fresh flask containing 5 ml of water and a few drops of phenolphthalein, extraction is complete if the indicator remains colorless.

The extractor cap is removed, and the rod and extractor are washed with distilled water neutralized to a phenolphthalein end point before use. The resulting sodium hydroxide solution is drawn into a clean flask and is titrated with 0.005*N* hydrochloric acid to a phenolphthalein end point. If a flame photometer is used to determine the sodium content, 100 ppm of lithium is added as an internal standard. The solution is filtered through a coarse sintered-glass filter, with a layer of Supercel as the actual filter medium, and made up to 100 ml.

Sample size is determined by adding an excess of standard hydrochloric acid to the amalgam with vigorous stirring and back-titrating the resulting solution with standard sodium hydroxide solution to a phenolphthalein end point.

Williams and Miller [202] have modified the procedure by employing high vacuum in an all-glass apparatus. By passing the blanket gas through sodium-potassium bubblers instead of hot copper to remove oxygen and by flaming the extractor instead of cooling it during amalgamation, Pepkowitz, Judd, and Downer [203] have modified the basic procedure so that a significant increase in precision is obtained. The absolute standard deviation of the differences between duplicate pairs is 0.0017 per cent in the range of 0.003 to 0.03 per cent sodium. Sodium-potassium alloys, liquid at room temperature, are handled by freezing the sample in the glass tubing on dry ice. The residual alloy in the rubber tube, A, is kept frozen by connecting sleeve A to a piece of glass tubing sealed at the end. This glass tube is immersed in a dry-ice slurry during extraction.

The procedure of White, Ross, and Rowan [204] is a clever adaptation of the Würtz-Fittig synthesis of hydrocarbons. An excess of *n*-butyl bromide is made to react with the sample of metallic sodium forming octane and sodium bromide. Sodium monoxide does not react. The procedure requires only simple apparatus, and other impurities may be determined on the same sample.

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The reagent *n*-butyl bromide must be purified by washing first with concentrated sulfuric acid and then with bicarbonate solution, drying over calcium chloride, and distilling. It is stored in a dark bottle in an argon atmosphere in contact with activated alumina. Hexane is distilled over sodium ribbon and stored in a dark bottle over sodium in an argon atmosphere.

Determination of Oxide by Reaction with n-Butyl Bromide.[204] A sealed sample, 1 to 2 g, is placed in a 4- by 20-cm tube with a reinforced bottom containing 100 ml of 50 per cent (v/v) *n*-butyl bromide in hexane. The glass tube is crushed by a heavy stirring rod flattened at one end. As the reaction proceeds, the rod is used to expose fresh sodium to the reagent. The tube is placed in a sand bath at 60 to 70°C. The reaction is complete in 1 to 2 hr. The tube is then cooled, and the residue is powdered to ensure complete reaction. About 100 ml of water free of carbon dioxide is then added, and the aqueous phase is separated by means of a separatory funnel. The aqueous phase is titrated to pH 7.0 with 0.001*N* nitric acid. The neutralized solution is diluted to 500 ml, and a 25-ml aliquot is titrated with 0.5*N* silver nitrate with eosin as the indicator to obtain the sample weight.

The remainder of the aqueous solution and the organic phase is available for the determination of metallic impurities. The absolute standard deviation of the procedure is about 0.004 per cent in the 0.02 to 0.06 per cent range.

Silverman and Shideler [205] prefer to purify the *n*-butyl bromide and hexane by passage through silica gel-Celite. Other changes in manipulation of the sample are suggested. Sodium–potassium alloys are handled by freezing the alloy and controlling the rate of reaction by the temperature. De Brun and Smythe [206] converted the hydroxide to carbonate and measured the absorbance of the carbonate in the infrared at 11.38 μ. Beer's law is not followed, but 10 ppm of the carbonate can be measured.

11–2 DETERMINATION OF OTHER TRACE IMPURITIES

The term "trace impurities" is applied in this section to those elements present in the bulk material either by design or as normal impurities in concentrations ranging from fractional parts per million to several hundred parts per million. This somewhat arbitrary range, therefore, excludes the determination of most elements that are present in alloying quantities. In some cases, however, reference is made to procedures available for the determination of alloying elements if the concentration approaches the low ranges implied by the term "traces."

Detailed procedures are given only for those elements of primary current interest. Only the briefest discussion is presented for elements considered to be of minor importance; these elements are generally present in only minute concentration. It should be noted that many

existing procedures applicable to elements in this category were developed hurriedly early in the history of the Manhattan Project, and little need for additional work has arisen since that time.

Some elements are not even listed, either because insufficient interest has been shown in the particular element to warrant the necessary developmental work or because the element is simply not present in detectable amounts. However, if an element is only briefly treated or is not listed, it may mean that it can be determined more easily by one of the specialized techniques, such as spectrography or radioactivation, and the particular chapters devoted to these methods should be consulted.

Reference to Sandell and Rodden is made liberally since most of the procedures given are spectrophotometric and many have been discussed in the *Analytical Chemistry of the Manhattan Project.* Some volumetric, potentiometric, and polarographic methods are also described. No comprehensive discussions of standard techniques, interferences, reagent purification, reactions, etc., are included; these topics are covered adequately elsewhere. Mention of these items is made, however, where necessary for adequate comprehension. Repetitious statements regarding conformity to Beer's law are not made; linearity of standard curves can be assumed unless a definite statement to the contrary is made. The wide variety of expressions used for concentrations in the detailed procedures results from the presentation of the procedures in the literature. Only a few changes, e.g., suitable wave length substituted for a filter number, were made in the procedures as originally written.

When more than one procedure for the determination of a particular element exists, the procedure selected for the detailed description in the chapter is believed to be the best on the basis of reported accuracy and precision, analysis time and equipment, and manipulations involved. Brief mention is made of the other available procedures.

The determination of the trace elements in uranium, thorium, zirconium, and some of their alloys, such as Zircaloys, are covered. (The Zircaloys are trade names for certain alloys of zirconium with tin, iron and tin, uranium, etc.) References to procedures are given for the analysis of titanium and niobium, which frequently can be analyzed by the procedures covered. The analysis of plutonium, beryllium, etc., is covered in the pertinent chapters.

11–2.1 Aluminum

(a) *In Uranium.* The blue-purple lake given by aluminum with hematoxylin in slightly basic solution [207, 208] is applicable to the analysis of uranium.[209] The solution is acidified after color development to stabilize the color and to change the color of excess dye from red to

yellow. Iron(III), giving a blue lake, interferes seriously; 1 μg is equivalent to 0.4 μg of aluminum when the absorbance is measured at 610 mμ. A correction can be made for iron determined by some other method;[209] or the aluminum can be measured at 610 mμ and the iron at 730 mμ[210] (wave lengths of 540 and 660 mμ, respectively, are recommended by Sandell[207]), and the aluminum concentration can be calculated with the aid of calibration curves prepared at both wave lengths. Moderately high concentrations of beryllium, gallium, chromium (III), cobalt, lead, lanthanum, manganese(II), silver, tin(II), titanium, and vanadium interfere.

An 8-hydroxyquinoline (oxine) procedure for uranium metal is described.[211] Oxine is added to a slightly alkaline solution containing carbonate to complex the uranium, and the oxinates are extracted with chloroform. The extract is partially purified by washing it with sodium acetate buffer; then the aluminum and other impurities are stripped from the chloroform with dilute sulfuric acid. The acid phase is extracted at pH 3.0, then at pH 4.5 with chloroform. The latter extract is diluted to volume, and the absorbance at 395 mμ is measured. Calibration is carried out by standard addition, i.e., by adding aluminum to aliquots of the sample solution. Agreement with spectrographic results is said to be good.

The only other reagent that has been applied to the spectrophotometric determination of aluminum in uranium is aurintricarboxylic acid[207, 208] (aluminon), which gives a red color with aluminum in slightly acid, neutral, or slightly basic solution. Procedures involving these different media are described in Rodden.[209] Many metal ions can interfere including titanium, manganese(II), nickel, beryllium, vanadium(IV), chromium(III), copper, iron(III), thorium, zirconium, rare earths, gallium, and indium.[207, 208, 212] Horton and Thomason[212] report an ion-exchange separation procedure in which the aluminum is separated from uranium and a large number of impurities prior to the final determination with aluminon. When a $9M$ hydrochloric acid solution is passed through a column of Dowex–1 anion resin, many ions that interfere are retained, but aluminum is not. The rare earths, manganese(II), vanadium(IV), chromium (III), nickel, titanium, beryllium, and thorium are among the ions that pass through and may interfere in the aluminon procedure. Chromium(III) can be volatilized with hydrochloric and perchloric acid. Manganese(II) and titanium in small amounts can be tolerated. Beryllium, thorium, and the rare earths are generally not found in interfering amounts in uranium. One gram of dry resin, occupying a volume of about 2 ml in $9M$ hydrochloric acid, retains 1.5 milliequivalents of uranium.

Eberle and Lerner [213] have utilized the red fluorescence given by aluminum with Pontachrome Blue Black R [207] for the analysis of uranium. The fluorescence response is very sensitive, but it is quenched by many ions, particularly iron, nickel, copper, chromium, and cobalt. Titanium, vanadium, gallium, and fluoride may also interfere. The uranium is removed by a peroxide precipitation. A mercury-cathode electrolysis then removes the iron, copper, cobalt, and other interferences. The effect of any impurities remaining is eliminated by calibrating with known amounts of aluminum added to aliquots of the sample solution. This procedure, described in detail below, has a lower limit of determination of about 1 ppm.

Fluorometric Determination of Aluminum in Uranium—Peroxide Precipitation, Mercury Cathode, Pontachrome Blue Black R. Procedure.[213] A 1-g sample of uranium metal is dissolved in 3 ml of concentrated nitric acid. The solution is evaporated to dryness, and the salt is baked gently on a hot plate until red-orange trioxide is formed. To the cooled trioxide are added 10 ml of water and 1 ml of glacial acetic acid, and the mixture is heated until dissolution is complete. The cooled solution is transferred to a 100-ml volumetric flask and diluted to 90 ml. After the addition of 5.0 ml of 30 per cent hydrogen peroxide, the volume is adjusted to 100 ml. The solution is mixed well and cooled in an ice bath for 30 min. The suspension is filtered through a dry double 12.5-cm Whatman No. 42 filter paper.

A 50-ml aliquot of the filtrate is evaporated to dryness. The residue is dissolved in 25 ml of water plus 1 ml of concentrated sulfuric acid. The solution is diluted to about 50 ml and then electrolyzed in a mercury-cathode cell for 30 min at 8 to 9 volts and 5 to 6 amp.

The solution is transferred to a beaker, and 2.0 ml of glacial acetic acid is added. The pH is adjusted to 4.7 with ammonium hydroxide (distilled water, held in a polyethylene bottle and cooled in an ice bath, saturated with tank ammonia). The volume is adjusted to 200 ml. Aliquots of 40 ml are placed in five beakers. To three aliquots are added 1.0, 2.0, and 4.0 ml, respectively, of a standard aluminum solution containing 1.0 μg per milliliter. All solutions are diluted to 50 ml. To each solution is added 0.75 ml of 0.1 per cent Pontachrome Blue Black R solution (0.250 g dissolved in 250 ml of 95 per cent ethyl alcohol; solution aged for two days before using; solution prepared fresh every two weeks; dye purchased from National Aniline Division of Allied Chemical Corp. as Superchrome Blue B). The solutions are heated just to boiling and then are cooled to room temperature.

A reagent blank is prepared and is used to adjust the zero point of the fluorometer. The fluorometer is also adjusted to give a maximum response with the sample aliquot to which was added 4.0 μg of aluminum. From the fluorescence measurements with the three standards, the average response of the fluorometer to 1 μg of aluminum is calculated. The value obtained is used to calculate the quantity of aluminum from the fluorescence of the sample aliquots.

(b) *In Thorium.* A fluorometric procedure is described which involves the removal of the thorium by an oxalate precipitation, de-

struction of the oxalate in an aliquot of the filtrate, and measurement of the fluorescence of the Pontachrome Blue Black R–aluminum complex.[214]

All the other reported procedures are based upon the use of 8-hydroxyquinoline (oxine). Different methods are used to isolate the aluminum prior to its determination spectrophotometrically or fluorometrically. In one procedure [215, 216] the thorium is removed by extraction with 2-thenoyltrifluoroacetone (TTA) in hexone from an acetate or dilute perchloric acid solution, and the aluminum is then extracted with oxine in chloroform in the presence of peroxide and nitrilotriacetic acid at pH 8.0. Either the absorbance at 390 mμ or the fluorescence of the aluminum oxinate is measured. This separation procedure eliminates the interference of thorium, iron, titanium, uranium, zirconium, vanadium, and molybdenum in the spectrophotometric procedure. The interference of copper, zinc, and nickel is eliminated by washing the oxine extract with a dilute sodium cyanide solution. Manganese and cobalt interfere, but they can be removed by a diethyldithiocarbamate extraction in the presence of tartrate at pH 8.0 after the TTA extraction of the thorium at pH 1.5. This separation also removes those interferences commonly encountered in the fluorometric procedure.

Margerum, Sprain, and Banks [217] recommend the extraction of aluminum with oxine in chloroform in the presence of 4-sulfobenzenearsonic acid or concentrated acetate buffer, either of which prevents the extraction of thorium. This procedure, capable of determining down to 2 ppm of aluminum, is described in detail below. Interference of Fe(III) is prevented by reduction and complexation of the Fe(II) with 1,10-phenanthroline. Large amounts of iron may still give a positive error; therefore Rubin and House [218] measure the absorbance at two wave lengths, 385 and 480 mμ, and subtract 80 per cent of the value at 480 mμ from that at 385 mμ. The interference of copper, nickel, cobalt, and zinc is said to be eliminated by washing the oxine extract with a dilute alkaline cyanide solution. Zimmerman and Banks,[219] however, report that nickel (and zirconium) does not interfere significantly and that the interference of copper, cobalt, and zinc is not eliminated by the alkaline cyanide wash. In this latter investigation a mixture of 3-sulfopoprionate and *N*,*N*,*N*′,*N*′-tetrakis-(carboxymethyl)-ethylenediamine (ENTA) was used instead of acetate to prevent the extraction of thorium because small quantities of acetate extracted and caused partial ionization of oxine with accompanying production of interfering color. This modified procedure is limited to the determination of over 100 ppm of aluminum.

Spectrophotometric Determination of Aluminum in Thorium—8-Hydroxyquinoline. Procedure.[217] A 2- to 3-g sample of thorium metal is dissolved in 50 ml of nitric acid (1+1) plus 1 to 2 ml of dilute fluosilicic acid (1 ml of 30 per cent acid diluted to 2 liters). The solution is evaporated to near dryness, and the residue is dissolved and diluted to 100 ml.

To an aliquot containing 1 g of sample are added 1 ml of 10 per cent hydroxylamine hydrochloride solution and 20 ml of 0.1 per cent 1,10-phenanthroline solution. After a few minutes 100 ml of concentrated acetate buffer solution (600 g of ammonium acetate and 600 ml of glacial acetic acid, dissolved and diluted to 2 liters; solution purified by three extractions with 1 per cent solution of oxine in chloroform, followed by washing with 100-ml portions of chloroform until all oxine is removed from aqueous layer) is added, and the pH is adjusted to 4.80. A reagent blank is prepared at this point.

The sample solution is extracted with 20 ml of 1 per cent oxine in chloroform for 3 min. The organic phase is transferred to another separatory funnel containing 25 ml of dilute acetate solution (200 g of ammonium acetate and 100 ml of glacial acetic acid, dissolved and diluted to 1 liter), 20 ml of 1,10-phenanthroline solution, 1 ml of hydroxylamine hydrochloride solution, and 50 ml of water. After the equilibration the organic phase is drawn off and is dried over sodium sulfate for 15 min. The absorbance is measured at 390 mμ against the reagent blank carried through the procedure.

The standard curve is prepared by adding 0 to 120 μg of aluminum to solutions containing 1 g of low-aluminum thorium and proceeding as above. The absorbance of each standard must be corrected for the absorbance of the 0-μg standard.

If zinc, nickel, cobalt, and copper interferences must be removed, the chloroform extract is washed with 100 ml of alkaline cyanide solution (40 g of ammonium nitrate, 20 g of potassium cyanide, and 10 ml of concentrated ammonium hydroxide dissolved in water; solution diluted to 1 liter). The absorbance is measured at 385 mμ. The standard-curve preparation must include this step.

(c) *In Zirconium.* Procedures involving the removal of zirconium and other impurities prior to the final determination spectrophotometrically with aluminon or fluorometrically with 8-hydroxyquinoline (oxine) or Pontachrome Blue Black R are described.

The application of the yellow-green fluorescence of aluminum oxinate in chloroform to the determination of aluminum has been studied only briefly.[207, 220, 221] Although the technique would appear to be more specific than spectrophotometric procedures with oxine since only the oxinates of aluminum, gallium, indium, zinc, and cadmium are fluorescent, many elements including iron, titanium, and vanadium quench the aluminum fluorescence. The fluorescence is sensitive, however, and the interference may still be less than that encountered in absorbance measurements.

Many prior separation schemes are used. Eberle[222] precipitates the bulk of the zirconium as salicylate from a sulfuric acid solution.

An aliquot of the filtrate is evaporated to dryness, the residue is fused with sodium potassium carbonate, and the melt is leached with water to remove the residual zirconium, iron, and other impurities. The fluorescence with Pontachrome Blue Black R is developed at pH 4.8 at 80°C. The lower limit of determination is about 10 ppm.

In another procedure [223] the zirconium is first converted to hydride by heating the metal in hydrogen at 400 to 900°C. The major portion of the hydride is oxidized to dioxide by heating with silica at 930°C for 30 min in an argon atmosphere. The residual zirconium, the aluminum, and some silicon are then volatilized as chlorides by reaction with dry hydrogen chloride at 850°C. The aluminum in the volatilized portion is further purified by a sodium carbonate–sodium tetraborate fusion similar to that described by Eberle [222] before the development of the fluorescence with Pontachrome Blue Black R. The determination of below 100 ppm is unreliable. This lengthy and tedious procedure is hardly satisfactory.

Freund and Miner [224] describe an ion-exchange separation in which a 1-g sample of zirconium in a solution 0.06*M* in hydrochloric acid and 0.8*M* in hydrofluoric acid is passed through a 30-g (dry weight) column of the strongly basic resin Dowex–1. The aluminum passes through the column along with some residual zirconium and iron (III), tin(IV), and vanadium(V). After a cupferron–chloroform separation, the aluminum is determined with aluminon in the presence of thioglycolic acid and carbonate.

This same ion-exchange separation, together with a subsequent mercury-cathode electrolysis and final determination by measurement of the fluorescence with oxine, is the basis of a satisfactory procedure for the analysis of zirconium and Zircaloys.[225] This procedure, with a lower limit of determination of about 5 ppm, is described below.

Fluorometric Determination of Aluminum in Zirconium and Zircaloy—Ion Exchange, Mercury Cathode, 8-Hydroxyquinoline. Special Reagents. All water used, including that for reagent preparation, is distilled water passed through a 40- by 4-cm polystyrene column containing Rohm & Haas MB–1 ion-exchange resin.

Ion-exchange Column. The column is prepared by shaking about 50 g (dry weight) of Dowex–1, 200 to 400 mesh, chloride form, twice with 200 ml of conditioning solution prepared by mixing 1710 ml of water, 108 ml of 3*N* hydrochloric acid, and 54 ml of 48 per cent hydrofluoric acid. The final washing is poured off, and the slurry is added to a 50- by 2.5-cm-ID polyethylene or polystyrene column fitted to a Fisher filtrator. The height of the settled resin should be about 12 in. The column is washed with 1 liter of the above conditioning solution, then with elutriant, i.e., 0.06*N* hydrochloric acid and 0.8*N* hydrofluoric acid (20 liters of solution, held in polyethylene, containing 100 ml of 12*N* hydrochloric acid and 600 ml of 48 per cent hydrofluoric acid) until the

resin is free of aluminum as determined by extraction with oxine as described below.

Procedure.[225] The calibration curve is prepared by placing from 0 to 200 μg of aluminum in platinum beakers and adding 350 ml of elutriant and 10 ml of 72 per cent perchloric acid. The beakers are covered, and the solutions are heated to perchloric acid fumes. The solutions are fumed strongly for 1 min. The solutions are cooled, the sides and cover of the beakers are washed down, and the fuming is repeated. The cooling, washing, and fuming step is repeated. About 4 to 5 ml of perchloric acid should remain in each beaker. The solutions are transferred to 100-ml volumetric flasks, are diluted to volume, and are transferred immediately into polyethylene bottles.

Ten-milliliter aliquots of each solution are placed in separate small beakers, and sufficient ammonium carbonate solution (100 g dissolved in 500 ml of water; amount required for the day's work extracted with 10-ml portions of 0.5 per cent oxine in chloroform until no color forms in extract) is added to each beaker to bring the pH to 8.3±0.2. The solutions are extracted with two 10-ml portions of 0.5 per cent oxine in chloroform for 2 min each time. The extracts are combined in 50-ml volumetric flasks containing 1 g of anhydrous sodium sulfate. The solutions are diluted to volume with 0.5 per cent oxine in chloroform and are shaken for 30 sec to allow the sodium sulfate to absorb any water. The fluorescence is measured. The reading of the 0-μg standard is subtracted from the reading of the other standards before the curve is plotted. A fluorescein solution [1.33 mg in 10 ml of water plus 0.5 ml of 50 per cent (w/v) sodium hydroxide solution; solution diluted to 1 liter] provides a convenient reference solution for the fluorescence measurements.

For the analysis of samples, a 1-g quantity of metal or alloy is placed in a platinum dish containing about 15 ml of water, and 3.0 ml of 48 per cent hydrofluoric acid is added dropwise. After dissolution is complete, 2.0 ml of 3*N* hydrochloric acid is added, and the solution is diluted to 100 ml. This solution is passed through the resin column; the effluent is collected in a polyethylene beaker. The aluminum is eluted with 250 ml of elutriant. (Suction is not used to increase the flow rate.) The 350 ml of effluent is transferred to a platinum beaker, and 10 ml of 72 per cent perchloric acid is added. The solution is evaporated to fumes and fumed strongly for 1 min behind a safety shield.

The solution is cooled, the sides and cover of the beaker are washed, and the solution is again fumed. The cooling, washing, and fuming are repeated; about 4 to 5 ml of perchloric acid should remain. The solution is diluted to about 40 ml and is transferred to a mercury-cathode cell. The solution is electrolyzed for 90 min at 7 amp. At least twice during the electrolysis, the electrodes and beaker sides should be washed down. Since 40 μg of iron in the sample, or 4 μg in the 10-ml aliquot, interfere by quenching the fluorescence, a spot test should be made near the end of the electrolysis. In two spot-plate depressions are placed, respectively, 1 drop of standard iron solution containing 0.5 μg per milliliter and 1 drop of sample solution. To each depression are added 1 drop of 10 per cent (w/v) hydroxylamine hydrochloride, 1 drop of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) solution (33 mg in 100 ml of solution), and 1 drop of 20 per cent (w/v) ammonium acetate

solution. If the sample solution shows considerable less color than the standard iron solution, the iron content of the sample solution is acceptable.

The solution is transferred to a 100-ml volumetric flask and is diluted to volume. A suitable aliquot, generally 10 ml, is extracted with oxine in chloroform, and the fluorescence is measured as described above.

A reagent blank is carried through the entire procedure, with the exception of passage through the resin column. The same volume of reagent blank and sample solution is extracted with the oxine–chloroform.

The resin is regenerated by passing 3*N* hydrochloric acid through the column until no zirconium hydroxide precipitates upon neutralizing the effluent with ammonium hydroxide. The hydrochloric acid is removed by washing the column with water until silver nitrate solution imparts only a faint turbidity to the effluent.

(d) *In Titanium.* Procedures for the determination of aluminum in titanium have been described.[226-237]

11–2.2 Antimony

(a) *In Uranium.* Although traces of antimony are generally determined spectrographically, a colorimetric procedure has been described.[238] The antimony is precipitated from acid solution as sulfide with arsenic as a carrier. After dissolution of the precipitate in ammonium sulfide, evaporation with sulfuric–nitric acid, and subsequent removal of the nitrate by fuming, the color of antimony with pyridine–iodide [207] is developed in the presence of sulfurous acid to prevent the interference of iodine and gum arabic to stabilize the suspension of the yellow pyridine antimony iodide. The absorbance is measured with a dark-blue filter.

(b) *In Titanium.* A procedure for the determination of antimony in titanium has been described by Aref'eva and Posdnyakova.[239]

11–2.3 Arsenic

(a) *In Uranium.* Traces of arsenic in uranium samples can be determined by the Gutzeit method [238, 240] in which arsenic is reduced to arsine by treatment with zinc and hydrochloric acid and the evolved arsine is led over a paper disk saturated with mercuric bromide. The disk is compared visually with standards.

Although the Gutzeit procedure is sensitive to about 0.1 μg of arsenic, it is troublesome and not as reproducible and accurate as recently developed procedures based upon the formation of molybdenum blue. In the molybdenum blue method, the heteropoly arsenomolybdic acid is produced by the reaction of As(V) with molybdic acid, and the complex is reduced with suitable reductants to strongly colored arsenic molybdenum blue. Silicate, phosphate, and germanate also form heteropoly acids reducible to molybdenum blue compounds. Brief discussions of the general reaction are given in Secs. 11–2.24(a) and

11–2.29(a), "Phosphorus in Uranium" and "Silicon in Uranium," respectively. The determination of both phosphorus and arsenic is described by Lafferty and Wade.[241] Under controlled conditions of acidity, both the phosphorus and arsenic molybdenum blue compounds are formed and measured. The arsenic is then reduced to unreactive As(III) in another sample, and the phosphorus molybdenum blue alone is produced and measured. The arsenic is calculated by difference. Germanium is assumed to be absent. The procedure, described in detail in Sec. 11–2.24(a), can determine down to 5 μg of arsenic in a 1-g sample.

The molybdenum blue reaction can be applied [207] after isolation of the arsenic by distillation from a hydrochloric acid solution containing bromide and a reducing agent in a Scherrer all-glass still [242, 243] according to the technique of Rodden.[244] This type of procedure is described by DeSesa [245] for the analysis of impure sodium uranate; undoubtedly it could be applied to purified uranium metal and oxides. Germanium, if present, accompanies arsenic in the distillation, but conditions can be adjusted during color development to avoid the interference of germanium.[207]

The volatility of arsenic trichloride and arsine should be kept in mind during sample dissolution. An oxidizing agent such as nitric acid should be present during dissolution and prolonged evaporations.

(b) *In Niobium.* A procedure for the determination of arsenic in niobium has been described by Nazarenko and coworkers.[246]

11–2.4 Beryllium

(a) *In Uranium.* Traces of beryllium in uranium are determined chiefly by the spectrograph. However, the yellow-green fluorescence of the beryllium complex with 3,5,7,2′,4′-pentahydroxyflavone (morin) [207] in alkaline solution has been used to determine microgram amounts in uranium metal or oxide.[247] The uranium is removed prior to color development by the extraction of uranium 1-nitroso-2-naphtholate with amyl alcohol. The beryllium recovery is, unfortunately, only 50 per cent.

The general separation and determination of small quantities of beryllium are discussed in Chap. 4, "Beryllium."

(b) *In Titanium.* Procedures for the determination of beryllium in titanium have been described by Covington and Miles [248] and by Hill.[249]

11–2.5 Bismuth

(a) *In Uranium.* Apparently little work has been carried out on the determination of bismuth since that reported in Rodden.[238] Three procedures are available.

In the presence of excess iodide ion, bismuth in acid solution forms a yellow-colored solution containing BiI_4 ion.[207, 238] Platinum, palladium, antimony, and tin can also give colored compounds with iodide. Lead, thallium, mercury, and silver form insoluble iodides that occlude bismuth. Oxidizing agents that liberate free iodine must be removed by reducing agents such as sulfite, hypophosphorous acid, or ascorbic acid. The colored bismuth product can be extracted by higher alcohols and esters; a mixture of amyl alcohol and ethyl acetate is frequently used. The maximum absorbance is at 460 mμ.

Tetraphenylarsonium chloride reacts with bismuth in the presence of iodide to form an orange precipitate of $(C_6H_5)_4AsBiI_4$ which is soluble in chloroform.[238] Other metals precipitated are antimony, cadmium, copper, lead, mercury, and silver. Gold, platinum, and tellurium give soluble colored products. Phosphate, chromate, cyanide, and thiosulfate interfere. Oxidizing agents liberating iodine must be removed. The absorbance in chloroform is measured at 510 mμ.

Diphenylthiocarbazone (dithizone) reacts with bismuth in acid or basic solution to give a colored product extractable with chloroform or carbon tetrachloride.[207, 238] In slightly basic solution containing cyanide, only bismuth, lead, thallium(I), and tin(II) react. In the presence of uranium, however, the extraction of bismuth may be incomplete.[238] For this reason a preliminary extraction of bismuth cupferrate is made in the analysis of uranium solutions. Bismuth and other metals are thus separated from uranium and from lead. In the subsequent dithizone extraction of a basic solution containing cyanide, pyrophosphate is added to prevent the extraction of thallium. Interference of tin is prevented by oxidation to tin(IV). Excess dithizone is washed from the extract with water containing ammonium hydroxide and cyanide. The procedure, described below, is applicable to the determination of 2 to 50 μg of bismuth.

Spectrophotometric Determination of Bismuth in Uranium—Dithizone. Procedure.[238] A 2-g sample of metal is dissolved in 20 ml of nitric acid (1+1). The solution is evaporated to about 10 ml and is diluted to 30 ml; then 7 ml of concentrated sulfuric acid is added. The solution is cooled, and concentrated ammonium hydroxide is added until a permanent precipitate forms; then 2 ml of concentrated nitric acid is added in excess of that necessary to clear the solution. The solution is diluted to 200 ml, cooled, and transferred to a separatory funnel. About 2 ml of 6 per cent (w/v) cupferron solution is added, and the solution is well mixed and then extracted with three 20-ml portions of chloroform. The extracts are filtered through dry Whatman No. 40 paper into a 100-ml beaker.

The chloroform is evaporated to dryness, and to the residue is added 3 ml of concentrated sulfuric acid. The solution is heated to fumes, and

1 ml of concentrated nitric acid is added dropwise. The solution is again heated to fumes until all organic matter has been oxidized. The solution is diluted to 20 ml, and a few drops of thymol blue indicator solution are added, followed by 2 ml of 40 per cent (w/v) ammonium citrate solution (previously made alkaline to litmus with ammonium hydroxide and extracted with dithizone solution until the extract remains green, then extracted with chloroform until the extract is colorless). Ammonium hydroxide is added until the solution is blue, then 6 drops are added in excess. To the solution are now added 10 ml of 5 per cent (w/v) sodium pyrophosphate solution (freshly prepared and treated as described above for the ammonium citrate solution) and 6 drops of 10 per cent (w/v) potassium cyanide solution. The solution is transferred to a separatory funnel and is extracted with three 7-ml portions of 0.006 per cent dithizone in chloroform. The combined organic phase is washed first with 5 ml of water and then, successively, with 40, 30, and 30 ml of dilute ammonium hydroxide–potassium cyanide solution (0.5 ml of concentrated ammonium hydroxide and 5 drops of 10 per cent potassium cyanide, diluted to 100 ml). The orange-red bismuth dithizonate solution is transferred to a 50-ml cylinder, diluted to 30 ml, and filtered through a Whatman No. 40 paper. The absorbance is measured in 1-cm cells at 505 mμ against chloroform as a reference. A correction is made for a reagent blank. The standard curve is prepared by carrying 0 to 50 μg of bismuth through the entire procedure.

(b) *In Thorium.* Thorium C (Bi^{212}) has been separated from thorium nitrate by electrodeposition at controlled potential in hot 0.5*M* hydrochloric acid upon a platinum or nickel cathode.[250]

(c) *In Zirconium.* A direct polarographic procedure has been reported for the analysis of zirconium metal, oxide, or tetrachloride.[251] A 1-g sample of metal or oxide is dissolved in 2 ml of 48 per cent hydrofluoric acid. Hydrochloric acid, 0.5 ml, and 0.25 g of boric acid plus 3 drops of 0.2 per cent methyl cellulose solution are added, and a polarogram is made of the bismuth reduction at about −0.15 volt vs. a saturated calomel electrode. The tetrachloride, 1 g, is dissolved in water; 2 ml of 10 per cent (w/v) hydroxylamine hydrochloride and 3 drops of 0.2 per cent methyl cellulose solution are added, and the solution is diluted to 10.0 ml before the polarography.

(d) *In Niobium.* A procedure for the determination of bismuth in niobium has been described by Nazarenko and Biryuk.[252]

11–2.6 Boron

(a) *In Uranium.* Boron is generally separated from matrix materials such as uranium before it is determined spectrophotometrically with suitable chromogenic reagents. The separation procedure involving the distillation of methyl borate is particularly useful in the range of about 0.1 ppm or lower to 5 ppm of boron. However, for slightly greater concentrations direct procedures can be applied if certain precautions are taken.

Curcumin is the chromogenic reagent favored by many workers because the reaction with boron is sensitive, instantaneous, and does not require the presence of concentrated acid. The color is intensified by oxalic acid or trichloroacetic acid and is extractable with organic solvents such as ethyl alcohol or acetone. A comprehensive study of the color reaction has been made recently by Spicer and Strickland.[253] Silverman and Trego [254, 255] determine as low as 0.3 μg of boron directly in 100-mg samples of uranium with curcumin by using sufficient oxalic acid above the quantity necessary for the color reaction to prevent the interference of uranium. Samples of uranium metal are dissolved under reflux in concentrated hydrochloric acid plus hydrogen peroxide. Borides insoluble in the acid mixture are worked up separately after fusion with sodium carbonate. A stable curcumin solution is prepared by dissolving the reagent in Carbitol (diethyleneglycol monoethyl ether) and diluting with acetone. The boron complex, produced under strictly controlled conditions, is extracted with acetone. To eliminate the effects of interfering impurities, a boron-free uranyl solution, prepared by evaporating a sample solution repeatedly to dryness with hydrochloric acid, is used as a reference solution in the optical measurements. Similar solutions are used to prepare the standard curve. Uranium (7 per cent)–zirconium alloys containing 0.015 per cent boron are analyzed directly with curcumin by Rynasiewicz and Consalvo.[256] The procedure is discussed in Sec. 11–2.6(c), "Boron in Zirconium."

Direct procedures based upon the reaction of boron with carmine [257] or carminic acid in concentrated sulfuric acid are also reported.[258, 259] The use of 93.4 per cent sulfuric acid is recommended.[259] At this concentration small amounts of peroxide used in the sample dissolution do not interfere. The interference of nitrate is prevented by adding a small amount of hydrochloric acid to the sulfuric acid.[257, 259] The blue complex, with a maximum absorption at 585 to 590 mμ is generally measured at 620 mμ if the uranium compound contains organic matter.[259] Color formation is usually complete within 2 hr with the 93.4 per cent acid, but the rate of reaction and the maximum absorbance obtainable depend somewhat upon the source of the reagent. The absorbance of the boron complex in uranium solutions is increased markedly if the solution is exposed to solar light.[259] The lower limit of determination is about 0.5 μg with 1 g of uranium in 25 ml of solution. Uranium–aluminum alloy fuel elements containing 0.1 per cent boron are also analyzed directly with carminic acid.[260] Compensation is made for the carminic acid complexes of uranium and aluminum, which absorb weakly at the working wave length of 585 mμ, by including uranium and aluminum in the reference solution used for the

absorbance measurements. Uranium–zirconium fuel samples are analyzed similarly [261] [see Sec. 11–2.6(c), "Boron in Zirconium"].

The conventional distillation of methyl borate followed by spectrophotometric determination of the boron in the distillate with curcumin is described in detail in Chap. 4, "Beryllium," Sec. 4–4.12(a). This procedure is applicable to many materials, including uranium, thorium, and zirconium metal and their alloys and compounds, with only minor changes due to sample dissolution. Uranium metal is dissolved in either 85 per cent phosphoric acid [262] or in a hydrochloric–nitric acid mixture.[263] If the latter dissolution is used, the solution is adjusted to about pH 4 by the addition of ammonium hydroxide before the distillation to avoid large amounts of acid in the distillate. The procedure is described below. The phosphoric acid dissolution is seldom used at the present time because of the difficulty in obtaining low blanks. The hydrochloric–nitric acid dissolution is also used for the analysis of uranium–aluminum alloys.[264]

In a procedure reported by the British,[265] the hydrochloric–nitric acid solution of the sample is adjusted to between pH 1.3 and 1.8, and a definite volume of solution is distilled off and discarded before the addition of methanol. This preliminary decrease in volume facilitates the subsequent distillation of the methyl borate. Minor variations in color development are also used. With 10-g samples, as low as 0.01 ppm can be determined. The sensitivity is thus about the same as that of the conventional procedure.

Carmine is also used as the chromogenic reagent after the methyl borate distillation.[266] The distillate is collected in 1 per cent sodium hydroxide solution. The solution is evaporated to dryness; then the residue is taken up in 1 ml of water plus 1 drop of concentrated hydrochloric acid and 5 ml. of concentrated sulfuric acid. To the solution is added 5 ml of 0.05 per cent carmine in concentrated sulfuric acid, and the absorbance is measured after 1.5 hr at 620 $m\mu$. The optimum range is 0.5 to 5 μg of boron.

To overcome the difficulties associated with the distillation separation, Eberle, Lerner, and Kramer [267] remove the uranium and other cations by ion exchange prior to color development with 1,1′-dianthrimide.[268, 269] Black oxide, produced from uranium metal by ignition, is dissolved in sulfuric acid (1+4) and hydrogen peroxide. After destruction of the excess peroxide with permanganate, the solution is passed through a column of Dowex–50 cation resin, 50 to 100 mesh, in the hydrogen form, supported in a Lusteroid tube. The column is washed with water, and the effluent and washings are collected in a quartz flask containing pyridine. The solution is evaporated to dryness, and the color is developed with 1,1′-dianthrimide in concentrated

sulfuric acid at 90°C for 2 hr. The absorbance is measured at 620 mμ. A standard curve must be prepared for each set of samples.

Two other procedures applicable to the analysis of uranium must be mentioned. Both are discussed, and the bromine–methanol procedure is given in detail, in Chap. 4, Sec. 4–4.12.

One procedure involves the extraction separation of the boron with chloroform as the tetraphenylarsonium fluoborate complex.[270] The BF_4^- ion is produced by dissolving the uranium in hydrochloric acid (1+4) plus hydrogen peroxide and adding ammonium bifluoride. After 18 hr the solution is extracted with tetraphenylarsonium chloride in chloroform. The extract is washed and evaporated to dryness after the addition of sodium hydroxide solution. The curcumin complex is developed in the presence of trichloroacetic acid instead of the customary oxalic acid.

The bromine–methanol dissolution and distillation procedure of Eberle and Lerner[271] described below is applicable to many metals including uranium, beryllium, thorium, and zirconium. With uranium samples a double distillation of the boron ester must be made because a trace of uranium distills over from the bromine–methanol medium in the first distillation. However, even with the double distillation, the separation is not as tedious as the conventional aqueous distillation. The recovery of the boron is complete with only a partial distillation of the methanol in each step. Fluorides do not interfere. Traces of bromine interfere with the formation of the curcumin complex. However, diaminochrysazin[272] is a satisfactory chromogenic reagent if large excesses of bromine are first consumed by the addition of a beryllium scavenger.

In all these procedures the necessity of keeping the blanks down to a reasonable level in the determination of boron in the 0.1- to 5-ppm range requires the use of quartzware, Corning 7280 boron-free glassware, or porcelain. Quartz is preferable for most operations. Polyethylene or soft-glass containers can often be used for storage. Pyrex glassware should ordinarily be avoided, although in some cases[254, 271] little contamination apparently results if an acid or neutral solution is in contact with the glass for only short periods. Stopcock grease can also be a serious source of contamination.

Spectrophotometric Determination of Boron in Uranium—Acid Dissolution, Distillation, Curcumin. Procedure.[263] A 0.5-g sample of uranium is dissolved under reflux in the reaction flask A of the apparatus described in Chap. 4, Sec. 4–4.12(a), Fig. 4.2, in 2.5 ml of nitric acid (1+4) plus 9 ml of hydrochloric acid (2+1) by gentle warming. The solution is cooled, and concentrated ammonium hydroxide is added dropwise until a precipitate forms and remains when the flask is shaken. Concentrated hydrochloric acid is then added until the precipitate just dissolves when the flask is shaken for 5 to 10 min. The pH at this point

should be about 4 when tested with pHydrion paper. To the solution is added 25 ml of 10 per cent calcium chloride solution in methanol. The flask is then connected for the distillation, and the procedure described in Sec. 4–4.12(a) is followed. With 5-cm cells the lower limit of determination is about 0.06 μg of boron. Blanks, however, are generally from 0.05 to 0.1 μg. In the range of 0.1 to 1.5 μg, the reproducibility is within 10 per cent.

Spectrophotometric Determination of Boron in Uranium—Bromine in Methanol Dissolution, Distillation, Diaminochrysazin. Procedure.[271] A 5-g sample of metal chips or chunks is pickled in 8*M* nitric acid, washed with water and ethanol, dried, and weighed. To the sample in the quartz reaction flask of the apparatus described in Chap. 4, Sec. 4–4.12(b), Fig. 4.4, is added 25 ml of methanol. The receiving flask contains 40 ml of methanol. To the reaction flask is added 2.0 ml of bromine, and the flask is quickly stoppered. The reaction is controlled by means of an ice bath around the reaction fla. . When dissolution is complete, 75 ml of methanol and 0.5 g of boron-free beryllium powder are added. The reaction is again controlled by the ice bath. The ice bath is then replaced by a hot-water bath at 85 to 95°C, and 60 ml of distillate is collected in the receiving flask. With a fresh receiving flask containing 45 ml of water in place, the original reaction flask is then replaced by the flask containing the methanol distillate, and 55 ml of methanol is distilled. The distillate is worked up as described in Sec. 4–4.12(b). The boron content of the scavenger beryllium is subtracted from the value found.

(b) *In Thorium.* Both the conventional acid dissolution–distillation–curcumin procedure and the bromine in methanol dissolution–distillation–diaminochrysazin procedure mentioned above under "Uranium" and described in detail in Chap. 4, Sec. 4–4.12, are applicable to thorium metal. The former procedure can also be applied to the analysis of oxide.

Minor variations of the conventional procedure exist as applied to thorium.[214, 263] The New Brunswick Laboratory procedure is identical to that described above for boron in uranium except for sample dissolution. For thorium metal or oxide, a 0.5-g sample is dissolved under reflux in 2.5 ml of nitric acid (1+4) plus 9 ml of hydrochloric acid (2+1); when the initial reaction subsides, 4 drops of hydrofluoric acid (1+9) are added, and the mixture is refluxed until the sample is completely dissolved. The remainder of the procedure is the same as that described. This procedure requires meticulous care when applied to the analysis of thorium. Although the reproducibility in the analysis of uranium is within 10 per cent, in the case of thorium it may not be as good. Some of the difficulty can be traced to the frequent plugging of the methyl alcohol delivery tube during the distillation.

No such difficulties appear in the bromine–methanol technique.[271] Fluoride is unnecessary in the dissolution step and, even if present, does not interfere. Distillation of the boron ester in the nonaqueous

690-457 O—64——51

system is simple and rapid. The reproducibility is within 10 per cent in the 0.2- to 1-ppm range.

Spectrophotometric Determination of Boron in Thorium Metal—Bromine in Methanol Dissolution, Distillation, Diaminochrysazin. Procedure.[271] A 5-g sample of chips or small chunks is pickled in hot nitric acid (1+1) containing a trace of fluoride ion. It is washed with water and then with alcohol, dried, and weighed. The procedure is identical with that described above for boron in uranium except that only a single distillation is used. The 55 ml of distillate is collected in 45 ml of water, and the mixture is worked up for color development as described. The boron content of the beryllium scavenger is subtracted from the boron value found.

(c) *In Zirconium.* Direct spectrophotometric procedures and those involving prior separation are available for the analysis of zirconium metal and alloys. As with uranium, direct procedures are useful for the determination of relatively large amounts of boron.

A direct carmine procedure similar to that described above for boron in uranium is reported by Consalvo [261] for the analysis of uranium–zirconium fuel clad with Zircaloy-2 and containing 100 to 350 ppm of boron as a burnable poison. Although uranium forms only a weakly absorbing complex with carmine and is innocuous at a uranium–boron ratio of less than 300, zirconium reacts to give a relatively large but reproducible blank. Therefore the absorbance is measured against a boron-free uranium–zirconium solution treated in the same manner as the sample solution. The procedure, described below, apparently has not been applied to the analysis of irradiated samples containing less boron.

Uranium (7 per cent)–zirconium or Zircaloy alloys containing 0.015 per cent boron are analyzed directly with curcumin by Rynasiewicz and Consalvo.[256] Fine chips of the sample are fused with sodium carbonate. The melt is dissolved in water, and the solution is converted to a chloride system by the addition of hydrochloric acid to the methyl red color change. The solution is evaporated to dryness, and the boron is extracted with 95 per cent ethyl alcohol.[273] The extract is made alkaline with sodium hydroxide; glycerol–mannitol solution is added, and the solution is evaporated to dryness. After the residue has been ignited over a burner, the conventional curcumin–oxalic acid–ethyl alcohol color development similar to that described in Sec. 4–4.12(a) is applied. The effect of the other impurity ions is negligible.

A direct quinalizarin procedure is also described for similar zirconium alloys containing from 0.02 to 0.5 per cent boron.[274] Samples up to 2 g are dissolved without loss of boron by gently refluxing with 20 ml of sulfuric acid (1+1). The solution is diluted to 100 ml, and a 5-ml aliquot is mixed with 5 ml of 0.01 per cent quinalizarin

in sulfuric acid (9+1). The mixture is diluted to 50 ml with concentrated sulfuric acid for the absorbance measurement at 617 mμ against a reagent blank as a reference. The results agree with those obtained with the distillation–curcumin procedure mentioned below.

The distillation separation of methyl borate followed by color development remains the best procedure for the determination of microgram amounts of boron in most metals including zirconium and Zircaloys. Zirconium is dissolved in either hydrofluoric acid [275] or sulfuric acid.[276] Zircaloy is dissolved in sulfuric acid.[277] If hydrofluoric acid is used, the pH of the solution is adjusted with ammonium hydroxide and methyl red indicator to about 4 to avoid large quantities of acid in the distillate. Calcium chloride in the methanol prevents the interference of the fluoride ion. The details of the distillation and color development with curcumin are described in Chap. 4, Sec. 4–4.12(a).

The bromine–methanol dissolution procedure described in Chap. 4, Sec. 4–4.12(b), is useful for either zirconium or Zircaloys.[271] The dissolution procedure is described in detail below.

Spectrophotometric Determination of Boron in Uranium–Zirconium Fuel—Direct, Carmine. Procedure.[261] A 0.5- to 1.5-g sample is dissolved under reflux with 10 ml of concentrated sulfuric acid plus 1 ml of water at 80°C for 4 to 16 hr in a quartz flask fitted with a quartz condenser. The solution is cooled, diluted with 25 ml of water, filtered, and made up to 100 ml. To a 1-ml aliquot in a 25-ml volumetric flask are added 1 ml of water and 2 drops of concentrated hydrochloric acid. The flask is cooled in an ice bath, and 10 ml of concentrated sulfuric acid is added. When the solution is at room temperature, 10 ml of 0.05 per cent carmine in concentrated sulfuric acid is added, and the solution is diluted to volume with concentrated sulfuric acid. After 1 hr the absorbance is measured at 585 mμ against 2 ml of water carried through the procedure. The absorbance must be corrected for the absorbance of a similar weight of boron-free uranium–zirconium sample carried through the procedure. The standard curve is prepared by carrying 2 ml of standards containing 1 to 10 μg of boron through the procedure.

Spectrophotometric Determination of Boron in Zirconium and Zircaloy—Bromine in Methanol Dissolution, Distillation, Diaminochrysazin. Procedure.[271] In the quartz reaction flask of the apparatus described in Sec. 4–4.12(b), Fig. 4.4, are placed a 1-g sample of shavings, 15 ml of methanol, and a Teflon stirring bar. The flask is connected to the apparatus and is cooled in an ice bath. The receiving flask contains 45 ml of water. To the reaction flask is added 2 ml of bromine, and the flask is quickly stoppered. The reaction is controlled by means of the ice bath. Zirconium reacts less vigorously than Zircaloy and may require occasional stirring to assist the dissolution. When dissolution is complete, 85 ml of methanol and 1 g of low-boron beryllium scavenger are added to the reaction flask. When the beryllium has

been completely dissolved, the distillation and color development are carried out as described in Sec. 4–4.12(b). Correction for the boron in the beryllium scavenger must be made.

(d) *In Titanium.* Procedures for the determination of boron have been described in the literature (see Refs. 231, 235, 278, and 279).

11–2.7 Cadmium

(a) *In Uranium.* Polarographic procedures have been used to determine traces of cadmium after a separation of the cadmium and other metals from the uranium. An ion-exchange separation is described.[280] The uranium is added as the nitrate to a column of Amberlite IR–120 in the hydrogen form and is eluted, along with copper and iron, with 0.5*N* oxalic acid. Cadmium, nickel, cobalt, and manganese are then eluted with 1*N* hydrochloric acid and are determined polarographically in a 6*M* calcium chloride supporting electrolyte.

The mercury-cathode electrolysis–polarographic method of Bricker, Furman, and coworkers[281, 282] described in Rodden[283] involves the electrolysis of many metals including cadmium into a mercury cathode, volatilization of the mercury in a stream of nitrogen or air, and polarographic determination of the cadmium in the residue. Cadmium and lead are determined in a 0.1*M* potassium chloride medium; copper, nickel, and the sum of the zinc and cobalt are determined in the same solution buffered with pyridine. Iron in the residue is determined spectrophotometrically with thiocyanate or 1,10-phenanthroline. Although this method was formerly very useful, it is seldom used at the present time because of the hazards of the mercury distillation and the relative ease of other separation techniques, e.g., solvent extraction.

The dithizone extraction–polarographic procedure,[284] described in detail in Chap. 4, "Beryllium," Sec. 4–4.11, is satisfactory for the determination of traces of cadmium, copper, lead, nickel, zinc, and cobalt. The uranium solution is complexed with citrate, 2 g per gram of uranium, and exhaustively extracted with dithizone in chloroform at pH 7.5 and 9.0. The treatment of the extract and the polarographic measurements are made as described in Sec. 4–4.11. The lower limit of determination for each metal is about 0.5 ppm with 4-g samples.

Spectrophotometric procedures for determining traces of cadmium are based upon the extraction of cadmium dithizonate from a strongly basic solution.[207] In a procedure described in Rodden,[285] the uranium is complexed with citrate, and the solution is extracted with dithizone in carbon tetrachloride at about pH 9.5. Since other metals accompany cadmium at this pH, the extract is washed with 0.01*N* hydrochloric acid to remove the cadmium and any zinc, lead, and thallium. Traces

of copper and nickel may also transfer to the acid and are removed by extracting the acid solution with dithizone. The acid solution is then made strongly basic with sodium hydroxide, and the cadmium dithizonate alone is extracted for the absorbance measurement. Zinc, in concentrations up to 150 times the cadmium, and milligram quantities of other metals forming dithizonates including thallium do not interfere. Rodriguez Pasques and Possidoni de Albinati [286] have studied the variables involved in this procedure and suggest some modifications regarding the optimum concentration of dithizone and purification of the carbon tetrachloride. These changes are included in the detailed procedure given below.

Schwebel and Rosenwasser [287] extract directly a strongly basic uranium solution complexed with sucrose. Traces of silver, copper, and nickel extract with the cadmium, however, and re-extraction with 0.05*N* sulfurous acid is necessary in the presence of these metals. In another modification these authors first extract copper with dithizone from acid solution and nickel with dimethylglyoxime from slightly alkaline solution before extracting the cadmium from the strongly basic solution. Both procedures are limited to 50-mg samples of uranium and have no advantages over that described below.

Spectrophotometric Determination of Cadmium in Uranium–Dithizone. Special Reagents. Ammonium Citrate Solution, 50 Per Cent and 10 Per Cent. A 50 per cent (w/v) solution is adjusted to pH 9.5 with ammonium hydroxide and is extracted with 10-ml portions of 0.02 per cent dithizone in carbon tetrachloride until the last extract remains green. The solution is then washed with carbon tetrachloride until excess dithizone is removed. The 10 per cent solution is made by diluting the 50 per cent solution.

Carbon Tetrachloride. Redistilled solvent is washed with 20 per cent sodium hydroxide solution, passed through a carbon tetrachloride-wetted filter paper, and stored over sodium hydroxide pellets.

Procedure.[285, 286] A 3-g sample is dissolved in 4 ml of concentrated hydrochloric acid and then 3 ml of concentrated nitric acid is added. The solution is evaporated to a syrupy consistency, and 70 ml of water and 10 ml of 50 per cent ammonium citrate solution are added. The solution is transferred to a separatory funnel. Two drops of thymol blue indicator solution (0.1 g dissolved in 2 ml of 0.1*N* sodium hydroxide solution plus 5 ml of 90 per cent ethyl alcohol; solution diluted to 250 ml with 20 per cent ethyl alcohol) are added. Concentrated ammonium hydroxide is then added until the indicator turns to green, and 5 ml in excess is added.

The solution is extracted with 5-ml portions of 0.02 per cent dithizone in carbon tetrachloride, for 1 min each time, until the extract remains green. The organic extracts are transferred to another separatory funnel and are washed with 5-ml portions of water until the aqueous phase is colorless. The aqueous phase is discarded. The organic phase is washed for 2 min with 10 ml of 0.01*N* hydrochloric acid and is dis-

carded. The acid phase is extracted with 5-ml portions of 0.004 per cent dithizone in carbon tetrachloride for 1 min each time until the last extract remains green. The extracts are discarded. The aqueous phase is washed with 10-ml portions of carbon tetrachloride until the last portion is colorless. The organic extracts are discarded.

To the acid solution are added 5 ml of 10 per cent ammonium citrate solution, 5.0 ml of 0.004 per cent dithizone, and 5 ml of 20 per cent sodium hydroxide solution. After a 30-sec equilibration, the organic phase is immediately filtered through a dry filter paper into a dry 1-cm cell. The absorbance is measured within 5 min at 520 mμ against a carbon tetrachloride reference; the color is not stable. The absorbance is corrected for a reagent blank.

For the standard-curve preparation, from 0 to 10 μg of cadmium is carried through the entire procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(b) *In Thorium.* The dithizone extraction–polarographic procedure,[284] mentioned above under "Cadmium in Uranium" and described in detail in Chap. 4, Sec. 4–4.11, is applicable to the analysis of thorium. The sample is dissolved in hot 8*M* nitric acid containing a trace of fluoride ion, and the thorium is complexed with citrate or tartrate prior to the exhaustive extractions at pH 7.5 and 9.0.

The polarographic determination of cadmium directly in 0.1*M* potassium chloride or hydrochloric acid solutions of thorium oxide below pH 3 is described by Menis and coworkers.[216] If interfering impurities are present, a preliminary 2-thenoyltrifluoroacetone (TTA)–chloroform extraction is made. After the extraction cadmium is determined in a 0.5*M* sodium tartrate supporting electrolyte at a half-wave potential of −0.80 volt vs. a saturated calomel electrode (S.C.E.).

The spectrophotometric determination [214] with dithizone is nearly identical to that described above under "Cadmium in Uranium." Ammonium citrate complexes the thorium, 5 g per gram of thorium. Minor differences in the procedure applied to thorium include the use of 0.05*N* sulfuric acid for backwashing the cadmium and the use of chloroform as the solvent.

(c) *In Zirconium.* A direct polarographic procedure has been used to determine traces of cadmium, bismuth, copper, lead, nickel, and the sum of the zinc and cobalt in zirconium metal.[251] A 1-g sample is dissolved in 2.0 ml of 48 per cent hydrofluoric acid plus 4 ml of water. After the addition of 0.5 ml of concentrated hydrochloric acid, 0.25 g of boric acid, and 3 drops of 0.2 per cent methyl cellulose solution, the solution is diluted to 10.0 ml and shaken until the boric acid dissolves. The polarographic waves of cadmium, bismuth, copper, and lead are measured at the highest possible sensitivity at half-wave potentials of −0.75, −0.15, −0.30 and −0.50 volt vs. S.C.E., respectively. For the determination of nickel and the combined zinc–cobalt, 1 g of tartaric acid and the maximum suppressor are added to a similar hydro-

fluoric acid solution of the sample; the pH is adjusted to between 7.0 and 7.5 with concentrated ammonium hydroxide; the solution is diluted to 10.0 ml for the polarography. The half-wave potentials of zinc and cobalt are nearly identical in this medium, −1.40 volt vs. S.C.E., and that of nickel is −1.15 volt vs. S.C.E. This procedure is generally unsatisfactory. The lower limit of about 5 ppm for each metal and the many interferences limit the value of the procedure.

The dithizone extraction–polarographic procedure [284] described in detail in Chap. 4, Sec. 4–4.11, is much more satisfactory than the direct polarographic procedure. The zirconium metal, dissolved in hydrofluoric acid, is further complexed with tartaric acid, 1 g per gram of zirconium, and the solution is exhaustively extracted with dithizone in chloroform at pH 7.5 and 9.0. The treatment of the extract and the polarographic procedure are described in Sec. 4–4.11. With 4-g samples a lower limit of determination of about 0.5 ppm of cadmium can be reached. Copper, lead, nickel, zinc, and cobalt can also be determined in the same solution with about the same lower limit of determination.

Spectrophotometric procedures with dithizone [207] are available. Read and Read [288] describe a procedure in which an initial extraction is made from a strongly basic solution of zirconium complexed with citrate. The extract is washed with 0.05*N* sulfurous acid to remove the cadmium and traces of other metals. The wash is made strongly basic, and the cadmium is finally re-extracted with dithizone for the optical measurements.

For the analysis of zirconium and Zircaloy, Burd [289] isolates the cadmium from a hydrofluoric–nitric acid solution of the sample containing boric acid and hydroxylamine by extraction of the diethyldithiocarbamate complex with chloroform at pH 1.0. The cadmium is stripped from the organic phase with 2.5*N* nitric acid. After destruction of the organic matter, the cadmium is extracted with dithizone–chloroform from a strongly basic solution containing tartrate, cyanide, and hydroxylamine according to the procedure developed by Saltzman.[290] The cadmium is stripped from the extract with 2 per cent tartaric acid, and a final dithizone extraction is made from the tartaric acid solution made basic with sodium hydroxide after the addition of cyanide and hydroxylamine. The lower limit of determination is 0.1 ppm with a 2-g sample. A similar procedure is reported by Chernikhov and Dobkina.[291]

Spectrophotometric Determination of Cadmium in Zirconium and Zircaloy—Diethyldithiocarbamate Separation, Dithizone. Procedure.[289] A 2-g sample is degreased with acetone and ethyl ether, washed with 20 ml of hydrochloric acid, rinsed with several portions of water, and dried. The weighed sample is dissolved in a platinum dish with 4 ml of 48 per

cent hydrofluoric acid (containing less than 0.02 ppm cadmium) plus 20 ml of water and 6 drops of concentrated nitric acid. After the addition of 50 ml of saturated boric acid solution and 1 ml of 20 per cent hydroxylamine hydrochloride solution, the pH is adjusted to 1.0 with dilute hydrochloric acid.

The solution is transferred to a separatory funnel and is extracted with three 2-ml portions of 2 per cent sodium diethyldithiocarbamate plus 15 ml of chloroform for 1 min each time. The solution is extracted with a final 15-ml portion of chloroform, and the combined organic phase is washed four times with 20-ml portions of 2.5*N* nitric acid. To the combined nitric acid washes in a pyrex beaker is added 3 ml of concentrated sulfuric acid. The solution is evaporated to fumes; the sides of the beaker are washed with water. Then 4 ml of concentrated nitric acid and 2 ml of 70 per cent perchloric acid are added. The solution is evaporated to near dryness.

The residue is dissolved in 10 ml of hot water, and the solution is cooled. Four drops of thymol blue solution (0.1 g of indicator ground in a mortar with 21.5 ml of 0.01*N* sodium hydroxide; solution diluted to 250 ml) are added, and the solution is titrated to a yellow color with 10*N* sodium hydroxide. The solution is transferred to a separatory funnel and diluted to about 25 ml. The following reagents are then added, with thorough mixing after each addition, in the order given: 1 ml of 25 per cent sodium potassium tartrate solution; 5 ml of 10*N* sodium hydroxide–1 per cent potassium cyanide (400 g of sodium hydroxide and 10 g of potassium cyanide dissolved in 400 ml; solution diluted to 1 liter and stored in polyethylene); and 1 ml of 20 per cent hydroxylamine hydrochloride solution.

The solution is extracted with 15 ml of ice-cold 0.008 per cent dithizone in chloroform for 1 min. The organic phase is drained into a separatory funnel containing 25 ml of ice-cold 2 per cent tartaric acid solution. The extraction is repeated with 10 ml of chloroform, and the extract is added to the tartaric acid.

The tartaric acid–chloroform phases are shaken for 2 min. The organic phase is discarded. The aqueous phase is washed with 5 ml of chloroform. The chloroform wash is removed as completely as possible; the last drops floating on the surface are evaporated by drawing air across the surface.

To the acid phase are added 0.25 ml of 20 per cent hydroxylamine hydrochloride solution, 15.0 ml of 0.0008 per cent dithizone in chloroform, and 5 ml of 10*N* sodium hydroxide–0.05 per cent potassium cyanide (400 g of sodium hydroxide and 0.5 g of potassium cyanide dissolved in 400 ml of water; solution diluted to 1 liter and stored in polyethylene). The separatory funnel is immediately shaken for 1 min, and the stem is washed with ethyl alcohol and dried with filter paper. The chloroform phase is drained into a dry 25-ml volumetric flask and is diluted to volume with chloroform. The absorbance is measured at 520 mμ in 2-cm cells against chloroform as a reference.

The absorbance is corrected for a reagent blank prepared by evaporating 4 ml of 48 per cent hydrofluoric acid, 20 ml of water, and 6 drops of concentrated nitric acid in a platinum beaker to near dryness, adding 50 ml of saturated boric acid solution, and proceeding as described for a sample.

The standard curve is prepared by carrying from 0 to 2 μg of cadmium in 50 ml of saturated boric acid solution through the entire procedure. The absorbance of each standard should be corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* A procedure for the determination of cadmium in titanium has been described by Aref'eva and Posdnyakova.[239]

(e) *In Niobium.* A procedure for the determination of cadmium in niobium has been described by Nazarenko and Biryuk.[252]

11–2.8 Calcium

(a) *In Uranium.* Spectrographic or flame photometric methods are more useful than chemical methods for the determination of traces of calcium in refined uranium materials. However, chemical procedures have been applied in the past after removal of the uranium by precipitation as peroxide or extraction with diethyl ether followed by conventional removal of the silica, the hydrogen sulfide, and the ammonium hydroxide groups. The calcium is precipitated with sodium carbonate and Fe(III) as a carrier, then it is precipitated as the oxalate and is titrated with permanganate in the usual manner.[247] An indirect spectrophotometric procedure has also been applied.[247] The calcium oxalate precipitate is isolated and dissolved in hydrochloric acid; a known amount of Fe(III) in slight excess and sulfosalicylic acid are added. The oxalate complexes a portion of the Fe(III). The remaining Fe(III) is determined by measuring the absorbance of the Fe(III)-sulfosalicylic acid complex.

(b) *In Thorium.* Calcium and magnesium are determined after a homogeneous precipitation of the thorium with urea in the presence of formate buffer by a conventional ethylenediaminetetraacetic acid (EDTA) titration.[292] Calcium has also been determined by complexing the thorium with sulfosalicylic acid, precipitating calcium oxalate, treating the oxalate with an excess of ceric sulfate, and back-titrating the Ce(IV) with ferrous ion.[247]

(c) *In Zirconium.* Calcium in zirconium has been determined volumetrically with permanganate after both complexing the zirconium and precipitating the calcium with oxalate.[293]

(d) *In Titanium.* Procedures for the determination of calcium have been described in the literature (see Refs. 230, 235, 294, and 295).

11–2.9 Chlorine, Bromine, and Iodine

(a) *In Uranium.* General methods for the determination of chloride, bromide, and iodide in uranium compounds are given in Rodden.[296] Little interest has been shown in the determination of iodide. Use has been made of the oxidation of iodide by iodate or dichromate and the extraction of the resulting iodine by chloroform or carbon tetrachloride for the spectrophotometric measurement.[296]

It has been necessary to determine bromide in uranium hexafluoride. The procedures are generally applicable to other uranium materials. One procedure [297] for hydrolyzed hexafluoride involves the oxidation of bromide by chromic–sulfuric acid mixture, distillation of bromine, reoxidation followed by extraction with carbon tetrachloride to separate entrained chromium, and color development with phenol red. A similar procedure [298] with direct oxidation and extraction and color development with fluorescein is reported for the analysis of hydrolyzed hexafluoride and uranyl nitrate. For difficulty soluble compounds such as the tetrafluoride and oxides, a preliminary distillation step is incorporated into the procedure. Another approach [299] involves the precipitation of silver bromide with added chloride as a carrier, formation of bromate with hypochlorite, reaction of the bromate with bromide to form bromine, and color development with rosaniline. Bromide can also be determined by effusion of bromine from a chromic–sulfuric acid medium and absorption by a solution of Fast Green dye in a Conway cell.[300]

To the variety of procedures for the determination of chloride in uranium compounds described in Rodden [296] can be added that in which chloride is oxidized by permanganate. The chlorine is swept by nitrogen into an iodide solution, and the liberated iodine is titrated with thiosulfate.[300] This procedure, developed for the analysis of hexafluoride, actually yields total chloride, bromide, and iodide.

Uranium metal is generally analyzed only for chloride, although many procedures give results for total halide. Turbidimetric and nephelometric procedures with and without separation of the chloride before precipitation with silver nitrate are described in Rodden [296] and elsewhere.[301, 302] The measurement of silver chloride turbidimetrically in 50 per cent ethylene glycol is recommended.[303] Dissolution of the metal in dilute nitric acid with gentle heat instead of in concentrated acid is said to reduce loss of chloride.[304] Several other developments have been reported. One [305] involves the coulometric titration at constant current with electrolytically generated silver ion; the end-point is determined potentiometrically with a silver–calomel electrode pair. Amperometric titrations with silver ion have been studied.[306, 307] A potentiometric titration with silver ion to a predetermined equivalence potential in 95 per cent methyl alcohol–5 per cent nitric acid medium is described.[308]

A rapid volumetric procedure [309] for the determination of chloride in metal is based upon the separation of silver chloride, the addition of iodide to an ammoniacal solution of the silver chloride to precipitate silver iodide, the dissolution of the silver iodide with potassium cyanide, and the back-titration of the excess cyanide with silver

nitrate. The end point is the appearance of a turbidity due to reprecipitated silver iodide. Large samples are required to determine traces of chloride.

The determination of down to 2 ppm of chloride in uranium, beryllium, or thorium metal or their oxides can be carried out by heating the sample held in a silicon boat in a current of steam at 1100 to 1200°C and determining the chloride in the condensate spectrophotometrically after the addition of mercuric thiocyanate and ferric alum.[310] Ferric thiocyanate is formed proportionally to the chloride present. Iodide, bromide, cyanide, and sulfide interfere. Sulfide can be oxidized by nitric acid at 50°C before color development. The procedure is described in detail in Chap. 4, "Beryllium," Sec. 4–4.17(c).

(b) *In Thorium.* Chloride in thorium metal and oxide is determined by the pyrohydrolysis–spectrophotometric procedure[310] described under "Chloride in Uranium" and given in detail in Chap. 4, Sec. 4–4.17(c). Thorium oxide–uranium oxide mixtures have been analyzed similarly.[311] After pyrohydrolysis, mercurous ion, which forms a strong chloride complex, is added. The excess mercurous ion is determined spectrophotometrically with diphenylcarbazone. A fusion pyrolysis has been applied to the analysis of thorium oxide.[216] The chloride, released by fusing the sample with sodium trimolybdate, is trapped in dilute sodium hydroxide solution. The solution is acidified with nitric acid, and the chloride is titrated potentiometrically with silver nitrate and a silver–silver chloride indicator electrode. Conventional nephelometric procedures are also available.[214]

(c) *In Zirconium.* Iodide in "crystal bar" zirconium is determined by oxidizing the iodide with chromic acid, extracting the resulting iodine with benzene, and measuring the absorbance at 295 mμ.[251] An iodine distillation followed by development of the color with starch has also been used.[251]

Chloride in zirconium sponge can be determined gravimetrically by the conventional silver chloride method[288] or volumetrically by potentiometric procedures.[312, 313] Thomason and Kelley[312] state that as little as 5 ppm can be determined by the potentiometric titration, but the procedure is most useful for amounts greater than 100 ppm.

Arc-melted zirconium and Zircaloy metals, which contain less chloride than sponge metal, are best analyzed at present by various turbidimetric or nephelometric procedures that differ only in minor details (see Refs. 223, 251, 291, and 314). From 5 to 100 ppm can be determined, although the results for less than 20 ppm are often erratic.[288] For this reason, chloride is frequently added to samples to bring the concentration over 20 ppm. Because of the apparent effect of chloride on the weld penetration in Zircaloy, a need exists

for a procedure capable of analyzing metal containing less than 5 ppm.[288]

Nephelometric Determination of Chloride in Arc-melted Zirconium and Zircaloy. Special Apparatus. If a Fisher Nefluoro–Photometer is used, the blank filter is placed in the left position, the 425-mμ filter in the center, and the 430+ in the right position. Any similar instrument may be used.

Special Reagents. Distilled water passed through a column of mixed-bed ion-exchange resin should be used for all reagents and dilutions.

Procedure.[314] The calibration curve is prepared by adding 0 to 125 μg of chloride to 100-ml flasks containing about 50 ml of water, 10 ml of nitric acid (1+1), and 25 ml of 0.85*M* boric acid. To the flask containing 125 μg of chloride is added 2.0 ml of 4.8 per cent silver nitrate solution (prepared fresh daily and kept protected from bright light). The solution is mixed and diluted to volume. A portion of this generating solution is placed in the clear ¾-in. cell. Silver nitrate solution is added to the 100-μg standard flask. The solution is mixed and diluted to volume. The scale reading is set to 100 with this solution as the reference solution in the black-fritted ¾-in. cell. The silver nitrate solution is then added to each of the remaining flasks, and scale readings are measured immediately after dilution to volume. The scale reading of the 0-μg standard is subtracted from the readings of the other standards.

To a sample weighing 1 g in a platinum beaker are added 10 ml of water, 10 ml of nitric acid (1+1), and 2 to 3 ml of 48 per cent hydrofluoric acid dropwise until the sample is in solution. External heat is not applied. If the sample contains less than 20 ppm of chloride, 20 μg should be added to the solution. After the addition of 25 ml of boric acid solution, the solution is transferred to a 100-ml flask, and 2.0 ml of silver nitrate solution is added. The solution is diluted to volume and mixed, and the optical measurement is made immediately. The scale reading is corrected for a reagent blank carried through the procedure.

The time between the addition of the silver nitrate and the optical measurements should be as constant as possible. A final correction is made for any chloride added.

Potentiometric Titration of Chloride in Zirconium Sponge. Special Apparatus. A Leeds & Northrup pH meter or a similar potential-measuring instrument is used.

Special Reagents. Silver Nitrate Solution, 0.01N. A stock 0.10*N* solution is prepared by dissolving 16.99 g of silver nitrate in water and diluting the solution to 1 liter. The solution is stable for at least six months if stored in the dark. The 0.01*N* solution, which is stable only for several weeks, is prepared by dilution of the stock solution.

Procedure.[313] The 0.01*N* solution is first standardized by titration against potassium chloride as a primary standard. To a 100-ml beaker are added 10 ml of standard 0.01*N* chloride solution (0.7455 g of potassium chloride in 1 liter of solution), 0.2 ml of concentrated nitric acid, and 30 ml of acetone. The solution is titrated with the 0.01*N* silver nitrate solution with a silver and mercury–mercurous sulfate–1*N* sulfuric acid (Beckman No. 40455) electrode pair connected to the potentiometer. The silver nitrate is added at a rate of 1 to 2 drops per second to the magnetically stirred (Teflon bar) solution until the voltage

change is 5 to 10 mv per drop of titrant, and then in 0.1-ml increments until the potential change is 15 to 20 mv per 0.1 ml. The addition of 0.1-ml increments is continued for an additional 0.5 ml. The potential readings are plotted against volume of titrant, and the end point is determined as the point at which the potential change per 0.1-ml addition is the greatest.

It is recommended that a control standard be analyzed first in duplicate. A 5-g sample of low-chloride arc-melted zirconium (<10 ppm chloride) is placed in a platinum beaker, and 5.0 ml of the standard chloride solution is added. About 15 ml of water is added, a watch-glass cover is applied, and the beaker is cooled to about 10°C in an ice bath. To the beaker is added 5 ml of 48 per cent hydrofluoric acid, 1 ml at a time. When the reaction nearly stops, the beaker is removed from the ice bath, and 4 ml of 48 per cent hydrofluoric acid is added, 2 ml at a time. When the sample has dissolved completely, 1 g of boric acid is added, and the solution is warmed gently and swirled until the boric acid dissolves. The solution is cooled to room temperature, and 0.2 ml of concentrated nitric acid and 30 ml of acetone are added. The solution is titrated with 0.01*N* silver nitrate as described above, and the end point is determined from a plot of the potential vs. volume curve. In the presence of the zirconium, the boric acid, and the hydrofluoric acid, the potential break is suppressed and is only about one half that obtained for the standardization of the silver nitrate.

Samples are analyzed in the same manner as that described for the control standard. A 5-g sample of low-chloride arc-melted zirconium (<10 ppm chloride) is analyzed to obtain the reagent blank.

(d) *In Titanium.* Procedures for the determination of chloride in titanium have been described in the literature (see Refs. 227, 235, 278, 294, and 315 to 324).

(e) *In Niobium.* A procedure for the determination of chloride in niobium has been described by the British.[325]

11–2.10 Chromium

(a) *In Uranium.* The sensitive diphenylcarbazide reaction with Cr(VI) in acid solution to give a red-violet product[207, 326] is used exclusively for the determination of traces of chromium in uranium. Only minor differences exist in the many procedures reported. Larger amounts of chromium, from 0.1 to 1.0 mg in the presence of uranium, can be determined by the chromate color intensified in the presence of Fe(III) and perchloric acid.[207, 326] The absorbance of the solution is measured before and after the addition of Fe(II) to reduce the dichromate. These larger amounts, greater than 100 μg, can also be determined by X-ray fluorescence after extraction of the bulk of the uranium with tributyl phosphate.[327]

Few metals interfere in the diphenylcarbazide procedure. Molybdenum(VI) gives a violet color much less intense than that of chromium. Mercury (I) and (II) give pale-blue colors eliminated by chloride ion. Iron(III) and vanadium(V) yield yellow colors; the vanadium color fades rapidly. The analysis of uranium, conse-

quently, can be carried out directly with little difficulty. Compensation for the uranium color itself is generally only made in the determination of chromium below 1 or 2 ppm.

Oxidation of the chromium to chromium(VI) in uranium solutions is carried out with permanganate,[326] bromate,[328] or persulfate and silver-ion catalyst.[263, 326, 328] Low results are experienced with permanganate oxidation if chlorides are used to destroy the excess permanganate.[329] Presumably some volatilization of chromyl chloride can occur. Sodium azide removes excess permanganate efficiently. If persulfate and silver ion are used, the absorbance should be measured immediately since silver reacts slowly with the reagent.[328]

In the procedure given below, it is assumed that the sample is completely soluble in nitric acid. In the case of uranium powder, some chromium may remain undissolved by this treatment.[328] A procedure for determining separately the chromium in this insoluble portion by bromate oxidation after dissolution in perchloric acid is described.[328] Excess bromate is destroyed by sodium chloride.

Spectrophotometric Determination of Chromium in Uranium—Diphenylcarbazide. Procedure.[263] A 1-g sample is dissolved in 5 ml of nitric acid (1+1). The solution is heated until the sample has been completely dissolved; then it is evaporated just to dryness. The residue is dissolved in 10 ml of 2*N* sulfuric acid, and the solution is diluted to about 90 ml. The pH is adjusted to 0.9 to 1.1 with 2*N* sodium hydroxide.

To the solution are added 10 ml of 0.25 per cent silver nitrate solution (0.5 g in 200 ml; solution stored in the dark) and 10 ml of 20 per cent (w/v) ammonium persulfate solution. A few glass beads are added, the beaker is covered with a watch glass, and the solution is boiled for 25 min. The volume is not allowed to decrease below 50 ml. The solution is cooled and transferred to a 100-ml volumetric flask containing 2 ml of diphenylcarbazide solution (0.2 g dissolved in 40 ml of acetone; solution prepared fresh daily). The solution is diluted to 100 ml, and the absorbance at 540 mμ in 5-cm cells is measured immediately against water.

The absorbance is corrected for a reagent blank. The standard curve is prepared with 0 to 10 μg of chromium as dichromate in 10-ml volumes of 2*N* sulfuric acid. The pH is adjusted to 0.9 to 1.1 with 2*N* sodium hydroxide, and the color is developed without the oxidation step. The absorbance of each standard is measured against the 0-μg standard.

For the highly precise determination of less than 2 ppm, compensation should be made for the absorbance of the uranium and other colored ions in the sample solution. Another 1-g sample is dissolved as above. The solution is evaporated, the residue is taken up in 10 ml of 2*N* sulfuric acid, and the solution is diluted to 100 ml. The absorbance of this solution is measured against water and subtracted, along with that of the reagent blank, from the sample absorbance. The absorbance of the sample blank seldom exceeds that given by 0.1 μg of chromium.

(b) *In Thorium.* The diphenylcarbazide method is applicable. The various procedures reported differ mainly in the oxidation of the Cr(III). Persulfate[214] is satisfactory. Permanganate, with the excess destroyed with hydrochloric acid, has been used,[214, 330] but losses of chromium with this technique are possible as mentioned previously under "Chromium in Uranium." Destruction of excess permanganate with sodium azide has been applied to the analysis of thorium oxide–uranium oxide slurries with satisfactory results.[311] Ammonium hexanitratocerate has been shown to be a better oxidant than perchloric acid, sodium bismuthate, or silver oxide in a study of the determination of chromium in thorium oxide slurries.[216] Dissolution of the oxide by repeated fuming with perchloric acid results in chromium loss. No loss results if a mixture of hydrochloric acid and hydrofluoric acid is used.[216]

Spectrophotometric Determination of Chromium in Thorium—Diphenylcarbazide. Procedure.[330] A 1-g sample of metal is dissolved in 25 ml of nitric acid (1+1) plus 2 drops of 48 per cent hydrofluoric acid. After the addition of 25 ml of 0.85*M* boric acid, the solution is diluted to a definite volume. To a 50-ml aliquot or less, 9 drops of concentrated sulfuric acid are added, and the solution is heated to boiling. Then 5 drops of 1 per cent silver nitrate solution and 5 ml of 10 per cent ammonium persulfate are added, and the solution is boiled for 10 min. The solution is cooled, 1.0 ml of 0.4 per cent diphenylcarbazide solution (0.4 g dissolved in 100 ml of 95 per cent ethyl alcohol; solution prepared immediately before use) is added, and the solution is diluted to 50 ml. The absorbance is measured immediately at 545 mμ in 1- to 5-cm cells against water as a reference. The absorbance is corrected for a reagent blank. The standard curve is prepared by carrying 0 to 100 μg of chromium through the procedure and correcting the absorbance of each standard for the absorbance of the 0-μg standard.

(c) *In Zirconium.* The diphenylcarbazide procedure with oxidation of the Cr(III) by either permanganate (Ref. 223) or persulfate and silver ion (Refs. 223, 263, 288, 331) is used exclusively for zirconium. The latter technique is applied in the analysis of zirconium and Zircaloy-3 for traces of chromium and in the analysis of Zircaloy-2 for alloying quantities. The fluoride used for sample dissolution can be either fumed off or complexed with boric acid.

Spectrophotometric Determination of Chromium in Zirconium and Zircaloy—Diphenylcarbazide. Procedure.[263] A 1-g sample in a platinum dish is covered with water and dissolved by the addition of 1 ml of sulfuric acid and sufficient 48 per cent hydrofluoric acid. The solution is warmed to obtain dissolution, and 25 ml of 0.85*M* boric acid solution is added. The pH is adjusted to between 0.9 and 1.1 with 2*N* sodium hydroxide, and the solution is diluted to about 90 ml. The procedure described above for "Chromium in Uranium" is then applied beginning with the oxidation of the Cr(III).

(d) *In Titanium.* Procedures for the determination of chromium in titanium have been described in the literature (see Refs. 226, 227, 231, 232, 235, 294, 332, and 333).

11–2.11 Cobalt

(a) *In Uranium.* A dithizone extraction–polarographic procedure,[284] described in detail in Chap. 4, "Beryllium," Sec. 4–4.11, can be applied. A mercury cathode electrolysis–mercury volatilization procedure,[281, 283, 334] with the final determination being carried out spectrophotometrically on the tetraphenylarsonium thiocyanate[334] complex mentioned below, has been used. An ion-exchange separation of the cobalt followed by polarography in 6*M* calcium chloride has also been recommended.[280] All these procedures are discussed briefly in Sec. 11–2.7(a).

The simultaneous spectrophotometric determination of cobalt, copper, and nickel in uranium is carried out by Chilton[335, 336] by extracting the diethyldithiocarbamates with carbon tetrachloride at pH 5.4 in the presence of pyrophosphate, citrate, and carbonate as shown in Sec. 11–2.12(a), "Copper in Uranium." Bismuth interferes.

The formation of a blue chloroform-soluble product between the cobalt thiocyanate complex and tetraphenylarsonium chloride is the basis of a spectrophotometric procedure developed by Potratz and coworkers.[337, 337a]

$$2[(C_6H_5)_4As]^+ + Co(SCN)_4^{-2} \rightarrow [(C_6H_5)_4As]_2Co(SCN)_4$$

Iron(III), copper(II), molybdenum (VI) and (V), and vanadium (V) interfere. The interference of Fe(III) and molybdenum is prevented by the addition of fluoride. Ferrous ion prevents the interference of pentavalent vanadium. Copper(II) is reduced by potassium iodide; the resulting iodine is destroyed by thiosulfate. The color due to cobalt, with a maximum absorption at 615 mμ, is stable in the dark for 24 hr. The method is most applicable in the range of 10 to 200 μg of cobalt.[334]

The red complex formed by cobalt with 1-nitroso-2-hydroxy-3,6-naphthalenedisulfonic acid (nitroso-R)[207] is the basis of a useful procedure for the determination of cobalt in a variety of uranium products including the metal.[338] A preliminary separation of cobalt and other impurities is made by extracting the potassium ethylxanthate complexes with chloroform. The nitroso-R products are then formed. Finally, treatment with hot nitric acid decomposes all the complexes except that of cobalt.

Spectrophotometric Determination of Cobalt in Uranium—Potassium Ethylxanthate Extraction, Nitroso-R. Procedure.[338] A sample weighing up to 2 g is dissolved in a slight excess of nitric acid, and the solution

is heated to remove much of the free acid. To a 250-ml separatory funnel are added 50 ml of 25 per cent (w/v) sodium citrate, the sample solution, and 10 ml of glacial acetic acid. The separatory funnel is shaken well, then 25 ml of 5 per cent (w/v) potassium ethylxanthate (prepared daily) is added.

The solution is extracted with six 10-ml portions of chloroform. The extracts are filtered through chloroform-wetted Whatman No. 54 paper and collected in a 100-ml flask. The chloroform is evaporated, and the organic matter is destroyed by adding two 4-ml portions of concentrated nitric acid and evaporating after each addition nearly to dryness. The residue is dissolved in 2 ml of hot concentrated hydrochloric acid.

The solution is diluted to about 40 ml with water, and 10 ml of saturated sodium acetate solution (200 g of sodium hydroxide dissolved in water; solution neutralized to litmus with glacial acetic acid and diluted to 1 liter) and 3 ml of 0.4 per cent (w/v) nitroso-R reagent solution are added. The solution is brought to a boil, 5 ml of concentrated nitric acid is added, and the solution is boiled for 1 to 2 min.

The solution is cooled and diluted to 100 ml, and the absorbance is measured in 1- or 5-cm cells at 420 or 500 mμ (Ilford 603 and Calorex H503 heat-resisting filters are used in a filter photometer) vs. a reagent blank carried through the procedure.

The standard curve is prepared by carrying 0 to 300 μg of cobalt in solutions containing 2 ml of concentrated hydrochloric acid through the color-development steps as described above. The absorbance of each standard is measured against the 0-μg standard.

(b) *In Thorium.* The dithizone extraction–polarographic procedure mentioned previously under "Cadmium in Uranium," Sec. 11–2.7(a), and described in detail in Sec. 4–4.11 is applicable.[284] Thorium is complexed with citrate or tartrate for the extractions.

LaMont and Johnson [311] determine microgram quantities of cobalt in thorium oxide–uranium oxide slurries directly with 1-nitroso-2-hydroxy-3,6-naphthalenedisulfonic acid (nitroso-R).[207] Interference by iron is prevented by complexation with fluoride after oxidation of Fe(II) with bromine.[339]

A sensitive method based upon the color produced with 1-(pyridylazo)-2-naphthol (PAN) has been proposed for the analysis of thorium oxide slurries by Goldstein, Manning, and Menis.[340] A prior separation of cobalt by ion exchange is required. Of the elements that accompany cobalt through the anion-exchange column, only copper interferes seriously in the color development. If copper is present, it can be removed by a separate step such as electrolytic deposition prior to the column separation. If the nickel to cobalt ratio is less than 10 and if only microgram quantities of iron, zinc, and cadmium are present, the ion-exchange step may be unnecessary.

Spectrophotometric Determination of Cobalt in Thorium—Anion Exchange, PAN. Special Reagents and Apparatus. A 1- by 5-cm column of Dowex 1–X10, 50 to 100 mesh, is washed with 50 ml of 10*M* hydrochloric acid before a sample is added. After the column has been used,

it is washed with 50 ml of water for regeneration. Because some elements such as zinc and molybdenum are irreversibly retained by the resin, the column is discarded before its capacity for retention of these ions is exceeded.

Procedure.[340] A 10*M* hydrochloric acid solution of the sample is prepared as follows: the metal, oxide, or oxide slurry is dissolved in nitric acid (1+1) containing a few drops of 48 per cent hydrofluoric acid; the solution is evaporated to dryness twice with concentrated hydrochloric acid; and the residue is taken up in 10*M* hydrochloric acid so that 10 ml contains not more than about 2.5 g of thorium. A 10-ml volume of the solution is heated just to boiling, and the hot solution is passed through the column at a rate of not more than 2 ml per minute. The column is washed with 20 ml of hot 10*M* hydrochloric acid, and the effluent and washings are discarded. The cobalt is eluted with 30 ml of 4*M* hydrochloric acid.

The eluate is evaporated to dryness, and the residue is dissolved in 15 ml of water plus 5 drops of concentrated hydrochloric acid. To the solution are added 2 ml of 10 per cent citric acid solution, 2 ml of 50 per cent (w/v) ammonium acetate solution, and 1 drop of a saturated solution of potassium periodate. The pH should now be about 4.5. Then 0.5 ml of the PAN reagent solution (0.1 g dissolved in 100 ml of ethyl alcohol) is added. The solution is transferred to a 60-ml separatory funnel and shaken for 3 min with 5 ml of chloroform. After a 15-min disengagement period, the chloroform phase is drained into a 1-cm cell, and the absorbance at 640 mμ is measured against a reagent blank. The quantity of cobalt is obtained by reference to a standard curve prepared by carrying solutions containing from 0 to 10 μg of cobalt through the complex-formation and -extraction steps and measuring the absorbance of each solution against the 0-μg standard.

(c) *In Zirconium.* A direct polarographic procedure,[251] discussed breifly in Sec. 11–2.7(c), "Cadmium in Zirconium," can determine the sum of the cobalt and zinc. This procedure is useful only when the zinc is either absent or is known from some other determination. The dithizone extraction–polarographic method,[284] which is discussed in the same section and described in detail in Chap. 4, Sec. 4–4.11, is more satisfactory. The lower limit of determination is about 1 ppm with a 2-g sample.

Spectrophotometric procedures all utilize the nitroso-R color reaction.[207] Zirconium metal can be analyzed directly.[341] A hydrofluoric acid solution of the metal is complexed with boric acid and citrate, and the color is developed at pH 8.0 ± 0.2. A pH of 6 in the presence of ammonium fluoride has been used.[342] Boiling the nitroso-R complexes in the presence of nitric acid destroys the interference of other impurities in the usual manner.[207]

Separation procedures are generally applied in the analysis of both zirconium and Zircaloys prior to color development with nitroso-R. Chernikhov and Dobkina [291] extract cobalt diethyldithiocarbamate from a fluoride solution at pH 1.0 with ethyl acetate or chloroform.

The cobalt is back-extracted by a mixture of nitric and hydrochloric acid, and the color reaction is applied.

Cobalt can be extracted as the potassium ethylxanthate complex by chloroform from a hydrofluoric acid solution containing boric acid, ammonium citrate, and acetic acid.[341] The extract is evaporated, and the organic matter is destroyed with nitric acid prior to color development.

A mercury-cathode electrolysis–mercury volatilization separation technique [281-283] has been applied to zirconium and titanium.[343]

Extraction of the 1-nitroso-2-naphtholate complex with chloroform from a hydrofluoric acid solution buffered with ammonium citrate at pH 8.2 is used by Tate, Wilson, Goward, and Beiter.[344] Hydrochloric acid decomposes the other heavy metal complexes of nitroso-R. This procedure, described in detail below, is applicable to the determination of 0.5 to 30 ppm with a 1-g sample of zirconium or Zircaloy.

Spectrophotometric Determination of Cobalt in Zirconium and Zircaloy—1-Nitroso-2-Naphthol Extraction, Nitroso-R. Procedure.[344] A 1-g sample is dissolved in 25 ml of water, 2 ml of 48 per cent hydrofluoric acid, and 1 ml of concentrated nitric acid in a platinum or polyethylene beaker. After the addition of 10 ml of ammonium citrate solution (50 g of citric acid dissolved in 100 ml of water; solution neutralized with 70 ml of concentrated amonium hydroxide), the pH is adjusted to 8.2 with concentrated ammonium hydroxide. The solution is transferred to a separatory funnel and is extracted three times with 5 ml of 1-nitroso-2-naphthol solution (200 mg dissolved in 5 ml of 1*N* sodium hydroxide; solution filtered and diluted to 100 ml) and 5 ml of chloroform for each extraction. The extracts are combined, and the chloroform is evaporated. Organic matter is destroyed by fuming the residue to dryness with 5 ml of concentrated nitric acid and 2 ml of concentrated sulfuric acid. If necessary, the acid addition and fuming are repeated.

To the cooled residue is added 5 ml of mixed acids [2.5 ml of concentrated hydrochloric acid and 5 ml of nitric acid (1+9), diluted to 100 ml]. The mixture is warmed, if necessary, to dissolve the residue. To the solution are added 2 ml of 0.1 per cent nitroso-R solution and 5 ml of 40 per cent sodium acetate solution (40 g of the trihydrate in 100 ml of solution). The solution is boiled for 45 sec. Then, 3 ml of hydrochloric acid (1+1) is added, and the solution is boiled for an additional 45 sec. The solution is cooled, transferred to a 25-ml volumetric flask, and diluted to volume. From 30 to 40 min after the addition of the nitroso-R reagent, the absorbance at 510 mμ is measured in 2-cm cells against water as a reference. The absorbance is corrected for a reagent blank.

To prepare the standard curve, from 0 to 30 μg of cobalt is added to 5 ml of concentrated nitric acid and 2 ml of concentrated sulfuric acid. The solution is fumed to dryness. The beaker sides are rinsed, the same quantity of acids is added, and the solution is again fumed to dryness. After the addition of 5 ml of mixed acids, the color development described above is applied. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of cobalt in titanium have been described in the literature (see Refs. 227, 235, 316, 342, and 343).

11–2.12 Copper

(a) *In Uranium.* The polarograph has been useful for the determination of traces of copper. A direct procedure is proposed by Horton and Thomason.[345] In a carbonate solution of uranium at pH 8.5 containing 0.25*M* ethylenediaminetetraacetic acid (EDTA), the half-wave potential of copper is −0.55 volt vs. a saturated calomel electrode. No other common impurity interferes. Media containing EDTA, nitriloacetic acid, or sodium citrate–ammonium carbonate are used similarly by Ball, Manning, and Menis.[346]

Procedures involving the separation of copper and other metals prior to polarography are available. A mercury-cathode electrolysis technique is described [347] in which the mercury is subsequently volatilized and the residue is analyzed.[281-283] This separation procedure, described briefly in Sec. 11–2.7(a), "Cadmium in Uranium," is rarely used at the present time. More useful is the dithizone extraction procedure [284] mentioned in Sec. 11–2.7(a) and described in detail in Chap. 4, "Beryllium," Sec. 4–4.11. This procedure, involving the exhaustive extraction of a uranium solution complexed with citrate at pH 7.5 and 9.0, can determine 1 ppm of copper in a 2-g sample.

Fairly large quantities of copper, greater than 1 mg, can be determined by an electrogravimetric procedure. Copper in uranyl sulfate solutions is deposited by internal electrolysis in a cell composed of a platinum cathode, a cadmium anode, and an alundum thimble separating the electrodes.[348]

Spectrophotometric methods utilize dithizone or sodium diethyldithiocarbamate (DDTC). In the dithizone–carbon tetrachloride extraction of copper from a 0.1 to 0.2*N* acid solution, platinum, palladium, gold, silver, mercury, bismuth, and tin(II) may accompany the copper.[207] Platinum and palladium are rarely found in significant amounts in uranium. The remaining elements can be washed out of the organic extract with 2 per cent potassium iodide in 0.01*N* hydrochloric acid.[349] Since these interfering elements are often present in insignificant amounts, the potassium iodide wash can be frequently omitted.[347]

The gold-yellow diethyldithiocarbamate complex of copper formed at pH 8.0 to 9.0 is extractable with solvents such as isoamyl alcohol, isoamyl acetate, chloroform, and carbon tetrachloride.[207] Iron, nickel, cobalt, bismuth, manganese, and uranium may also react with the reagent to give colored products soluble in isoamyl alcohol. However, uranium does not react when complexed with citrate. Pyro-

phosphate prevents iron and manganese interference. Nickel can be precipitated by dimethylglyoxime, bismuth by ammonium hydroxide, before extraction to prevent the interference of these metals.[347] The dimethylglyoxime also prevents the interference of cobalt. The absorbance is measured at 430 to 440 mμ.

A similar procedure is used by Chilton to determine copper, cobalt, and nickel simultaneously.[335, 336] The pH of a uranium solution containing citrate and pyrophosphate is adjusted to 5.4 with sodium carbonate solution, and the diethyldithiocarbamates are extracted with carbon tetrachloride. The absorbance of the copper maximum at 436 mμ, the cobalt maximum at 367 mμ, and the nickel maximum at 328 mμ are measured. By means of the molar absorptivities of each element at these wave lengths, simultaneous equations can be derived for each element. Bismuth must be absent.

A satisfactory diethyldithiocarbamate procedure[350, 351] free of interference is based upon the preliminary extraction of copper, iron, and vanadium cupferrates with chloroform at pH 1.5 to 2.0. After destruction of the cupferrates, more than 100 μg of iron is removed as the hydroxide. No copper is lost in the hydroxide precipitation if an excess of ammonium hydroxide in the presence of ammonium chloride is used. If less than 100 μg of iron is present, the citrate present during the color development with diethyldithiocarbamate prevents any interference. Iron can be determined with thioglycolic acid in the solution obtained after destruction of the cupferrates.

Spectrophotometric Determination of Copper—Cupferron Separation, Diethyldithiocarbamate. Special Reagents. Cupferron Solution, 5 Per Cent. A solution prepared by dissolving 25 g of reagent in 500 ml of water is filtered through Whatman No. 41 paper in a Buchner funnel. The filtrate is transferred to a 1-liter beaker, and 50 ml of sulfuric acid (1+19) is added with stirring. The mixture is cooled, and the precipitate is filtered through Whatman No. 41 paper in a Buchner funnel. The precipitate is washed with 200 ml of water, transferred to a 1-liter breaker, and dissolved in 250 ml of ammonium hydroxide (1+15). The solution is filtered as before. The solution is diluted to 500 ml and transferred to a 1-liter separatory funnel. After the addition of 1 drop of 30 per cent hydrogen peroxide, the solution is extracted with three 20-ml portions of chloroform. The extracts are discarded.

Sodium Citrate, 25 Per Cent. A 25 per cent (w/v) solution is purified by adding 5 ml of 2 per cent sodium diethyldithiocarbamate solution and concentrated ammonium hydroxide until the solution is alkaline to litmus and extracting with chloroform until the extracts show no trace of brown color.

Procedure.[350, 351] A 5-g sample is dissolved in 20 ml of nitric acid (1+1). The solution is cooled and diluted to 50 ml. To the solution are added 3 ml of concentrated sulfuric acid and then concentrated ammonium hydroxide until a permanent precipitate of ammonium

diuranate is obtained. The precipitate is redissolved by the dropwise addition of concentrated nitric acid; then 0.5 ml in excess is added. The pH of the solution is checked at this point with a meter and is adjusted to 1.5 to 2.0. (If iron is also to be determined on a portion of the extract, the pH should be adjusted to 1.0 to 1.5.)

The solution is transferred to a separatory funnel, 5 ml of 5 per cent cupferron is added, and the solution is extracted with three 10-ml portions of chloroform. The extracts are filtered through Whatman No. 42 paper wetted with solvent into a 75-ml Kjeldahl flask and are evaporated to dryness. To the residue is added 2 ml of concentrated sulfuric acid. The flask is heated to fumes of sulfur trioxide; then concentrated nitric acid is added dropwise until the solution clears. The solution is cooled and diluted with 20 ml of water.

The solution is transferred to a beaker, and 5 ml of concentrated hydrochloric acid is added. Concentrated ammonium hydroxide is added until iron precipitates; then 5 ml in excess is added. (If the iron content is small or if the blank is being prepared, phenolphthalein is used to indicate the end point.) The solution is warmed to coagulate the ferric hydroxide; then it is filtered through Whatman No. 41 paper into a separatory funnel.

Concentrated nitric acid is added to the solution until it is just acid to phenolphthalein. The solution is cooled. To the solution are added 5 ml of 25 per cent sodium citrate solution, sufficient concentrated ammonium hydroxide solution to make the pH 8.0 to 9.0, and 0.5 ml of 2 per cent sodium diethyldithiocarbamate solution. The copper complex is extracted with 10-ml portions of chloroform until the last extract is colorless. (Three extracts are normally sufficient.) The extracts are filtered through a solvent-wetted Whatman No. 41 paper and diluted to 50 ml with chloroform.

The absorbance is measured at 440 mμ in 5-cm cells against chloroform as a reference. The absorbance is corrected for a reagent blank. The standard curve is prepared by carrying from 0 to 60 μg of copper through the diethyldithiocarbamate extraction procedure beginning with the addition of nitric acid to the phenolphthalein end point. The absorbance of each standard is measured against the 0-μg standard as a reference.

(b) *In Thorium.* The dithizone extraction–polarographic procedure,[284] mentioned in Sec. 11–2.7(a) and described in detail in Chap. 4, Sec. 4–4.11, is applicable. Thorium is complexed with citrate or tartrate before the exhaustive extractions at pH 7.5 and 9.0.

Spectrophotometric methods employ sodium diethyldithiocarbamate (DDTC) or 2,9-dimethyl-1,10-phenanthroline (neo-cuproine) as the chromogenic reagent. The reagent DDTC is discussed briefly under "Copper in Uranium." A thorium solution containing citrate, pyrophosphate, and dimethylglyoxime at a pH over 9 is treated with DDTC and extracted with isoamyl alcohol.[214] The absorbance of the extract is measured at 440 mμ. Ethylenediaminetetraacetic acid (EDTA) is used instead of citrate in a similar procedure for the analysis of thorium oxide slurries.[216]

Neo-cuproine [352] is satisfactory for the determination of traces of copper in thorium metal [330] or thorium oxide–uranium oxide slurries.[311, 353] The procedures are identical to that described in detail for "Copper in Zirconium." A 1-g sample of metal is dissolved in 25 ml of hydrochloric acid (1+1) containing 2 drops of 48 per cent hydrofluoric acid. When the reaction ceases, 1 ml of concentrated nitric acid is added, and the solution is boiled, cooled, and diluted to about 35 ml. The pH is adjusted to 1.0 or below, and the colorimetric procedure is applied.

(c) *In Zirconium.* A direct polarographic procedure,[251] described briefly in Sec. 11–2.7(c), is available for the determination of traces of copper and other metals in zirconium. The dithizone extraction–polarographic procedure,[284] also mentioned in Sec. 11–2.7 and described in detail in Sec. 4–4.11, is more satisfactory. The metal is dissolved in hydrofluoric acid and exhaustively extracted, after the addition of tartaric acid, at pH 7.5 and 9.0 with dithizone in chloroform. With 2-g samples a lower limit of about 1 ppm can be determined. No common impurity interferes.

For the spectrophotometric determination of traces of copper, the analyst is offered a variety of chromogenic reagents. Conventional dithizone or diethyldithiocarbamate procedures,[207] described previously for "Copper in Uranium," are said by Read and Read [288] to be satisfactory for the analyses of zirconium metal.

Wood and Clark [354] describe a diethyldithiocarbamate procedure for the determination of 5 to 100 ppm of copper in zirconium and Zircaloy–2. The sample is dissolved in a mixture of sulfuric and fluoboric acid. The zirconium is complexed with citrate prior to the extraction of the complex from alkaline solution with chloroform. More than 0.5 per cent iron and 0.005 per cent nickel give high results, but the addition of ethylenediaminetetraacetate (EDTA) to the solution before the extraction overcomes these interferences. The interference of over 0.25 per cent manganese is prevented by washing the extract with dilute ammonium hydroxide and thereby precipitating manganese hydroxide in the aqueous phase.

Another diethyldithiocarbamate procedure [355] for the analysis of zirconium, Zircaloy–2, and zirconium–uranium alloys involves the precipitation of zirconium as the hydroxide and nickel as the dimethylglyoxime complex prior to the extraction. The sample, however, must contain over 20 ppm.

The extraction of the green pyridine–thiocyanate complex with chloroform from a fluoride solution containing citrate or tartrate is used by Chernikhov and Dobkina.[291]

For the analysis of zirconium, titanium, and their alloys containing over 50 ppm of copper, Wood and Clark [354] recommend the use of bis-

cyclohexanoneoxalyldihydrazone. The blue copper complex formed in a citrate or borate buffer solution at pH 9.0 is measured directly, without extraction, at 595 mμ. Large amounts of manganese, tin, chromium, iron, nickel, molybdenum, or vanadium do not interfere. A high salt concentration, however, inhibits the color development and limits the procedure to amounts of copper over 0.005 per cent.

The 2,9-dimethyl-1,10-phenanthroline (neo-cuproine) [356] procedure of Gahler [352] has been applied to the analysis of zirconium and Zircaloys.[357, 358] Goward and Wilson [357] produce and extract the neocuproine complex of Cu(I) at pH 4 to 6 in the presence of tartaric acid and hydroxylamine hydrochloride. Pollock, Read, Zopatti, and Read,[358] on the other hand, suggest that, in the presence of the large amounts of tin found in Zircaloy, the complex be formed at pH 1.0 before the extraction at pH 5.0 for more reproducible results. Under these conditions the reagent is specific for copper.[359]

Spectrophotometric Determination of Copper in Zirconium and Zircaloy—Neo-Cuproine. Procedure.[358] A 5- to 10-g sample is placed in a platinum dish containing 50 ml of sulfuric acid (1+4). Hydrofluoric acid, 48 per cent, is added dropwise until the zirconium dissolves. If the sample is Zircaloy, concentrated nitric acid is then added a few drops at a time, and the dish is warmed to dissolve the tin and copper. When the sample has dissolved completely, the solution is cooled, diluted to 100 ml, and quickly transferred to a polyethylene bottle.

An aliquot containing up to 150 μg of copper is transferred to a 100-ml beaker. The pH is adjusted to 1.0 with ammonium hydroxide (1+1) or hydrochloric acid (1+1). The following reagents are then added with stirring after each addition: 10 ml of hydroxylamine hydrochloride solution (20 g dissolved in 100 ml; solution prepared fresh daily); 10 ml of 30 per cent sodium citrate solution; and 10 ml of neo-cuproine solution (0.1 g of hemihydrate dissolved in 100 ml of 95 per cent ethyl alcohol). After 10 min the pH is adjusted to 5.0 with ammonium hydroxide (1+1), and the solution is transferred to a separatory funnel previously rinsed with 95 per cent ethyl alcohol. The solution is extracted for 45 sec with 10 ml of chloroform. The organic phase is filtered through a wad of dry filter paper placed in the cone of a small dry funnel into a dry 25-ml volumetric flask containing 4 ml of absolute ethyl alcohol. The extraction is repeated with 5 ml of chloroform, and the chloroform is transferred to the flask as before. The wad of filter paper is washed dropwise with 2 ml of chloroform and removed. The funnel is washed with 2 ml of absolute ethyl alcohol. The washings are added to the flask and the volume is adjusted with absolute ethyl alcohol.

The absorbance is measured at 457 mμ in 1-cm cells against water as the reference. The absorbance is corrected for a reagent blank treated in the same manner as the sample.

The standard curve is prepared by carrying from 0 to 200 μg of copper through the entire procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of copper in titanium have been described in the literature (see Refs. 227, 235, 239, 316, 354, 360, and 361).

(e) *In Niobium.* A procedure for the determination of copper in niobium has been described by Reed.[362]

11–2.13 Fluorine

(a) *In Uranium.* All procedures for the determination of traces of fluorine in uranium involve the prior separation of the fluorine. Four main separation techniques have been utilized. Steam distillation of fluosilicic acid formed by reaction of the fluoride with glass beads or powdered silica in acid solution is widely used.[363] Distillation of hydrogen fluoride from strong sulfuric acid solution in a platinum still swept out with nitrogen is satisfactory for small volumes of sample solutions.[363] Pyrohydrolysis with superheated steam at 700 to 900°C can be applied to uranium fluorides and metal.[363-366] Combustion of metal in a stream of oxygen in quartz followed by steam distillation is also reported.[302, 363]

Of the many methods available for the determination of fluoride after separation, only those that have been applied to the analysis of uranium materials are briefly mentioned here. Most of them have been described in Rodden [363] in detail. The fluoride can be titrated with thorium nitrate solution in the presence of sodium alizarin sulfonate or Chrome Azurol S indicator. The end point is the change from the color of the dye to the color of the thorium lake produced upon the addition of excess thorium. A potentiometric method involving the change in potential of an Fe(III)/(II)–gold electrode upon the addition of fluoride has been used. An amperometric procedure based on the precipitation of fluoride with thorium nitrate and the measurement of the catalytic nitrate reduction wave is described. Other amperometric procedures involve the reduction by fluoride of the catalytic wave of nitrate in the presence of uranium. Spectrophotometric methods depend on the bleaching effect of fluoride on the colored complexes of many metals, e.g., peroxytitanic acid, iron(III) salicylate, or zirconium–alizarin lake. A similar fluorometric method involves the quenching of the fluorescence given by the morin complex of aluminum. Even an enzymatic method has been used, the fluoride specifically inhibiting the activity of hog-liver esterase in hydrolyzing ethyl butyrate.

Recent investigations favor procedures involving the steam distillation of fluosilicic acid followed by spectrophotometric determination by the bleaching of the thorium–Chrome Azurol S [367] or the zirconium–Alizarin Red S lake,[368] or by titration of the distilled fluoride with thorium nitrate to a Chrome Azurol S end point.[369-371] For the distilla-

tion step the uranium may be dissolved in sulfuric acid by anodic oxidation,[368] in nitric acid,[371] or in perchloric acid plus hydrogen peroxide.[369, 370] Phosphoric acid has been recommended in the past.[302]

In the titration of fluoride with thorium nitrate, stoichiometric relations are not strictly followed. Accordingly, the thorium solution is standardized against sodium fluoride. Large amounts of aluminum or iron may interfere in the distillation by complexing the fluoride.[369] The procedure described below [370] was developed for uranium powder and oxide, but it is also applicable to turnings and massive metal.[369] The lower limit of determination is about 5 ppm.

Volumetric Determination of Fluoride in Uranium—Distillation. Special Apparatus. The steam distillation apparatus, similar to that shown in Fig. 4.9B in Chap. 4, "Beryllium," consists of a steam generator, a distilling flask, and a condenser. Connection between the steam generator and distilling flask can be of polyethylene tubing; standard-taper joints are used elsewhere.

Procedure.[370] The apparatus is assembled. In the distilling flask are placed 40 ml of 70 per cent perchloric acid, 10 ml of water, and a few silica chips. Steam is passed through the apparatus for 15 min with the distillation temperature held at 140°C. The distillate and contents of the distilling flask are discarded.

The apparatus is reassembled. A 100-ml cylinder receiver containing 3 ml of 4 per cent sodium hydroxide solution is placed under the condenser so that the condenser tip dips below the surface of the solution. To the distilling flask are added a 2-g sample of metal, 40 ml of 70 per cent perchloric acid, 10 ml of water, and 8 ml of 30 per cent hydrogen peroxide in the order given. The flask is warmed gently until dissolution is complete. The flask is heated and maintained at 140°C, and steam is passed through until 100 ml of distillate is collected. The distillate is transferred to a 200-ml cylinder, and 10 ml of 25 per cent (w/v) hydroxylamine hydrochloride solution is added. The solution is diluted to 150 ml and allowed to stand for at least 2 hr, preferably overnight, to destroy any peroxide.

A 50-ml aliquot in a 100-ml beaker is adjusted to pH 3.0 on a meter with perchloric acid and sodium hydroxide solution, and 1 ml of 0.02 per cent (w/v) Chrome Azurol S indicator solution and 0.5 ml of buffer solution (50 ml of 22.4 per cent monochloracetic acid neutralized to phenolphthalein with 20 per cent sodium hydroxide solution; an additional 50 ml of monochloracetic acid added to the neutral solution to give a pH of 3.0; solution diluted to 1 liter) are added.

A blank determination is carried out by adding the same volume of hydrogen peroxide as used for the sample to a 150-ml beaker, adding 1 ml of 4 per cent sodium hydroxide solution, evaporating the solution almost to dryness, and transferring the residue to the distillation flask. After the addition of 40 ml of 70 per cent perchloric acid, 100 ml of distillate is collected. Hydroxylamine hydrochloride solution is added, and the solution is treated exactly as described above.

The blank solution is transferred to a 100-ml Nessler tube and is titrated with a standard thorium nitrate solution (0.138 g of tetrahydrate

in 1 liter of solution) until the indicator changes to a red-purple color. The sample aliquot is titrated to the same color.

The thorium nitrate solution is standardized by adding 0, 5, 10, 20, 30, and 50 μg of fluorine to 150-ml beakers containing 1 ml of 4 per cent sodium hydroxide solution and 3.3 ml of hydroxylamine hydrochloride solution. Each solution is diluted to 50 ml, the pH is adjusted to 3.0, and 1 ml of indicator and 0.5 ml of buffer solution are added. The 0-μg standard is titrated. Then the other solutions are titrated to a color matching the 0-μg standard. The average fluoride equivalent of 1.0 ml of thorium nitrate solution is then calculated after suitable correction for the reagent blank is made.

(b) *In Thorium.* A separation of traces of fluoride by pyrohydrolysis at 700 to 800°C followed by titration of the fluoride with thorium nitrate solution and sodium alizarin sulfonate has been applied to thorium metal.[372] The techniques are discussed briefly under "Fluoride in Uranium." Pyrohydrolysis at 1000°C also has been used to separate fluoride from thorium oxide–uranium oxide slurries.[311] The separated fluoride is then determined spectrophotometrically by an indirect method in which thorium is added to the condensate to form the strong fluoride complex, and the excess thorium is measured as the 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (thorin) complex. Menis and coworkers [216] separate the fluoride by a similar fusion pyrolysis in the analysis of thorium oxide slurries. The sample is fused in a silica reaction tube with sodium metabismuthate under a stream of moist oxygen.[373] The fluoride is absorbed in a small volume of sodium hydroxide solution; thus the large volumes of condensate in the usual pyrohydrolysis technique are avoided. The fluoride is titrated with thorium nitrate solution.

The pyrohydrolysis–thorium nitrate titration procedure is identical to that described in detail in Chap. 4, Sec. 4–4.16(a).

(c) *In Zirconium.* Zirconium is analyzed for fluorine by a pyrohydrolysis–thorium nitrate titration procedure.[374] The pyrohydrolysis step is based upon the apparatus and technique of Warf, Cline, and Tevebaugh,[364, 365] while the titration procedure is essentially that of Armstrong.[375] Zircaloy is analyzed similarly.

Volumetric Determination of Fluorine in Zirconium and Zircaloy—Pyrohydrolysis. Special Apparatus. The apparatus shown in Fig. 4.8 of Chap. 4 is modified to permit oxygen to flow through the boiling water and through the system.

Procedure.[374] A weighed sample of zirconium in a platinum boat of 5 to 6 mil thickness is placed in the platinum reaction tube. The oxygen flow is regulated with a calibrated flow meter so that 150 to 200 ml of distillate is condensed in the receiver in 45 to 60 min of pyrohydrolysis. The end of the copper-jacketed platinum condenser is kept just above the surface of the distillate in the receiving dish. The furnace is kept at 700 to 900°C. A temperature of 1200°C and a bed of U_3O_8 in the boat are necessary for Zircaloy.

A 0.01 per cent (w/v) thorium nitrate solution is standardized against reference solutions containing from 1 to 25 μg of fluoride. Each solution is diluted to about 40 ml, the pH is adjusted to 3.0 with dilute acid or alkali, and the solution is transferred to a Nessler tube containing 0.25 ml of 0.01 per cent (w/v) sodium alizarin sulfonate solution. Each solution is titrated to the pink end point, and a calibration curve is plotted.

A 40-ml aliquot of the distillate is treated in the same manner. The color of the solution at the end point is matched with that of one of the titrated reference solutions. A reagent blank should be determined for the entire procedure.

11–2.14 Germanium

(a) *In Uranium.* The spectrograph is generally used to determine traces of germanium in uranium after an initial separation. Quantities down to 1 μg are separated from most other elements by distillation of the tetrachloride from a 5*N* hydrochloric acid solution of the sample followed by a hydrogen sulfide precipitation from 6*N* sulfuric acid with kieselguhr as a carrier.[376] Apparently no other procedures, such as those involving the heteropoly germanomolybdic acid or germanium molybdenum blue,[207] have been applied to the analysis of uranium.

(b) *In Zirconium.* Booth and Bakes[377] describe a procedure for the determination of traces of germanium in zirconium oxide based upon the study of Luke and Campbell.[378] Germanium chloride is extracted from a 8 to 9*M* hydrochloric acid solution of zirconium with carbon tetrachloride. After a back-extraction into an aqueous solution, the germanium is determined spectrophotometrically with 9-phenyl-2,3,7-trihydroxy-6-fluorone (phenylfluorone). The optimum range is 5 to 50 μg of germanium.

Although this procedure was developed for the analysis of zirconium oxide, presumably metal can be analyzed in a similar fashion. However, a study should be made of the possible loss of germanium either on converting the metal to oxide before dissolution or on dissolving directly in nitric–sulfuric–hydrofluoric acid mixture and taking to fumes.

Spectrophotometric Determination of Germanium in Zirconium Oxide—Carbon Tetrachloride Extraction, Phenylfluorone. Procedure.[377] A sample to provide about 30 to 40 μg of germanium in an aliquot of the final solution no greater than 10 ml is fused with potassium bisulfate in a platinum crucible. The cooled melt is extracted with hot water, and the solution is diluted to volume. An aliquot of 10 ml or less is transferred to a separatory funnel, and 2 ml of 50 per cent (v/v) sulfuric acid plus sufficient concentrated hydrochloric acid are added to make the solution 8 to 9*M* in hydrochloric acid.

The solution is extracted first with 20 ml of carbon tetrachloride, then with an additional 5 ml, transferring the organic phases to another

separatory funnel. The combined extract is washed with 2 ml of 80 per cent (v/v) hydrochloric acid. The organic phase is transferred to a third separatory funnel and back-washed with 10 ml of water. The aqueous phase is filtered into a 50-ml volumetric flask, and the following reagents are added in the order given: 1.5 ml of 50 per cent sulfuric acid; 10 ml of pH 5.0 buffer solution (225 g of sodium acetate trihydrate dissolved in 180 ml of warm water, 120 ml of glacial acetic acid added, solution cooled and diluted to 500 ml); 3 ml of gum acacia solution (0.5 g dissolved in 50 ml of hot water, solution filtered through Whatman No. 42 paper, prepared fresh daily); and 10 ml of phenylfluorone solution (0.05 g dissolved in 50 ml of methanol and 1 ml of concentrated hydrochloric acid, solution diluted to 500 ml with methanol, stable 1 month, polyethylene unsuitable for storage). The solution is mixed, allowed to stand for 5 min, then diluted to volume with 10 per cent (v/v) hydrochloric acid. The absorbance is measured at 510 mμ against water as a reference. The absorbance is corrected for a reagent blank.

The calibration curve is prepared by carrying 0, 20, and 50 μg of germanium through both the extraction and color-development steps. Correction should again be made for the reagent blank. [A standard germanium solution of 10 μg per milliliter is conveniently prepared by dissolving 0.144 g of the dioxide in 3 ml of 5 per cent (w/v) sodium hydroxide solution, adding 10 per cent (v/v) sulfuric acid solution until the solution is just acid, diluting to 1 liter, and diluting 10 ml of this stock solution to 100 ml.]

11–2.15 Gold in Uranium

The spectrograph has been relied on exclusively for the determination of traces of gold in uranium compounds either by direct examination or after a partial separation step.[347] Two separation procedures are useful. In one the gold and other elements are extracted from an acid solution with dithizone. In the other the uranium is removed by a hydroxide precipitation, and the gold and platinum in the filtrate are precipitated by stannous chloride with tellurium as a carrier.[347] For the analysis of uranium–gold alloys, a volumetric procedure is described [347] in which chlorauric acid is titrated with hydroquinone and *o*-tolidine or *o*-dianisidine as the indicator.

11–2.16 Hafnium

(a) *In Uranium.* Hafnium has been determined spectrographically in the cupferron group concentrate of samples high in zirconium.[379]

(b) *In Zirconium.* The determination of hafnium in zirconium is generally carried out spectrographically. However, X-ray fluorescence procedures are available [380, 381] with which the lower limit of determination appears to be about 0.016 per cent.

11–2.17 Iron

(a) *In Uranium.* Traces of iron in purified metal, compounds, and certain alloys are generally determined by direct spectrophotometric procedures. Occasionally a separation method is applied to remove interferences and to concentrate the iron before the determination by

such techniques as polarography or X-ray fluorometry. A group separation is sometimes made when it is desired to determine certain other metals along with the iron.

Many separation schemes applicable to the analysis of uranium have been discussed in Rodden.[334] The procedures suitable for the determination of traces of iron will be mentioned only briefly here. A cupferron extraction with diethyl ether, amyl acetate, or chloroform separates iron, copper, titanium, and other refractory elements from uranium.[334] If iron and copper both are to be determined in the extract, the optimum pH for extraction[351] is 1.5. Both the separation and determination of iron can be made[334] with 8-quinolinol (oxine) at pH 2.0. Vanadium interferes, and some loss of iron occurs. Uranium has been precipitated as the peroxide prior to spectrophotometric determination of the iron to remove the background color of the uranyl ion.[382] Electrolysis of iron and other metals with a mercury cathode with subsequent volatilization of the mercury has been used to determine iron spectrophotometrically.[281-283, 334] This technique, discussed briefly in Sec. 11–2.7(a), "Cadmium in Uranium," is lengthy and hazardous. An ion-exchange–polarographic procedure is reported by Horton and Thomason[383] for the determination of iron in homogeneous reactor fuel solutions containing large amounts of copper, chromium, nickel, and cobalt. Copper is first plated out on a cadmium coil. In 0.3*M* sulfuric acid uranium and other elements are retained on a column of anion resin Dowex-1. Iron(III) in the effluent is determined in 0.5*M* sodium citrate by measuring the reduction wave with a half-wave potential at −0.15 volt vs. a saturated calomel electrode. The extraction of iron (Fe^{59}) from 10*M* nitric acid solutions of homogeneous reactor fuel by 2-thenoyltrifluoroacetone (TTA)-xylene is fairly selective.[384] The yields average 70 to 80 per cent. Zirconium also extracts if present. The extraction of uranium with tributyl phosphate (TBP) from 6*N* nitric acid prior to X-ray fluorometric determination of iron is satisfactory[327] for amounts greater than 100 μg. Chromium, nickel, and zirconium can be determined similarly.

Most available chromogenic reagents for the determination of iron[207, 385] have been applied to the spectrophotometric determination of traces in uranium without previous separation. The ferrous iron reagents are generally preferred because ferric iron complexing anions such as oxalate, fluoride, or phosphate generally do not interfere. The most commonly used reagent, 1,10-phenanthroline,[207, 334, 386] is favored because of the stability and sensitivity of the colored complex and the relative freedom of the color reaction from interferences. Procedures that utilize the similar 2,2′-bipyridine and dimethylglyoxime have been described.[334]

The ferric iron reagents 1,2-dihydroxybenzene sulfonic acid (tiron), salicylic acid, thiocyanate, and 8-quinolinol (oxine) are used only infrequently.[334] The mixed ferrous–ferric iron reagent, thioglycolic acid, is preferred by some [387, 388] since no provision need be made to obtain a single valence state. In the absence of cobalt, which interferes seriously, procedures with this reagent are rapid. Uranium, which also reacts with the reagent, must be complexed with carbonate. Thioglycolic acid is also recommended for the iron determination after a separation of copper and iron cupferrates from uranium solutions.[351]

The general use of 1,10-phenanthroline is covered thoroughly by Sandell [207] and Rodden.[334] Only a few pertinent remarks need be made here. In addition to colored ions, other elements can interfere if present in more than trace amounts. Silver and bismuth give precipitates. Zinc, cadmium, and mercury(II) depress the color due to iron, but this effect can be diminished by the use of an excess of reagent. Mercury (I) and (II), beryllium, tungsten, molybdenum, titanium, tin (II) and (IV), and other elements can interfere in one way or another. Control of pH in some instances prevents these interferences. For example, molybdenum does little harm over pH 5.5. Copper, cobalt, and nickel give fairly sensitive colored complexes. Citrate in large quantities interferes if it is introduced before the reduction of the iron. Moderate amounts of tartrate can be tolerated. Oxalate and pyrophosphate interfere below pH 6. Fluoride does not interfere above pH 4. Perchlorate is apt to interfere by precipitation of 1,10-phenanthroline perchlorate. The quantitative effects of many cations and anions are listed in Rodden.[334]

Iron(III) is reduced by hydroxylamine or hydroquinone. However, in the presence of citrate, hydroquinone must be used.[207]

In the analysis of essentially pure uranium metal and compounds, generally no provisions must be made for the interferences mentioned above. The background color due to colored impurities and uranium is eliminated by measuring the iron complex color against a sample solution as a reference. The optimum pH for color development appears [302] to be about 3.0. Above pH 3 the absorbance of uranium becomes appreciable; above pH 4 the uranium precipitates. In the analysis of uranium–molybdenum alloys with the molybdenum content up to 20 per cent, the pH must be 6.0 to 6.5 in the presence of tartrate to reduce the interference of molybdenum.[389, 390] Color formation in the presence of uranium is usually complete within a few minutes at room temperature. However, with some samples it has been found necessary to warm the solution and allow it to stand for 10 to 30 min for full color development. This treatment perhaps should be made routine.

Spectrophotometric Determination of Iron in Uranium—1,10-Phenanthroline. Procedure.[203] A 1- to 2-g sample (previously cleaned in warm 6*N* nitric acid, rinsed in water and acetone, and dried) is dissolved in a minimum amount of 6*N* nitric acid. When dissolution has been completed, 5 ml of concentrated hydrochloric acid is added, and the solution is evaporated to near dryness on a steam bath.

The residue is dissolved in about 20 ml of water, and 10 ml of 10 per cent (w/v) hydroxylamine hydrochloride solution is added. After 10 min, 10 ml of 0.1 per cent 1,10-phenanthroline solution is added. The pH is adjusted with a pH meter to between 2.5 and 3.0 with dilute ammonium hydroxide. The solution is then diluted to 50 ml.

The absorbance is measured at 515 mμ in 2-cm cells against a reference composed of a similar sample solution carried through the same procedure except that the 1,10-phenanthroline is omitted. The absorbance must be corrected for a reagent blank. The standard curve is prepared by carrying 0 to 20 μg of iron through the procedure. The absorbance of each standard is measured against the 0-μg standard.

(b) *In Thorium.* Iron can be determined spectrophotometrically with thiocyanate.[214] Boric acid ties up the fluoride used in the sample dissolution. Ethyleneglycol monobutyl ether has been used to stabilize the color.[391]

The color of ferric ion in hydrochloric acid has been utilized to determine iron directly down to 0.002 per cent.[392] It is stated that other impurities usually present in thorium metal do not interfere.

The ferrous reagents, 2,2′-bipyridine[216] and 1,10-phenanthroline (see Refs. 214, 311, 330, 393, and 394), remain the most satisfactory. Procedures with and without the addition of a complexing agent for thorium are described. With citrate or tartrate present, the pH is adjusted to either 3.5 (Refs. 214 and 330) or 5 (Ref. 214). In the analysis of thorium oxide–uranium oxide slurries, a pH range of 5 to 7 has been used with citrate present.[311] Color formation is slow; standing periods of 1 and 24 hr are recommended.[214, 330] In the absence of citrate, a pH of about 2.5 is used.[214, 263] Color development is rapid and is generally complete within a few minutes. More accurate and more reproducible results are obtained at this pH if any fluoride, used in the sample dissolution, is fumed off with perchloric acid prior to color development.[263]

A typical procedure[263] is identical to that described above for "Iron in Uranium" with minor exceptions. The pH is adjusted to 2.5. The absorbance can be measured against a reagent blank as the reference solution. The sample solution is prepared differently. Thorium metal is dissolved in either hydrochloric acid (1+1) or nitric acid (1+1) containing a trace of fluoride ion. When dissolution has been completed, 5 ml of 70 per cent perchloric acid is added. The solution is evaporated and fumed strongly for 5 to 10 min, cooled, and diluted to about 25 ml for the color development as described.

(c) *In Zirconium.* The spectrophotometric determination of iron in zirconium with 1,2-dihydroxybenzene-3,5-disulfonic acid (tiron)[395] is described by Beaumont.[396] The blue complex formed at pH 4.7 with Fe(III) is only a quarter as sensitive as that produced with 1,10-phenanthroline, but both iron and titanium can be determined with the same solution.

The yellow color of Fe(III) in 6*M* hydrochloric acid is utilized by Silverman and Trego[397] to determine down to 20 ppm of iron in 1-g samples of zirconium. Smaller amounts, down to 4 ppm, can be determined by a crystallization separation of most of the zirconium in 5- to 10-g samples from 9*M* hydrochloric acid in which the hydrated zirconyl chloride is fairly insoluble. Although many elements would be expected to interfere, only the necessary removal of copper and tin is mentioned.

Thiocyanate[288, 291] and sulfosalicylic acid[291, 385] have been used. The latter reagent is recommended for the analysis of zinc–zirconium alloys by Ayers and Banks,[385] who studied the application of both salicylic acid and 1,10-phenanthroline to the analysis of zirconium and zinc–zirconium alloys.

Zirconium and Zircaloys are best analyzed for iron with 1,10-phenanthroline. Several procedures exist,[288, 331] each differing in the pH and other conditions for maximum color development. Since hydrofluoric acid is necessary for dissolution, the fluoride is either complexed with boric acid[288] or fumed off.[288, 331] The former technique generally gives a smaller blank, although the use of sulfuric acid assists in dissolving Zircaloys. A pH of 3.5 to 7 can be used.[288] Citrate or tartrate complexes the zirconium. If the sample size is small, less than 100 mg, a complexing agent is unnecessary; the pH is raised after the iron reduction just to the point of precipitation, and the solution is cleared with acetic acid.[288]

Color formation in the presence of citrate or tartrate is slow. Standing periods of from 30 to 120 min at room temperature before making the optical measurements are recommended.[288] A standing period of 30 min at 60 to 70°C is stated to be necessary for full color development.[331] This precaution is also used at the New Brunswick Laboratory.

Spectrophotometric Determination of Iron in Zirconium and Zircaloy—1,10-Phenanthroline. Procedure.[288, 331] A 1-g sample is covered with water in a platinum dish, and 2 ml of 48 per cent hydrofluoric acid is added dropwise. When the reaction subsides, 5 ml of concentrated sulfuric acid is added. When dissolution appears to be complete, the solution is evaporated to fumes and carefully fumed for a few minutes. The dish is washed with about 50 ml of water, and the solution is again evaporated to fumes. The solution is diluted to about 50 ml.

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To the solution are added 5.0 ml of 50 per cent (w/v) tartaric acid solution, 1 ml of 10 per cent (w/v) hydroxylamine hydrochloride solution, and 5.0 ml of 0.2 per cent 1,10-phenanthroline solution. The pH is adjusted between 5.5 and 6.0 with dilute ammonium hydroxide. The solution is transferred to a 100-ml volumetric flask and diluted to volume. The flask is placed in a water bath at 60 to 70°C for 30 min. The solution is cooled. The absorbance is measured at 508 mμ in 1-cm cells against water as a reference. The absorbance is corrected for a reagent blank. The standard curve is prepared by carrying 0 to 500 μg of iron through the procedure beginning with the addition of the tartaric acid. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of iron in titanium have been described (see Refs. 226, 227, 231–235, 294, 315, 316, 333, and 398–405).

(e) *In Niobium.* Procedures for the determination of iron in niobium have been described.[390, 406–408]

11–2.18 Lead

(a) *In Uranium.* Traces of lead in uranium can be determined polarographically after separation of the lead and other impurities either by a mercury cathode electrolysis and subsequent volatilization of the mercury [281–283, 376] or by an exhaustive dithizone extraction at pH 7.5 and 9.0 followed by destruction of the dithizone.[284] Both procedures are discussed briefly in Sec. 11–2.7(a). The preferred dithizone extraction–polarographic procedure is described in Chap. 4, "Beryllium," Sec. 4–4.11.

Spectrophotometric procedures utilize dithizone.[376, 409, 410]

In the dithizone–chloroform extraction of an ammoniacal solution containing citrate and cyanide, only tin(II), thallium(I), and bismuth extract to any extent along with lead. In the analysis of uranium, steps are generally taken to prevent the interference of bismuth. Provision is sometimes made to avoid the possible interference of thallium(I), although often it is ignored because it is seldom present in significant amounts and its extraction is hindered by citrate.[207] Tin(II) is oxidized during sample dissolution. Copper and iron in large amounts may cause difficulty by oxidizing dithizone,[207] but this effect is prevented by the customary addition of hydroxylamine hydrochloride before extraction.[207, 376, 409]

Bismuth can be removed by washing the dithizone–chloroform extract with an ammonium hydroxide–cyanide solution.[409] Thallium, if present, is removed by a second wash of the extract with dilute potassium cyanide solution.[207, 409]

In another procedure,[376] described in detail below, the interferences are eliminated by a double-extraction technique.[411] The extract made from an alkaline solution containing citrate, cyanide, and hydroxyla-

mine is washed with dilute nitric acid, which removes the lead. The wash is adjusted to pH 2.0, and any traces of bismuth that survived the washing step are extracted with dithizone. After the addition of ammonium hydroxide, cyanide, and hydroxylamine, the lead is finally re-extracted for the optical measurement.

Spectrophotometric Determination of Lead in Uranium—Dithizone. Special Reagents. Ammonium Citrate Solution, 40 Per Cent. A solution of 40 g dissolved in 100 ml of water is purified by adjusting the pH to about 8.5 with ammonium hydroxide and extracting with 0.001 per cent dithizone in chloroform until the extracts are green. The solution is washed with chloroform to remove residual dithizone.

Hydroxylamine Hydrochloride Solution, 20 Per Cent. About 65 ml of solution containing 20 g of salt is adjusted to pH 9.0, and a slight excess of 4 per cent sodium diethyldithiocarbamate solution is added over that required to react with lead and other metals present. The solution is extracted with chloroform until the extract no longer turns yellow when shaken with a dilute copper solution. The volume is then adjusted to 100 ml.

Sodium Cyanide, 10 Per Cent. A saturated solution containing about 50 g in 100 ml of solution is extracted with 0.001 per cent dithizone in chloroform until the extracts are green. The solution is washed thoroughly with chloroform and diluted so that 100 ml of solution contains 10 g.

Procedure.[376] A 1-g sample of uranium is dissolved in a minimum of nitric acid (1+1). The solution is heated to remove oxides of nitrogen and then is cooled, and 3 ml of ammonium citrate solution is added. The pH is adjusted to 8.5 to 9.0, and the solution is transferred to a separatory funnel. To the solution are added 0.5 ml of hydroxylamine hydrochloride solution and 1 ml of sodium cyanide solution. The solution is extracted with 5-ml portions of 0.001 per cent dithizone in chloroform until the last portion is distinctly green. If more than three portions are necessary, the quantity of reagents used hereafter should be doubled. The combined extracts are collected in another separatory funnel and back-extracted with 20 ml of 1 per cent (v/v) nitric acid. The chloroform phase is discarded.

The aqueous phase is adjusted to pH 2.0 with dilute ammonium hydroxide, and the solution is extracted with 5-ml portions of 0.001 per cent dithizone until the extract is green. The aqueous phase is washed with 5-ml portions of chloroform until the wash is colorless. The organic phases are discarded. To the solution are added 4 ml of ammonium hydroxide–cyanide solution (75 ml of concentrated ammonium hydroxide plus 100 ml of 10 per cent purified sodium cyanide diluted to 500 ml) and 2 drops of hydroxylamine hydrochloride solution. The solution is then extracted with 10.0 ml of 0.001 per cent dithizone. The dithizone–chloroform solution is separated, and the absorbance in 1- or 5-cm cells is measured at 510 mμ against chloroform as a reference. The absorbance must be corrected for a reagent blank carried through the procedure.

The standard curve is prepared by adding 0 to 50 μg of lead to 20 ml of 1 per cent nitric acid, adding 4 ml of the ammonium hydroxide–cyanide solution and 2 drops of hydroxylamine hydrochloride solution,

and extracting with dithizone. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(b) *In Thorium.* Although the dithizone extraction procedures discussed above under "Lead in Uranium" undoubtedly can be applied to the analysis of thorium, polarographic procedures alone have been described.

The dithizone extraction–polarographic procedure, mentioned in Sec. 11–2.7(a), "Cadmium in Uranium," and described in detail in Chap. 4, Sec. 4–4.11, is satisfactory for the determination of traces of lead.[284] Thorium is dissolved in nitric acid containing a trace of fluoride and is complexed by citrate or tartrate for the exhaustive dithizone extractions at pH 7.5 and 9.0. Lead in the dithizone extract is determined polarographically in a 0.1N potassium chloride supporting electrolyte. A similar procedure [412] involves an extraction at pH 9.5, a re-extraction of the lead from the chloroform extract with 0.5N hydrochloric acid, and a supporting electrolyte 0.1N in ammonium acetate and 0.025N in potassium thiocyanate. The half-wave potential of lead in this medium is -0.5 volt vs. a saturated calomel electrode.

(c) *In Zirconium.* A direct polarographic procedure [251] is available for the analysis of zirconium metal. However, because of the frequent interferences encountered and the relative insensitivity inherent in this type of procedure, the dithizone extraction–polarographic procedure [284] described in detail in Chap. 4, Sec. 4–4.11, is preferred. Both methods are discussed briefly in Sec. 11–2.7(c).

A dithizone spectrophotometric procedure,[288, 413] satisfactory for the analysis of both zirconium and Zircaloys, is given below.

Spectrophotometric Determination of Lead in Zirconium and Zircaloy—Dithizone. Special Reagents. Ion-exchange Water. Distilled water is passed through a column of Rohm & Haas MB–1 ion-exchange resin. This water is used in all solutions.

Buffer Solution, pH 3.4. To 9.1 ml of concentrated nitric acid diluted to about 500 ml is added dilute ammonium hydroxide to pH 3.4. To the solution are added 2.042 g of potassium acid phthalate and 19.9 ml of 0.1N hydrochloric acid.

Procedure.[413] A 1-g sample suspended in about 10 ml of water in a platinum beaker is dissolved by the dropwise addition of 48 per cent hydrofluoric acid. When dissolution has been completed, 10 ml of concentrated sulfuric acid and 5 ml of nitric acid (1+1) are added, and the solution is evaporated to fumes. When the solution has cooled, it is diluted to 100 ml.

A 10-ml aliquot is diluted to about 40 ml in a platinum dish, and 10 ml of 40 per cent ammonium citrate solution [40 per cent (w/v) solution previously extracted with successive portions of 0.0015 per cent dithizone in chloroform until the last portion remains green, then washed with chloroform until the washings are colorless] is added. Ammonium

hydroxide (solution prepared by passing tank ammonia through ice-cooled water until a specific gravity of 0.92 is obtained) is added until the solution is alkaline. Then 5 ml of 10 per cent potassium cyanide solution (sulfide free) and 1 ml of 20 per cent hydroxylamine hydrochloride solution are added, and the pH is adjusted to 9.0 to 9.5 with 10 per cent sodium hydroxide solution.

The solution is transferred to a 250-ml separatory funnel and extracted with 5-ml portions of 0.001 per cent dithizone in chloroform. When the last portion of dithizone solution remains green, the combined extracts in another separatory funnel are washed with 50 ml of pH 3.4 buffer solution. The chloroform phase is discarded.

To the aqueous phase is added 7 ml of ammonium hydroxide–cyanide solution (20 g of sulfide-free potassium cyanide dissolved in 150 ml of concentrated ammonium hydroxide; solution diluted to 1 liter, extracted with portions of dithizone solution until the last portion is green, then washed with chloroform until washings are colorless). The solution is now extracted with 5-ml portions of dithizone solution until the color of the last portion remains green. The same volume of dithizone solution must be used for both sample and standard solutions. For 5 to 50 μg of lead, 15 ml is adequate. The extracts are diluted to 50 ml with chloroform in a volumetric flask. If water appears to be present, the solution is filtered through a dry filter paper (previously rendered lead free by washing with dilute nitric acid and water, and dried in an oven at low heat). The absorbance is measured immediately at 510 mμ in covered 1-cm cells against chloroform. The absorbance is corrected for a reagent blank carried through the procedure.

The standard curve is prepared by adding 0 to 50 μg of lead to platinum beakers, diluting to 40 ml, and continuing with the extraction procedure as described above. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* A procedure for the determination of lead in titanium has been described by Chernikhov and Dobkina.[316]

(e) *In Niobium.* A procedure for the determination of lead in niobium has been described by Nazarenko and Biryuk.[252]

11–2.19 Magnesium

(a) *In Uranium.* All procedures available for the determination of magnesium involve the prior separation of the uranium and many other elements by various means. Ammonium hydroxide precipitation in the presence of an ammonium salt is used, but it is said to occlude much magnesium.[247] A double precipitation is recommended.[247, 302] A thorough washing of the precipitate minimizes the loss.[247] Others recommend that a correction factor of 1.12 be applied.[414] A single 8-hydroxyquinoline (oxine) precipitation at pH 5 has been used.[415] The uranium can also be removed by a peroxide precipitation or by an ether extraction.[247] In these latter two separation procedures, the magnesium is further separated by conventional sulfide, ammonium hydroxide, and oxalate precipitations.

Fairly large quantities of magnesium can be determined gravimetrically or volumetrically.[247] After a double ammonium hydroxide precipitation and an oxine precipitation at pH 3 to 3.8, a final oxine precipitation from ammoniacal solution is made. The magnesium oxinate is weighed after drying for 3 hr at 135°C. In another procedure the oxinate is titrated in the usual manner. Precipitation as the phosphate has also been used after removal of the uranium, the silica, the hydrogen sulfide and ammonium hydroxide groups, and calcium with oxalate.[247]

Similar separation procedures are utilized for the spectrophotometric determination of traces of magnesium. Titan yellow, methylbenzothiazole(1,3)-4,4′-diazoaminobenzene-(2,2′)-disulfonic acid, which gives a red lake with magnesium precipitated with sodium hydroxide,[207, 247] has been applied after removal of the uranium and other metals by a single ammonium hydroxide precipitation in the presence of ammonium ion. Aluminum, arsenic, beryllium, bismuth, cadmium, cobalt, copper, lanthanum, manganese, nickel, tin, and zinc may interfere. Calcium ion intensifies the color of the lake. Titan yellow has been shown to be superior to Magneson II, 3-hydroxy-1-*p*-nitrophenyl-3-phenyltriazine, in regard to sensitivity and conformity to Beer's law.[414] Chlorazol Brilliant Yellow 3 G.S. has been used after an ether extraction, a double ammonium hydroxide precipitation, and a precipitation of other interfering elements with diethyldithiocarbamate.[416]

These procedures that depend upon lake formation suffer greatly from factors of dye variability, rapid fading of the color, and interference from many metals. A procedure involving the formation of a complex of magnesium with Eriochrome Black T, 1-(1-hydroxy-2-naphthylazo)-2-hydroxy-5-nitro-4-naphthalene sulfonic acid, overcomes these difficulties. The very slightly dissociated, soluble, intensely red complex is formed in the pH range of 7 to 10.[417, 418] Uranium, which also reacts with the reagent to give a colored product, is separated without loss of magnesium by an oxine precipitation at pH 5. The residual uranium and other metal oxinates are extracted with chloroform. The pH is then adjusted to 10.1, and the complex with Eriochrome Black T is formed. The effect of calcium, which interferes at pH 10.1, can be overcome by developing the color at pH 7 to 8, but the sensitivity for magnesium is thereby reduced materially. Iron(III), chromium(III), cobalt, aluminum, nickel, and molybdate, commonly found in uranium materials, do not interfere.[415]

Spectrophotometric Determination of Magnesium in Uranium—Eriochrome Black T. Procedure.[415] A solution containing at least 5 μg of magnesium in a volume of 20 ml or less is placed in a quartz beaker.

The excess acid is neutralized, and the volume is adjusted to about 25 ml. To the solution is added 5 ml of acetate buffer solution [380 ml of 50 per cent (w/v) sodium acetate and 10 ml concentrated hydrochloric acid diluted to 1 liter]. The solution is warmed to 60 to 70°C, and a sufficient quantity of a 10 per cent solution of oxine in acetone is added to precipitate the uranium and attending impurities. The solution is kept warm and is stirred for 3 to 5 min, then it is filtered. The precipitate is washed with warm water, and the filtrate and washings are collected in a separatory funnel. The solution is extracted with five 10-ml portions of chloroform. The aqueous phase is filtered to remove droplets of chloroform.

The pH of the solution or an aliquot of the solution is adjusted to a value between 9.8 and 10.6 with ammonium hydroxide. The solution is placed in a 50-ml volumetric flask, and 1.0 ml of 0.1 per cent (w/v) Eriochrome Black T in methanol is added. The solution is diluted to volume with water and mixed. The absorbance is measured in 1- to 5-cm cells at 520 mμ against a water reference. The absorbance must be corrected for a reagent blank carried through the procedure.

The calibration curve is prepared by diluting standard solutions containing from 0 to 30 μg of magnesium to about 30 ml, adjusting the pH to within ±0.1 pH unit of the previous value used, transferring the solutions to 50-ml volumetric flasks, adding 1.0 ml of the dye, diluting to volume, and measuring the absorbance of each standard against the 0-μg standard.

(b) *In Thorium.* Magnesium has been determined spectrophotometrically with Eriochrome Black T.[216] Thorium, which also forms a colored complex with the reagent, must be removed by extraction with 2-thenoyltrifluoroacetone (TTA) in chloroform at pH 1.7. The pH is then adjusted to 10 for color development; the absorbance is measured at 520 mμ. Calcium interferes and must be determined in some other manner, e.g., flame photometrically, so that a correction can be applied.

Magnesium and calcium have been determined[292] also by a conventional ethylenediaminetetraacetic acid (EDTA) titration after removal of the thorium by a homogeneous precipitation with urea in the presence of formate.[419]

(c) *In Zirconium.* For the determination of greater than 50 ppm of magnesium in sponge metal, the zirconium can be volatilized as the tetrachloride as described in Sec. 11–1.10(d), followed by further removal of impurities by a double ammonium hydroxide precipitation.[223] The magnesium is finally determined gravimetrically with 8-hydroxyquinoline (oxine). Although this procedure is apparently satisfactory for sponge, which contains up to 1000 ppm of magnesium, it is inapplicable to arc-melted zirconium and Zircaloy, which generally contain less than 50 ppm. Another procedure applicable only to sponge metal involves the precipitation of the zirconium as the normal selenite. After removal of the iron, calcium, etc., by the usual

hydroxide and oxalate precipitations, the magnesium is precipitated with oxine and determined volumetrically.[293]

More satisfactory procedures involve an ion-exchange separation of the zirconium as fluozirconate on a column of strong-base anion resin.[224] For sponge metal a mercury-cathode electrolysis is used to remove the iron, and the magnesium is determined flame photometrically at 382 mμ with an oxyhydrogen flame.[420] For arc-melted metal and Zircaloy,[421] the mercury-cathode electrolysis must also be used for the removal of iron, tin, chromium, nickel, and other elements, followed by an 8-hydroxyquinoline (oxine) extraction at pH 4.5 to 5.0 to remove residual iron, zirconium, copper, and aluminum. Magnesium is then extracted at pH 10.0 to 10.2 with chloroform in the presence of 2-*n*-butoxyethanol (butyl cellosolve), added to assist the extraction of the magnesium oxinate.[422] The oxinate is measured spectrophotometrically. This lengthy but versatile procedure, suitable for the determination of 5 to 100 ppm on a 1-g sample basis, is described below.

Spectrophotometric Determination of Magnesium in Zirconium and Zircaloy—Ion Exchange, Mercury Cathode, Oxine Separation, Oxine. Special Apparatus. The tubing for the resin column is polyethylene, 1 in. in inside diameter by 26 in. long.

Special Reagents. All water used, except where noted, is distilled water passed through an Amberlite MB–1 mixed-bed ion-exchange resin column and stored in polyethylene.

Procedure.[421] About 70 g of Dowex–1, 200 to 400 mesh, 8 per cent cross linked, in the chloride form, is washed in a polyethylene bottle with several portions of 3*N* hydrochloric acid. The resin is transferred to the column, which is fitted with a cotton plug, and is washed with 200 ml of 3*N* hydrochloric acid and then with distilled water until only a faint turbidity persists on the addition of 5 per cent silver nitrate solution. The column is then washed with 200 ml of ion-exchange water and 100 ml of elutriant (594 ml of 48 per cent hydrofluoric acid plus 396 ml of 3*N* hydrochloric acid diluted to 18.8 liters; stored in polyethylene).

A 5-g sample is placed in a platinum beaker containing about 50 ml of water and is dissolved by the careful addition of 15 ml of 48 per cent hydrofluoric acid. When dissolution has been completed, 30 ml of 1*N* hydrochloric acid is added, and the solution is transferred to a 500-ml polyethylene cylinder and diluted to volume. A 100-ml aliquot is passed through the resin column at a flow rate of 3 to 5 ml per minute. The solution is collected in a platinum beaker. Three portions of elutriant with a total volume of 100 ml are passed through the column.

To the combined effluent is added 6 ml of concentrated sulfuric acid, and the solution is evaporated to about 3 ml. The lid and sides of the beaker are rinsed down, and the solution is taken to fumes. This step is repeated. The solution is cooled, diluted to 30 ml, and warmed until the salts are all in solution. The solution is transferred to a mercury-cathode electrolysis cell and is electrolyzed at 8 to 10 amp for 90 min. During the electrolysis the sides and cover of the cell are rinsed every 20 min.

The solution is drained into a 400-ml beaker and evaporated to dryness. The residue is taken up in 3 to 5 drops of concentrated nitric acid, and the solution is transferred to a 100-ml beaker. The solution is evaporated to dryness, and the residue is taken up in 5 ml of 1*N* hydrochloric acid. The solution is transferred to a 125-ml separatory funnel with about 25 ml of water. To the funnel are added 5 ml of sodium acetate buffer solution (40 g of sodium acetate trihydrate dissolved in 100 ml; solution stored in polyethylene) and 10.0 ml of 3 per cent oxine solution (15 g in 500 ml of chloroform), and the mixture is shaken for 30 min. The chloroform phase is discarded. The extraction is carried out three more times.

To the aqueous phase is added 2.0 ml of butyl cellosolve solution [50 per cent (v/v) aqueous solution], and the pH is adjusted to 10.0 to 10.2 by the addition of 6 ml of ammonia buffer (30 g of ammonium chloride dissolved in 200 ml of water plus 500 ml of concentrated ammonium hydroxide; solution diluted to 1 liter and stored in polyethylene). The solution is equilibrated for 1 min with 20.0 ml of 3 per cent oxine solution. The organic phase is drained into a dry stoppered flask, and 5 ml of 95 per cent ethanol is added. After the solution has been kept for 30 min in a water bath at 30±2°C, the absorbance at 378 mμ in 2-cm cells is measured against chloroform. The absorbance is corrected for a reagent blank carried through the entire process except the ion-exchange step.

The calibration curve is prepared by adding 0 to 10 ml of a standard magnesium solution containing 10 μg per milliliter to a 125-ml separatory funnel, 5 ml of 1*N* hydrochloric acid, and 5 ml of sodium acetate buffer solution, adjusting the volume to about 35 ml, and extracting at this pH of 4.5 to 5.0 with 10.0 ml of the 3 per cent oxine solution. The butyl cellosolve is then added, the pH is adjusted to 10.0 to 10.2, the final extraction is made with 20.0 ml of the oxine solution, and the absorbance measurements in the presence of ethanol are made as described above. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of magnesium in titanium have been described in the literature (see Refs. 227, 229–231, 235, 278, 294, 315, 321, 402, and 423–430).

11–2.20 Manganese

(a) *In Uranium.* An ion-exchange–polarographic procedure has been reported.[280] A solution of uranyl nitrate is added to a column of cation resin, Amberlite IR–120. The uranium and any iron and copper are eluted with 0.5*N* oxalic acid. The manganese, cadmium, cobalt, and nickel are then eluted with 1*N* hydrochloric acid. The manganese is determined polarographically in a 6*M* calcium chloride supporting electrolyte.

Conventional volumetric procedures have been used. In one [431] the Mn(II) is oxidized to permanganate with persulfate and silver-ion catalyst, and the permanganate is titrated with arsenite. In another procedure [432] the manganese, iron, and nickel are separated by precipi-

tation with sodium carbonate after removal of the silica and acid-insoluble sulfides by the usual methods. The Mn(II) is then oxidized by bismuthate, and the permanganate is titrated with ferrous ion. These volumetric procedures are only applicable to amounts of manganese over 50 ppm even when samples as large as 5 g are used.

The most useful procedures are all based upon the spectrophotometric determination of the permanganic acid obtained by oxidation of the Mn(II). The recommended oxidant is metaperiodate, although persulfate with silver-ion catalyst has been used.[431] Few substances interfere.[207] Traces of chloride are oxidized by the excess periodate and thus are rendered innocuous. Larger amounts that may survive the oxidation step and subsequently reduce the Mn(VII) must be removed by a preliminary evaporation step with nitric and sulfuric acids. This treatment also removes other interfering reducing agents such as iron(II), sulfite, and nitrite. Moderate amounts of colored ions such as cobalt, copper, and nickel can interfere. Uranium (VI) also absorbs slightly at the absorption maximum of the permanganate ion at 525 mμ. The effect of these colored ions can be eliminated by correcting the absorbance of the sample solution for the absorbance of either an unoxidized sample solution or an oxidized solution decolorized by a reducing agent such as hydrogen peroxide, nitrite, or sodium azide. The addition of phosphoric acid is helpful in decolorizing Fe(III) and preventing the precipitation of Fe(III) periodate.

The separation of manganese by extraction with diethyldithiocarbamate–chloroform at pH 8.2 to 8.6 prior to the oxidation step is also used.[351, 433] Platinum gauze assists the oxidation with periodate. The results with this separation–oxidation procedure may be 10 to 15 per cent low in the 1- to 25-ppm range.

Spectrophotometric Determination of Manganese in Uranium—Direct Periodate Oxidation. Procedure.[263] A 2- to 5-g sample is dissolved in 25 ml of concentrated nitric acid, and the solution is boiled for a few minutes in a covered beaker. The beaker cover and sides are washed down, and 5 ml of 85 per cent phosphoric acid and some glass beads are added. The solution is again brought to a boil. To the solution is added 0.5 g of solid potassium periodate. Boiling is continued, with occasional stirring, until the periodate is completely dissolved. The solution is placed on a steam bath for 15 min to develop the color completely. The solution is cooled and diluted to 50 ml. The absorbance is measured at 525 mμ in 5- or 10-cm cells against an identical sample solution carried through the procedure but with the periodate omitted. The absorbance is corrected for a reagent blank measured against all the reagents except the periodate.

The standard curve is prepared by adding 0 to 100 μg of Mn(II) to a nitric–phosphoric acid solution of low-manganese uranium dissolved as

above and containing the same weight of uranium. The absorbance of each standard after oxidation is measured against the 0-μg standard as the reference.

For the analysis of less than 10 ppm of manganese, a slightly modified procedure gives more reproducible results. After the sample solution has been oxidized and diluted quickly to volume, it is again placed on the steam bath until it is hot. The absorbance of the hot solution is measured quickly against water. A few drops of dilute hydrogen peroxide (1 ml of 30 per cent solution diluted to 100 ml) are then quickly added to the cell, the solution is mixed, and the absorbance is again measured immediately. The absorbance of the decolorized solution is subtracted from the sample absorbance. Correction for a reagent blank is also made. The standard curve is prepared in the same way with 0 to 10 μg of manganese added to low-manganese uranium solutions. Each standard is corrected for the absorbance of the decolorized solution and for the absorbance of the 0-μg standard.

(b) *In Thorium.* Spectrophotometric procedures based upon the oxidation of Mn(II) to permanganic acid by either persulfate [214] or periodate [214, 434] are available. The periodate procedures resemble that described above under "Manganese in Uranium" with a few exceptions. The sample dissolution generally requires the presence of a trace of fluoride ion. Phosphoric acid cannot be used to eliminate the effects of Fe(III). The absorbance often can be measured simply against a reagent blank if only small amounts of colored ions are present. However, for the analysis of less than 10 ppm of manganese, it is recommended that the absorbance be measured against a sample solution decolorized with sodium azide as described below for zirconium. It is not necessary to have thorium present in the solution used for the standard-curve preparation.

A 5-g sample is dissolved in 40 ml of concentrated nitric acid containing a few drops of 48 per cent hydrofluoric acid. The solution is evaporated to 25 ml, and 10 ml of concentrated nitric acid is added before the periodate oxidation.

(c) *In Zirconium.* Spectrophotometric procedures involving the oxidation of Mn(II) to permanganic acid with persulfate and silver-ion catalyst are reported.[288, 291] Oxidation with periodate [288, 435] apparently is preferred. As in the analysis of thorium and titanium, phosphoric acid cannot be used to eliminate the interference of Fe(III). The absorbance of colored impurities in zirconium metal is generally ignored. However, for the analysis of less than 10 ppm of manganese or for the analysis of Zircaloys containing large amounts of alloying elements, correction for the absorbance of colored elements can be made by determining the absorbance of the oxidized sample solution decolorized with sodium azide. This technique is described in detail below, and is suitable for the determination of 10 to 200 ppm with a 1-g sample. Larger samples can be used.

Zirconium metal is dissolved in sulfuric acid (1+1) plus hydrofluoric acid. Fluoride and reducing agents are removed by adding perchloric acid and evaporating the solution to fumes.[288] The solution is diluted, 0.5 g of potassium periodate is added, and the solution is boiled for 5 min. The solution is allowed to stand for 24 hr before it is diluted, and the absorbance is measured at 525 mμ. Nitric acid can be used instead of perchloric acid to oxidize reducing impurities.[288, 435] In this case maximum color development is said to be achieved with 15 to 20 min of boiling.

Spectrophotometric Determination of Manganese in Zirconium or Zircaloy—Direct Periodate Oxidation. Procedure.[435] A 1-g sample is suspended in 40 ml of sulfuric acid (1+1) in a platinum beaker, and 48 per cent hydrofluoric acid is added dropwise until dissolution is complete. About 4 drops of concentrated nitric acid are added, and the solution is evaporated to fumes. The solution is transferred to a pyrex beaker, cooled, and diluted with about 50 ml of water.

To the solution is added 0.3 g of potassium periodate. The solution is boiled for 15 min, cooled, and diluted to 100 ml. The absorbance is measured in 10-cm cells at 525 mμ against water as a reference. To the remaining portion of the sample solution is added 10 mg of sodium azide crystals (hood!). The solution is warmed for a few minutes. When the solution is cool, the absorbance is again measured. This blank absorbance and the absorbance of a reagent blank are subtracted from the sample absorbance.

The standard curve is prepared by adding 0 to 200 μg of manganese in 25 ml of water to 40 ml of sulfuric acid (1+1) and 0.3 g of potassium periodate and continuing the oxidation as described above. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of manganese in titanium have been described in the literature (see Refs. 226, 227, 232, 235, 294, 315, 316, 332, 333, 400, 429, and 436).

(e) *In Niobium.* A procedure for the determination of manganese in niobium has been described by Reed and Goward.[437]

11–2.21 Mercury in Uranium

The determination of traces of mercury in uranium compounds has been carried out by a dithizone procedure.[285] In the extraction of a 0.25*M* hydrochloric acid solution of the sample, small amounts of copper and bismuth do not interfere. Palladium and gold interfere, but these elements are rarely encountered. Silver is assumed not to extract from the chloride system.

Traces of mercury in uranyl sulfate solutions can be determined polarographically.[346] The supporting electrolyte is ethylenediaminetetraacetic acid (EDTA), nitriloacetic acid, or sodium nitrate–ammonium carbonate.

11–2.22 Molybdenum

(a) *In Uranium.* Traces of molybdenum in uranium are determined spectrophotometrically by methods in which reactions of molybdenum with phenyl hydrazine, 3,3′,4′,5,7-pentahydroxyflavone (quercetin), thiocyanate, or toluene-3,4-dithiol (dithiol) are utilized.

In hot mineral acid solution, phenyl hydrazine gives a red color with molybdate.[207] The color is stable and the sensitivity of the reaction is fairly high. Few elements interfere except those with sufficiently strong color.[326] Uranium is best precipitated as the peroxide prior to color development. Other colored impurities present may be removed as hydroxides.

Molybdenum in strongly acid solutions of uranyl sulfate is extractable with α-benzoinoxime in chloroform. After the extraction the molybdenum–quercetin complex is formed by the addition of an alcoholic solution of quercetin to a portion of the extract. The yellow complex is measured at 420 mμ.[438] Tungsten and vanadium interfere.

In acid solution containing a reducing agent such as stannous chloride, thiocyanate gives an orange-red color [207] with Mo(VI). This well-known reaction of Mo(V) is applicable to the analysis of uranium.[326]

A critical investigation of the molybdenum and tungsten thiocyanate procedures has been carried out by Crouthamel and Johnson.[439] Reduction of the Mo(VI) by cuprous chloride in a homogeneous acetone–aqueous medium is recommended for maximum formation and stability of the molybdenum complex. The increase in stability of the complex in organic solvents over that in water is also noted by Sandell.[207] *n*-Butyl acetate,[300, 326] 1-hexanol,[263] or a mixture of diethyl ether–petroleum ether [440] are used to extract the complex from uranium solutions prior to the optical measurements. If *n*-butyl acetate is used, some uranium accompanies the molybdenum and must be washed out with sulfuric acid (1+9). The *n*-butyl acetate procedure is applicable to uranium–thorium mixtures.[353] A direct procedure, without extraction, for the analysis of uranium alloys is also reported.[441]

As discussed under the determination of tungsten, both molybdenum and tungsten give slightly soluble products with toluene-3,4-dithiol (dithiol) which are extractable with organic solvents to which a blue-green color is imparted.[207] In the determination of molybdenum, the interference of tungsten can be prevented by extracting in the presence of citrate,[207] or by extracting the molybdenum from a cold solution containing less acid than that required for the tungsten complex.[442, 443]

Ashbrook [444] extracts the molybdenum–dithiol complex with carbon tetrachloride in the presence of hydrazine sulfate. Granger [445] rec-

ommends a different procedure. Extraction of the complex is avoided by adding to the reaction mixture a water-soluble organic solvent, *n*-butyl alcohol, in which the complex is soluble. The procedure is rapid and is capable of determining molybdenum down to 1 ppm in uranium metal. Uranium–molybdenum and molybdenum–niobium alloys can also be analyzed. A differential spectrophotometric technique is described for these samples. If citrate is added to the reaction mixture to avoid tungsten interference, no impurity commonly found in uranium metal or the alloys mentioned above interferes.

Spectrophotometric Determination of Molybdenum in Uranium—Dithiol, n-*Butyl Alcohol–Aqueous Medium. Procedure.*[445] A weight of sample is taken such that, when dissolved and diluted, a 10-ml aliquot contains up to 30 μg of molybdenum and up to 1 g of uranium. The sample is dissolved in hydrochloric acid (1+3). When the reaction ceases, 30 per cent hydrogen peroxide is added dropwise with stirring until the solution clears. The solution is evaporated without boiling just to dryness. The salts are not baked. The residue is dissolved in 10 ml of hydrochloric acid (1+3), and the solution is warmed to ensure complete dissolution of the molybdenum trioxide. The solution is filtered through 5.5-cm Whatman No. 40 paper, and the paper is washed with hydrochloric acid (1+19). The solution is then diluted to volume.

A 10-ml aliquot is placed in a 50-ml volumetric flask, and 20 ml of concentrated hydrochloric acid is added. After the solution has been well mixed, 15 ml of *n*-butyl alcohol is added, and the solution is again mixed and cooled to room temperature. If tungsten is present, 2 g of citric acid is added and dissolved. To the flask is now added 4 ml of dithiol solution [1 g dissolved in 500 ml of 1 per cent (w/v) sodium hydroxide; 7 ml of 76 per cent thioglycolic acid added to solution; final solution stored in the refrigerator], and the contents are mixed. The flask is placed in a constant-temperature bath at 20°C for 30 min. The solution is diluted to volume with *n*-butyl alcohol.

The absorbance is measured at 680 mμ in 5-cm cells against water or a reagent blank. The standard curve is prepared by carrying 10-ml volumes of solution containing 0 to 50 μg of molybdenum through the procedure.

(b) *In Thorium.* Traces of molybdenum in thorium oxide slurries have been determined by first extracting the molybdenum from a 1.5*M* hydrochloric acid solution with α-benzoinoxime in chloroform and then forming the molybdenum-3,3′,4′,5,7-pentahydroxyflavone (quercetin) complex in a portion of the extract by the addition of quercetin in ethyl alcohol.[438] The absorbance is measured at 420 mμ. Interfering tungsten and vanadium are seldom found in these samples.

The classic thiocyanate reaction,[207, 326] mentioned above under "Molybdenum in Uranium," is applicable to the analysis of thorium.[214] *n*-Butyl acetate is generally used to extract the colored complex; 1-hexanol extracts too much thorium. The *n*-butyl acetate procedure,

described below, has also been applied to the analysis of thorium oxide–uranium oxide slurries.[353] 1-Hexanol has been used by Zibulsky [446] after the thorium has been precipitated with sodium hydroxide. Very little loss of molybdenum occurs in the precipitation step. The filtrate is acidified with sulfuric acid, the thiocyanate complex is produced, and the complex is extracted with 1-hexanol for the optical measurements at 470 mμ.

Spectrophotometric Determination of Molybdenum in Thorium—Thiocyanate, n-Butyl Acetate Extraction. Procedure.[214] A sample containing at least 20 μg of molybdenum is dissolved with 10 ml of concentrated nitric acid per gram of sample and 5 to 10 drops of 0.05*M* hydrofluoric acid. When dissolution has been completed, 15 ml of 70 per cent perchloric acid is added, and the solution is heated to fumes of perchloric acid. When the solution has cooled, 20 ml of water is added, and the solution is transferred to a separatory funnel. To the funnel are added 5 ml of 5 per cent sodium thiocyanate solution and 10 ml of stannous chloride solution (250 g plus 200 ml of concentrated hydrochloric acid added to 1200 ml of water). The solution is extracted for 1 min with 20 ml of *n*-butyl acetate, and the aqueous phase is discarded. The organic phase is washed with 5 ml of the thiocyanate solution plus 15 ml of the stannous chloride solution for 1 min. The organic phase is drained into a 50-ml volumetric flask. The separatory funnel is rinsed with two 10-ml portions of *n*-butyl acetate; the rinses are added to the volumetric flask. The extract is diluted to volume. The absorbance is measured at 470 mμ against a reagent blank.

The standard curve is prepared by carrying 0 to 100 μg of molybdenum through the entire procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(c) *In Zirconium.* The dithiol procedure, discussed above and also under the determination of tungsten, Sec. 11–2.39, is applicable to the determination of molybdenum in zirconium.[447] Both the molybdenum- and tungsten-dithiol complexes are extracted with carbon tetrachloride from a solution of the metal at controlled acidity and temperature: the molybdenum complex from a 2 to 3*M* hydrochloric acid solution at room temperature; the tungsten complex from 5 to 8*M* hydrochloric acid at 90°C.

The thiocyanate procedure is satisfactory for the analysis of zirconium and Zircaloy. The complex is extracted with *n*-butyl acetate or isopropyl ether.[288, 291, 448] The development of the complex by reduction with cuprous ion in a homogeneous acetone–aqueous medium, recommended by Crouthamel and Johnson [439] to ensure maximum formation and stability of the complex, is also reported [288] and is described in detail below.

Spectrophotometric Determination of Molybdenum in Zirconium and Zircaloy—Thiocyanate, Acetone–Aqueous Medium. Procedure.[288] A 1- to 5-g sample in a platinum dish is covered with water and dissolved by

the addition of 20 drops of sulfuric acid per gram of sample plus sufficient 48 per cent hydrofluoric acid added dropwise. The solution is warmed to complete the dissolution, and then is evaporated to fumes. The sides of the dish are washed with water, and the solution is again evaporated to fumes. The salts are dissolved in water, and the solution is diluted to a suitable volume.

An aliquot of 15 ml or less containing up to 1 g of zirconium is placed in a 50-ml volumetric flask, and the volume is adjusted to 15 ml with water. The sulfuric acid concentration is adjusted so that the concentration in the final 50-ml volume will be between 0.3 and 1.0*M*. The solution is cooled; 7 drops of 0.1*M* cuprous chloride in hydrochloric acid (0.495 g in 50 ml of concentrated acid) are added, and the flask is swirled. Then 28 ml of 1.0*M* ammonium thiocyanate in acetone (38.1 g in 500 ml of acetone; solution prepared just before use) is added, and the flask is swirled. The sides of the flask are washed down with 2 to 3 ml of water, and 15 drops of 10 per cent stannous chloride [5 g in 50 ml of hydrochloric acid (1+4)] are added. The solution is diluted to volume and mixed well. The absorbance is measured in 5-cm cells at 460 mμ against water. The color is stable for 1 hr.

The absorbance is corrected for a reagent blank prepared in the same manner. The standard curve is prepared as above with 0 to 40 μg of molybdenum in aliquots of a standard solution conveniently made by dissolving molybdenum metal in sulfuric acid.

(d) *In Titanium.* Procedures for the determination of molybdenum in titanium have been described in the literature (see Refs. 226, 227, 232, 235, 294, 316, 333, 401, and 449–451).

(e) *In Niobium.* Procedures for the determination of molybdenum in niobium have been described by Reed et al.[452, 453]

11–2.23 Nickel

(a) *In Uranium.* Various separation–polarographic procedures are available. Kelley, Thomason, and Horton [454] retain the uranium on an anion resin, Dowex A–1, elute the nickel with 6*N* hydrochloric acid, and obtain the nickel reduction wave at −0.78 volt vs. a saturated calomel electrode in 0.1*M* pyridine–0.1*M* pyridinium chloride. A cation-exchange procedure is also described.[280] This latter procedure, together with a mercury-cathode electrolysis [281-283] and a dithizone extraction separation,[284] all used individually prior to polarography, are discussed briefly under Sec. 11–2.7. A detailed description of the dithizone extraction–polarographic procedure is given in Chap. 4, "Beryllium," Sec. 4–4.11. One change in the procedure must be made when uranium is analyzed: the exhaustive extractions are made at pH 7.5 and 9.5.

Greater than 100 μg of nickel can be determined by X-ray fluorescence after extraction of the uranium with tributyl phosphate (TBP).[327]

Although diethyldithiocarbamate is recommended by Chilton [335, 336] for the simultaneous spectrophotometric determination of nickel, copper, and cobalt [Sec. 11-2.12(a), "Copper in Uranium"], the recommended chromogenic reagent for nickel is dimethylglyoxime.[207] The classic dimethylglyoxime reaction involving the production of the nickelic complex by suitable oxidants is readily adapted to the analysis of uranium.[334] Separation of the uranium as peroxide as formerly suggested [334] is not necessary. Citrate or tartrate prevents the precipitation of the uranium in the alkaline medium employed, and the resulting uranium and iron(III) complexes absorb only slightly above 500 mμ. The maximum absorption of the nickelic dimethylglyoxime complex occurs near 450 mμ, but, in practice, the less sensitive maximum near 540 mμ is used if no separation is carried out. The shape of the absorption curve apparently depends somewhat on the oxidant employed [455] and on the pH of the solution when the oxidant is added.[207, 455] Traces of copper and cobalt, which give similar but much less sensitive colors with the reagent, can ordinarily be ignored in the analysis of uranium. Appreciable amounts of chromium may give high results.

Of the oxidants that have been used in the past to oxidize the nickelous complex to the red nickelic complex, bromine is perhaps the most widely used. However, the color produced with bromine is fairly unstable, increasing slowly for 10 to 20 min and then fading; standardized conditions, therefore, should be rigidly followed for accurate results. Greater alkalinity in the final solution may increase the stability.[207] As a result of a study of various oxidants, Rodden and Petretic [456] report that ammonium persulfate gives a more stable color than that produced by bromine. Druschel, Menis, and Rowan [455] recommend potassium persulfate chiefly because of its better stability and uniformity as compared to the ammonium salt. Iodine is also reported to be more satisfactory than bromine.[457]

In the presence of more than trace quantities of copper, cobalt, chromium, iron, and other impurities, the nickel can be first separated as the nickelous dimethylglyoxime complex by extraction from ammoniacal solution with chloroform.[207, 458] Small amounts of copper accompanying the nickel are removed by washing the extract with 2 per cent (v/v) ammonium hydroxide.[207] The nickel is then washed out of the extract with 0.5*M* hydrochloric acid,[207, 459] or the chloroform is evaporated to dryness, and the residue is taken up in dilute acid.[263] The nickel is finally determined as the nickelic dimethylglyoxime complex. A typical extraction procedure is described below under "Nickel in Zirconium."

In another preliminary separation procedure, Haslam, Russell, and Wilkinson [432] precipitate nickel and manganese with sodium carbonate

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after the removal of the silica and acid-insoluble sulfides. Iron is added before the precipitation to serve as a collector. The precipitate is dissolved in acid, and the nickel is determined as the nickelic dimethylglyoxime complex in the usual manner. This separation procedure, however, is lengthy, and offers little advantage over the extraction procedure described previously.

The various direct procedures applied to uranium [263, 460, 461] differ only in minor details. The New Brunswick Laboratory procedure described below is selected as typical.

> *Spectrophotometric Determination of Nickel in Uranium—Direct Dimethylglyoxime. Procedure.*[263] A 1-g sample is dissolved in 5 ml of nitric acid (1+1), and the solution is evaporated to dryness on a steam bath. The residue is taken up in 2 ml of concentrated nitric acid plus about 8 ml of water. The solution is transferred to a 50-ml graduated cylinder, and 10 ml of 20 per cent (w/v) ammonium citrate solution is added.
>
> To the solution is now added 2 ml of 0.1*N* iodine solution (12.7 g of iodine and 25 g of potassium iodide in 1 liter of solution). The absorbance measurements should be made from 15 to 30 min after this step.
>
> To the solution are added 10 ml of concentrated ammonium hydroxide and water to bring the volume up to 48 ml. Then 2 ml of dimethylglyoxime solution [1 per cent (w/v) in ethyl alcohol] is added. The solution is mixed well.
>
> The absorbance is measured in 5-cm cells at 538 mμ against a similar 1-g sample carried through the procedure but with the omission of the dimethylglyoxime. With this reference solution the absorbance of uranium and other colored ions is eliminated. The reagent blank is determined by carrying 5 ml of nitric acid (1+1) through the entire procedure and measuring the absorbance of this solution against one similarly prepared but without the addition of dimethylglyoxime. The standard curve is prepared by carrying 10 ml of solution containing 2 ml of concentrated nitric acid and from 0 to 100 μg of nickel through the procedure beginning with the addition of the citrate and measuring the absorbance of each standard against the 0-μg standard.

(b) *In Thorium.* The dithizone extraction–polarographic procedure discussed briefly in Sec. 11–2.7(a) under "Cadmium in Uranium" and described in detail in Chap. 4, "Beryllium," Sec. 4–4.11, is satisfactory.[284] Thorium is complexed with citrate or tartrate for the exhaustive extractions at pH 7.5 and 9.0.

Direct spectrophotometric procedures employ dimethylglyoxime [214] or 1,2-cycloheptanedionedioxime.[214, 462] The nickelic complex is formed in ammoniacal solution containing citrate; bromine is the preferred oxidant with both chromogenic reagents.

LaMont and Johnson [311] analyze thorium oxide–uranium oxide slurries by extracting the nickelous dimethylglyoxime with chloroform from an ammoniacal solution containing citrate and measuring the

absorbance at 380 mμ. A similar extraction of the nickelous complex followed by removal of the nickel from the chloroform extract with 0.5*N* hydrochloric acid and production of the nickelic dimethylglyoxime with bromine in the usual manner is recommended.[214, 330] One such procedure is identical to that described in detail below under zirconium. The sample solution is prepared by dissolving thorium metal or oxide in hot 8*M* nitric acid containing a trace of fluoride ion; perchloric acid is added, and the solution is heated to fumes and diluted.

(c) *In Zirconium.* A direct polarographic procedure[251] and a procedure requiring the dithizone extraction of nickel and other metals prior to polarography[284] are both described briefly under Sec. 11–2.7(c). The latter method, described in detail in Chap. 4, "Beryllium," Sec. 4–4.11, is the more satisfactory of the two. The lower limit of determination is about 1 ppm with 2-g samples of zirconium.

Direct spectrophotometric procedures with dimethylglyoxime are satisfactory for both zirconium metal and Zircaloys (see Refs. 223, 291, 331, 463, 464). The absorbance is generally measured at 520 or 540 mμ to minimize the effect of Fe(III), although the more sensitive 440-mμ wave length[464] is sometimes used. At 440 mμ the approximate maxium permissible amounts in a 50-ml volume of the metals commonly occurring are said to be:[464] zirconium, 0.5 g; tin, 10 mg; iron, 1 mg; copper, 0.3 mg; and chromium, 0.2 mg. Either iodine or bromine is used as the oxidant in these direct procedures. The typical procedure is so similar to that described above under "Nickel in Uranium" that it need not be given in detail here. Samples are dissolved in hydrofluoric acid, hydrofluoric–nitric acid or hydrofluoric–sulfuric acid mixtures. The fluoride can be complexed with boric acid, or it can be fumed off. Citrate complexes the zirconium.

Spectrophotometric procedures with a preliminary separation step involving the extraction of nickelous dimethylglyoxime followed by the production of either nickelic dimethylglyoxime[223, 293] or the diethyldithiocarbamate complex[223] are available. One such extraction procedure, applicable to zirconium and Zircaloy, is described in detail below because it can be used for the analysis of uranium, thorium, titanium, and other metals in the event that iron, copper, and chromium are present in interfering quantities or when more sensitivity is required than that obtainable with the direct procedure.

Spectrophotometric Determination of Nickel in Zirconium and Zircaloy—Dimethylglyoxime Extraction, Dimethylglyoxime. Procedure.[223] A 1-g sample in a platinum dish is dissolved in a mixture of 20 ml of water, 5 ml of concentrated sulfuric acid, 2 ml of concentrated nitric acid, and 2 ml of 48 per cent hydrofluoric acid. The solution is evaporated to fumes and cooled. To the solution are added 30 ml of

water, 5 g of citric acid, concentrated ammonium hydroxide to make ammoniacal, and 2 ml of 1 per cent (w/v) dimethylglyoxime in ethyl alcohol.

The solution is extracted with three 3-ml portions of chloroform. The aqueous phase is discarded. The combined extracts are washed with 5 ml of ammonium hydroxide (1+49). The aqueous phase is washed with 2 ml of chloroform, which is added to the washed chloroform extract.

The nickel in the extract is stripped with two 5-ml portions of 0.5*N* hydrochloric acid. To the acid extract in a 25-ml volumetric flask are added 5 drops of saturated bromine water and concentrated ammonium hydroxide until the bromine color is destroyed plus 4 drops in excess. Then 0.5 ml of 1 per cent dimethylglyoxime solution is added, and the solution is diluted to volume. The absorbance is measured in 1-cm cells at 460 mμ against water as a reference.

A reagent blank is carried through the entire procedure. The standard curve is prepared by carrying 10-ml portions of 0.5*N* hydrochloric acid containing from 0 to 100 μg of nickel through the color development steps and measuring the absorbance of each standard against the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of nickel in titanium have been described in the literature (see Refs. 227, 235, 239, 316, 333, and 429).

11–2.24 Phosphorus

(a) *In Uranium.* The spectrophotometric determination of traces of phosphorus in uranium metal or compounds is carried out by the formation of either phosphorus molybdenum blue or the yellow phosphovanadomolybdic acid complex.

Anderson and Wright [465] prefer the latter compound because of the near specificity of the color reaction [466, 467] and the many variables involved in the quantitative production of the reduced heteropoly acid. Reducing agents interfere by reducing the complex to molybdenum blue. Oxalate, citrate, and tartrate, which complex molybdenum, bleach the color. Fluoride causes erratic results. Chromium(VI) interferes seriously.[468] Volatilization of the chromium as chromyl chloride removes this interference efficiently.[468] Arsenic in large amounts also interferes, but it can be removed as the tribromide.[469] The color of the uranyl ion interferes; therefore the uranium must be extracted first with tributyl phosphate (TBP)–carbon tetrachloride (1+1) from a 5 to 8*M* nitric acid solution.[465] The raffinate is washed with Varsol, a high-boiling petroleum ether, to remove the TBP. The color is developed by the addition of ammonium molybdate–ammonium vanadate reagent solution and is measured at 400 mμ. Interference by hydrolysis of the TBP during the extraction step is said to be insignificant. The lower limit of determination is about 10 ppm.

The molybdenum blue procedures depend upon the formation of the heteropoly molybdophosphoric acid and its subsequent reduction to a blue compound. The molybdophosphoric acid is often extracted by such solvents as isobutyl alcohol and *n*-butyl alcohol before the reduction. The literature on the molybdenum blue reaction is voluminous; however, the variables involved in the color development and the extraction of the molybdophosphoric acid have been the subjects of investigations.[470-472] The molybdenum blue reaction is not specific for phosphorus; arsenic(V), germanium, and silicon also form heteropoly acids with molybdenum yielding blue compounds upon reduction. Some selectivity for phosphorus can be obtained by controlling the acidity; for example, molybdosilicic acid is not formed [238, 470] above an acidity of about 0.9*N*. In direct procedures the reduction conditions must be carefully regulated because the molybdate reagent itself can be reduced to a blue product. However, if the heteropoly acid is separated from the excess molybdate by extraction, the subsequent reduction is less erratic. The chief interferences in the extraction technique are arsenic(V) and germanium, although traces of gold(III), tungsten(VI), and vanadium(V) can also interfere.[472] Arsenic is best removed by volatilization as the bromide; germanium, as the bromide or chloride.[472] Arsenic(V) can also be reduced with hydriodic acid and removed by heating with hydrochloric acid.[238] Reducing agents such as thiosulfate and tin(II) must also be absent during formation of the heteropoly acid. Direct molybdenum blue procedures applied to uranium utilize hydrazine [238] or stannous chloride (Refs. 238, 241, 263, 473) as the reducing agent. The New Brunswick Laboratory procedure [263] is described in detail below.

Lafferty and Wade [241] adjust the conditions of heteropoly acid formation and reduction to obtain both the phosphorus and arsenic molybdenum blue, the absorbances of which at 730 mμ are additive. The arsenic(V) in another aliquot of the sample is then reduced with sulfur dioxide or volatilized as the bromide, and the phosphorus color alone is produced and measured. Arsenic is calculated by difference. Satisfactory results for both elements are obtained if the ratio of one element to the other is not greater than 20. Chloride must be fumed off; fluoride must be complexed with aluminum sulfate. Sulfamic acid prevents the interference of nitrite. The lower limits of determination are 1 μg of phosphorus and 5 μg of arsenic on a 1-g sample basis. The procedure is described below.

Extraction procedures applied to uranium are described in Rodden.[238] Solvents used are ethyl acetate–amyl alcohol (1+2), or *n*-butyl alcohol. Stannous chloride is the reductant.

During sample dissolution and subsequent treatment of sample solutions, the volatility of compounds such as phosphine and ortho-

phosphoric acid should be borne in mind. An oxidizing acid should be present during dissolution. Perchloric acid is better than sulfuric acid for fuming operations.

Spectrophotometric Determination of Phosphorus in Uranium—Direct Molybdenum Blue. Procedure.[238, 263] A 1-g sample, previously pickled in nitric acid (1+1), washed well with water then alcohol, and air dried, is dissolved in a covered platinum dish with 10 ml of nitric acid (1+1). When dissolution has been completed, 3 ml of 70 per cent perchloric acid and 1 ml of 48 per cent hydrofluoric acid are added, and the dish is heated on a steam bath for 1 hr. The solution is then evaporated on a hot plate to fumes.

The solution is transferred to a 250-ml Erlenmeyer flask. If arsenic is present, 5 ml of hydrobromic acid (1+4) is added, and the flask is heated until perchloric acid condenses on the neck of the flask. The solution is cooled, the flask is washed down with 10 ml of water, and 15 ml of 10 per cent (w/v) sodium sulfite is added.

The solution is heated to boiling, and 70 per cent perchloric acid is added dropwise to produce a clear solution. To the flask is added 20 ml of freshly prepared ammonium molybdate–hydrazine sulfate solution [25 ml of 2 per cent (w/v) ammonium molybdate in 11*N* sulfuric acid diluted to 80 ml with water; 10 ml of 0.15 per cent (w/v) hydrazine sulfate solution added; solution diluted to 100 ml]. The solution is digested on the steam bath for 15 min, then it is cooled rapidly in an ice bath and diluted to 50 ml with dilute ammonium molybdate–hydrazine solution (20 ml of reagent solution diluted to 100 ml). The absorbance is measured at 650 mμ in 1- to 5-cm cells against water as a reference. The absorbance must be corrected for a reagent blank and for the absorbance due to the uranyl ion. The uranyl color is measured by carrying a 1-g sample through the same procedure except that the molybdate–hydrazine reagent is omitted. The standard curve is prepared by carrying from 0 to 50 μg of phosphorus in 10-ml portions of nitric acid (1+1) through the procedure. The 0-μg standard is the reagent blank.

Spectrophotometric Determination of Phosphorus and Arsenic in Uranium—Molybdenum Blue. Procedure.[241] A 1-g sample is dissolved in a minimum of nitric acid (1+1). The solution is evaporated to near dryness and diluted with 5 ml of water. Then about 0.2 g of sulfamic acid is added, and the solution is adjusted to pH 2.0 to 2.5 with dilute low-phosphorus "electrolytic" sodium hydroxide solution. To the solution are added 5 ml of 8.4*N* sulfuric acid and 5 ml of 0.025*M* ammonium molybdate. The volume is adjusted to 49.5 ml, and 0.5 ml of 1 per cent (w/v) stannous chloride solution is added. In 5 to 10 min, the absorbance at 730 mμ in 5-cm cells is measured against water to obtain the sum of the phosphorus and arsenic.

Another sample is dissolved as above, 2 ml of concentrated sulfuric acid is added, and the solution is fumed until the excess sulfuric acid is removed. The residue is dissolved in about 10 ml of water, and sulfur dioxide is bubbled through the solution for 15 min. The excess sulfur dioxide is removed from the solution by a brisk flow of nitrogen or carbon dioxide. The pH is adjusted to 2.0 to 2.5, and the procedure is continued as described above to obtain the absorbance due to phosphorus alone.

The absorbances must be corrected for reagent blanks and also for the color due to uranium and other ions. The latter correction can be obtained by measuring the absorbance against water of the same weight sample processed as described except for the addition of the molybdate. Standard curves for both phosphorus and arsenic must be prepared. A given amount of phosphorus yields an absorbance about 2.4 times that from the same weight of arsenic. The arsenic content is calculated from the difference in absorbance of the two sample solutions.

(b) *In Thorium.* The spectrophotometric determination of phosphorus as the yellow phosphovanadomolybdic acid complex,[468] described above under "Phosphorus in Uranium," has been applied to the analysis of thorium oxide slurries [216] and thorium nitrate.[474] Fluoride used in the sample dissolution should be fumed off with perchloric acid before color development.[468] If sodium chloride is added to the sample solution during the fuming process, interfering Cr(VI) is also removed.[468] Direct molybdenum blue procedures, described under "Phosphorus in Uranium" and "Phosphorus in Zirconium," undoubtedly are also applicable to the analysis of thorium. Extraction of molybdophosphoric acid with isobutanol prior to the reduction to molybdenum blue with stannous chloride has been applied to the analysis of thorium nitrate.[475] The procedure is similar to that described below under "Phosphorus in Zirconium." The sample solution is prepared by dissolving the metal or oxide in hot nitric acid (1+1) containing a trace of fluoride ion. The fluoride is fumed off with perchloric or sulfuric acid before producing the heteropoly acid.

(c) *In Zirconium.* Molybdenum blue procedures, direct or with prior extraction of the heteropoly molybdophosphoric acid, are available. Zirconium metal is analyzed by a direct procedure [288] with hydrazine as the reductant similar to that described above for "Phosphorus in Uranium." The absorbance is measured at 760 mμ. Arsenic is generally not present in interfering quantities. Fluoride is fumed off with perchloric acid. With 1-g samples 20 to 1000 ppm can be determined.

Reinhold [476] recommends the extraction technique for the analysis of zirconium and Zircaloys. With 0.25-g samples the optimum range is 5 to 80 ppm. This procedure is described in detail below.

Spectrophotometric Determination of Phosphorus in Zirconium and Zircaloy—Isobutyl Alcohol Extraction, Molybdenum Blue. Procedure.[476] A 0.25-g sample is dissolved in a platinum beaker with 10 ml of perchloric acid (1+1) and 1 ml of 48 per cent hydrofluoric acid, the latter added dropwise. The solution is evaporated to fumes. The residue is dissolved in 40 ml of water. When the solution is cool, 5 ml of 10 per cent sodium molybdate solution (10 g of dihydrate dissolved in 100 ml) is added, and the mixture is allowed to stand for 10 min.

The solution is transferred to a separatory funnel and is extracted for 1 min with 40 ml of isobutyl alcohol. The aqueous phase is dis-

carded. The organic phase is washed twice with 25-ml portions of water, and the aqueous phases are discarded. The organic phase is equilibrated for 30 sec with 25 ml of 0.01*M* stannous chloride reagent (2.3 g of dihydrate dissolved in 170 ml of concentrated hydrochloric acid; solution diluted to 1 liter). The aqueous phase is discarded. The organic phase is diluted to 50.0 ml, and the absorbance at 725 mμ in 2-cm cells is measured against isobutyl alcohol as a reference. The absorbance is corrected for a reagent blank.

The standard curve is prepared by carrying 0 to 20 μg of phosphorus added to 10 ml of perchloric acid (1+1) and 1 ml of 48 per cent hydrofluoric acid through the entire procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of phosphorus in titanium have been described in the literature (see Refs. 235, 316, and 477).

11–2.25 Platinum Metals: Ruthenium, Rhodium, Palladium, Osmium, Iridium, Platinum

(a) *In Uranium.* Although the platinum group metals are generally determined spectrographically, some spectrophotometric procedures are available and are briefly described below. The comprehensive review of colorimetric methods for each of the platinum metals reported by Beamish and McBryde [478] should prove valuable for any future developmental work.

Traces of osmium in uranium metal or oxide can be determined [479, 480] by distilling the tetroxide and measuring the osmium spectrophotometrically at 540 mμ as the red complex produced with thiourea.[207] The osmium is distilled from either a hydrochloric acid–hydrogen peroxide solution [479] or a nitric acid solution in an all-glass still into a hydrochloric acid (1+1) solution saturated with sulfur dioxide. If a nitric acid solution is used, the oxides of nitrogen in the distillate must be destroyed with urea before color development.[480] With 5-g samples of metal, recoveries of not less than 70 per cent are obtained with quantities of osmium down to 5 μg.

The solution remaining after removal of the osmium from the nitric acid solution can be used for the determination of traces of ruthenium.[479, 480] Permanganate is added to obtain the stronger oxidizing conditions necessary for the distillation of the ruthenium tetroxide. The distillate is collected in a hydrochloric acid–sulfur dioxide solution and determined colorimetrically as the blue thiourea complex.[207] With 5-g samples of metal, at least 90 per cent of the ruthenium in quantities down to 5 μg are recovered.

The colorimetric determination of traces of rhodium is carried out [207, 479] by dissolving the metal in aqua regia, evaporating the solution to dryness to remove nitrate, forming the chlorocomplexes by adding stannous chloride, and extracting the complexes with ethyl

acetate. Platinum and palladium interfere. It is recommended that the extract be examined spectrographically for platinum and palladium if the concentration obtained appears to be greater than 4 ppm.

Traces of palladium, iridium, and platinum are generally determined spectrographically after the application of one of the various separation procedures described in Chap. 12, "Spectrochemical Analysis." However, a spectrophotometric procedure developed for the determination of palladium in ores[479] can undoubtedly be applied to the analysis of metal. Palladium is coprecipitated with added tellurium by treatment of a hydrochloric acid solution of the sample with stannous chloride. The tellurium is volatilized by ignition, and the complex of palladium with *p*-nitrosodiphenylamine is produced and measured at 490 mμ.[207] Platinum(IV) interferes by its color; it does not react with the reagent. The same is true for the other platinum metals. Platinum(II) and large amounts of gold and silver interfere.

(b) *In Thorium.* Ruthenium in thorium oxide slurries can be determined spectrophotometrically as the β-nitroso-α-naphthol complex measured at 560 mμ.[216] A prior volatilization separation by fusion pyrolysis is required.

Palladium in thorium oxide slurries is reacted in dilute chloride solution with α-furildioxime.[216] The yellow complex is extracted into chloroform and determined spectrophotometrically at 380 mμ.

Palladium in uranium oxide–thorium oxide slurries is determined by extraction of the complex with 1,2-cyclohexanedionedioxime (nioxime) from a 3 per cent (v/v) hydrochloric acid solution with chloroform.[353] At a pH below 2.0, nickel does not react. The absorbance is measured at 390 mμ; 10 to 150 ppm can be determined.

(c) *In Zirconium.* Platinum in 7 per cent uranium–zirconium–platinum alloys containing about 0.25 per cent platinum can be determined by analyzing the insoluble portion after dissolution of the sample in hydrofluoric–nitric acid.[481] The residue is ashed and dissolved in aqua regia. The nitrate is removed by evaporation to dryness after additions of hydrochloric acid, and the platinum is determined by reduction with stannous chloride to the yellow chloroplatinous ion measured at 325 mμ.[207, 481]

11–2.26 Rare Earths and Scandium

In Uranium. The rare earths are generally determined spectrographically after a separation of the uranium and other elements. The various separation techniques applied to the analysis of uranium, thorium, zirconium, titanium, and other metals are discussed in Chap. 12, Sec. 12–2.

A spectrophotometric procedure is available for 100 to 200 μg of total rare earths.[482] The chromogenic reagent is 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo) benzenearsonic acid (arsenazo). The colored complexes are developed at pH 7.0±0.1. Each rare-earth complex has about the same absorbance at 570 mμ in the range of 100 to 200 μg per 50 ml. A value for the apparent molar absorptivity of $2.75(\pm 0.05) \times 10^4$ is used to obtain the total rare earths. Arsenazo also gives colored products with uranium(VI), copper(II), aluminum, vanadium(IV), thorium, zirconium, iron(III), titanium(IV), and chromium(III) under the conditions used for the determination of the rare earths. Anions forming slightly dissociated complexes with rare earths also interfere: fluoride, phosphate, tungstate, oxalate, citrate, tartrate, and salicylate. The rare earths are separated from U(VI) and Fe(III) by the use of the quaternary ammonium anion resin Dowex 1-X8. Nitrate and chloride interfere in the separation and must be fumed off. In a 0.5 per cent (v/v) sulfuric acid solution containing 1 g of ammonium thiocyanate per 25 ml, uranium and iron are retained on a column of the resin. The rare earths are eluted with 0.5 per cent sulfuric acid.

Traces of cerium down to about 20 μg can be determined [483] by extracting the uranium as the thiocyanate with ethyl acetate, and oxidizing the cerium to Ce(IV) with persulfate and silver ion. The absorbance of the Ce(IV) and permanganate, produced by the oxidation of any manganese present, is measured at 360 mμ. Correction is made for the permanganate by determining its concentration from the absorbance shown at 525 mμ. The absorbances are measured against a reference solution prepared by reducing a portion of the oxidized solution with oxalic acid, which selectively reduces ceric and permanganate ions. Small amounts of iron, nickel, copper, aluminum, chromium, and vanadium can be tolerated.

The spectrophotometric determination of traces of scandium in various uranium materials can be carried out with Alizarin Red S.[484] Because of the nonselectivity of this reagent, various separation schemes must be applied to isolate the scandium in a relatively pure state. A hydrochloric or sulfuric acid solution of the sample is extracted with cupferron–chloroform to remove zirconium and other metals. Thorium is removed by an iodate precipitation, with mercury as a carrier, from a nitric acid system. A tributyl phosphate extraction of the scandium from concentrated hydrochloric acid solution then removes the bulk of the remaining elements with the exception of uranium. The scandium is removed from the uranium and residual contaminants by a series of tartrate precipitations with yttrium as a carrier. Finally, the yttrium is removed by extraction of the scandium with tributyl phosphate from a hydrochloric acid system. After

the scandium is washed from the tributyl phosphate with water, the color is produced at pH 3.5 with Alizarin Red S and is measured at 520 mμ.

11–2.27 Rhenium in Uranium

Although traces of rhenium in uranium materials are generally determined spectrographically, a spectrophotometric procedure based upon the extraction of the thiocyanate complex [207] by amyl alcohol has been described for the analysis of large samples.[431] After an initial extraction of a dilute hydrochloric acid solution to which thiocyanate and stannous chloride are added, the amyl alcohol extract is evaporated to dryness, and the residue is oxidized with nitric acid. The nitrate is removed by evaporation with hydrochloric acid, and the resulting hydrochloric acid solution is treated with cupferron to remove any molybdenum, tungsten, or tin present. The rhenium is then again extracted as the thiocyanate complex, and the absorbance of the yellow amyl alcohol extract is measured at about 430 mμ.

11–2.28 Selenium in Uranium

Selenium has been determined volumetrically after separation from uranium by distillation of the tetrabromide.[485] The separated selenium is reduced to the elemental form with hydroxylamine. The selenium is dissolved, sodium thiosulfate and potassium iodide are added, and the excess thiosulfate is titrated with potassium iodate to a dead-stop end point. The titration is said to be reproducible to within 2 μg of selenium.

11–2.29 Silicon

(a) *In Uranium.* The reaction of soluble silicates with molybdic acid to form the yellow heteropoly silicomolybdic acid has been utilized both polarographically and spectrophotometrically for the determination of traces of silicon in uranium. Strickland [486] studied the formation of the α and β forms of the complex. The β form is the analytically important compound produced in the recommended procedures. The polarographic reduction of the β form gives two waves. DeSesa and Rogers [487] noted that in 1*M* ammonium nitrate the first wave measured at +0.23 volt vs. a saturated calomel electrode is suitable for the determination of silicon. Interference of phosphorus and arsenic, which also form molybdate complexes in acid solution, is eliminated by the precipitation of ammonium molybdophosphate and molybdoarsenate in the supporting electrolyte. The same polarographic medium has been applied to the analysis of uranium.[488] Copper, iron, and vanadium interfere; the interference of the former two elements is reduced by the addition of salicylic acid. In this

procedure, the current is measured at −0.13 volt vs. the mercury pool.

The spectrophotometric sensitivity of the yellow color of the silicomolybdic acid, when measured in the ultraviolet, compares favorably with that of the reduced complex, the silicon molybdenum blue.[487] The variables involved in the production of the β yellow form for analytical purposes have been studied rather thoroughly.[486, 487, 489] The removal of the interference caused by the corresponding compounds of phosphorus and arsenic by the use of citrate, oxalate, and tartrate, excess phosphate, and solvent extraction is discussed by DeSesa and Rogers.[487] The use of tartrate is recommended.

The color of uranium solutions interferes with the spectrophotometric measurement of the yellow silicomolybdic acid. Two procedures involving the prior separation of the uranium have been reported. Guenther and Gale[490] extract U(IV) cupferrate with chloroform. Wright[491] extracts U(VI) from nitric acid solution with tributyl phosphate (TBP) in carbon tetrachloride. The hydrolysis of the TBP does not contribute enough phosphorus to cause a significant error.

The most favored procedures for the determination of silica involve the reduction of the yellow β-silicomolybdic acid to molybdenum blue. Both stannous chloride and a mixture of 1,2,4-aminonaphthol sulfonic acid and sodium bisulfite are used frequently for the reduction. Other reducing agents have been applied.[492]

Because silica is insoluble in the common acids and because silicic acid is easily dehydrated, care must be taken in the determination of trace amounts to convert all the silicon, including colloidal silica, to reactive silicate. The use of added fluoride is effective,[489] but the treatment must be carefully carried out to avoid loss of silicon as the tetrafluoride. Appropriate treatment with ammonium hydroxide[487] and sodium carbonate[493] is also effective for solubilizing the silica. Fusion with sodium carbonate is also recommended for those samples containing fluoride because of the danger of silicon tetrafluoride loss when such samples are dissolved in acid.[493]

Another disturbing factor is the loss of silicon as silanes during sample dissolution. For example, silanes may be evolved when uranium metal is dissolved in hydrochloric acid. An oxidizing acid is generally used to avoid this loss, but with certain alloys a small loss may still result.[493] Ignition of the metal to oxide and subsequent fusion with sodium carbonate is frequently used.

Procedures for the analysis of uranium involving the preliminary extraction of the yellow silicomolybdate complex with amyl alcohol–ethyl acetate or *n*-butyl alcohol are described in Rodden.[493] Oxalic acid decreases the phosphate interference. Reduction to molybdenum blue

is carried out with stannous chloride. A special separatory funnel designed to avoid contact with ground-glass surfaces is described.

A direct procedure is available [494] which involves the dissolution of uranium in a nitric–hydrochloric acid mixture and filtration of the insolubles, which are treated separately. After formation of the silicomolybdate complex, oxalic acid is added to decompose phospho- and arsenomolybdates, sodium sulfite is added to prevent subsequent fading of the molybdenum blue, and sulfuric acid is added to prevent reduction of molybdic acid to a blue product. Reduction of the heteropoly acid is carried out with stannous chloride. The insoluble portion is fused with sodium hydroxide, and the silicon content is determined in a similar manner. Uranium–molybdenum alloys containing up to 12 per cent molybdenum are analyzed identically.[495]

In the satisfactory procedure of Ziegler, Nelson, and King [496] used at the New Brunswick Laboratory, the metal is ignited to black oxide, the oxide is fused with sodium chlorate–sodium carbonate mixture, and the melt is dissolved in hydrochloric acid. Reduction of the heteropoly acid is carried out with 1,2,4-aminonaphthol sulfonic acid–sodium bisulfite.

Spectrophotometric Determination of Silicon in Uranium—Direct Molybdenum Blue. Procedure.[496] A sample of metal, previously cleaned in nitric acid, is ignited to black oxide in a platinum crucible over a burner. To a 1-g sample of oxide are added 0.2 g of potassium chlorate and 1.0 g of sodium carbonate, and the mixture is pulverized and mixed in a tungsten carbide mortar. The mixture is fused in a covered platinum crucible for 20 min at the maximum heat of a blast burner. The fused cake should be bright orange, with no trace of black oxide left. The cake is dissolved in 5 ml of concentrated hydrochloric acid, and the solution is transferred to a plastic beaker and diluted to about 30 ml.

The pH is adjusted to 0.85 with ammonium hydroxide (distilled water saturated with tank ammonia; solution stored in plastic). To the solution is added 4 ml of ammonium molybdate solution (10 g in 100 ml of solution; solution prepared daily and stored in plastic), and the pH is adjusted to 1.2. At this point the uranium will precipitate. If phosphate is present, 4 ml of 10 per cent tartaric acid is added. After 10 min, 15 ml of concentrated hydrochloric acid is added, followed by 2 ml of reducing solution (27 g of sodium bisulfite, 2 g of sodium hydroxide, and 0.5 g of 1,2,4-aminonaphthol sulfonic acid in 250 ml of solution; solution stored in plastic). The solution is diluted to 100 ml in a graduated cylinder and is poured back into the plastic beaker. The absorbance is measured at 820 mμ in 1- to 5-cm cells against water as a reference.

A sample blank is prepared by fusing another 1-g sample of oxide, dissolving the melt in 5 ml of concentrated hydrochloric acid, and diluting the solution to 100 ml. The absorbance of this solution against water is subtracted from the sample absorbance to eliminate any interference of colored ions in the solution. A reagent blank must also be

prepared; its absorbance is measured and subtracted from the sample absorbance.

A standard curve is prepared by fusing 5 g of sodium carbonate and 1 g of potassium chlorate, dissolving the melt in 25 ml of concentrated hydrochloric acid, and diluting the solution to 100 ml. Aliquots of 20 ml, to which is added 0 to 50 μg of silicon, are carried through the procedure beginning with the adjustment of the pH to 0.85. The standard silicon solution is conveniently prepared by fusing NBS No. 81 silica sand in sodium carbonate and dissolving the melt in water.

(b) *In Thorium.* Direct molybdenum blue procedures are satisfactory. Reduction of the silicomolybdic acid is carried out by sulfite [214, 330] or a mixture of 1,2,4-aminonaphthol sulfonic acid and bisulfite–sulfite.[497] The latter reagent is used by Menis and Manning [497] in the analysis of thorium oxide. The oxide is dissolved in 4*M* nitric acid containing a small amount of hydrofluoric acid. If the temperature of the acid mixture is kept at 70 to 80°C, no silica is lost. Procedures for the analysis of metal specify dissolution in warm nitric acid [214] or hydrochloric acid at room temperature,[330] both acids containing small amounts of hydrofluoric acid. Presumably no silica is lost by either dissolution step. In all these direct procedures, tartrate is added before the reduction step to eliminate phosphate interference and to redissolve the thorium molybdate that precipitates under the conditions of the silicomolybdic acid formation.

Spectrophotometric Determination of Silica in Thorium—Direct Molybdenum Blue. Procedure.[214, 497] A 0.5- to 1-g sample of metal or oxide in a platinum dish is dissolved in a mixture of 5 ml of concentrated nitric acid, 25 ml of water, and 2 drops of 48 per cent hydrofluoric acid by warming the mixture to about 80°C and stirring occasionally. Water is added occasionally to keep the volume nearly constant. When dissolution is complete, the solution is cooled, transferred to a 100-ml polyethylene cylinder containing 30 ml of saturated boric acid solution, and diluted to volume.

An aliquot of 50 ml or less containing 2 to 40 μg of silicon is transferred to a 250-ml polyethylene beaker. The volume is adjusted to about 50 ml, and 15 ml of 10 per cent ammonium molybdate solution [100 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ dissolved in 1 liter] is added. The pH is adjusted on a meter to 0.9 to 1.4 with silica-free ammonium hydroxide (water, in a polyethylene bottle, saturated with tank ammonia). After 5 min, 20 ml of 20 per cent tartaric acid is added. After 2 min, 1 ml of reducing solution (solution A prepared by dissolving 90 g of sodium bisulfite in 800 ml; solution B prepared by dissolving 7 g of sodium sulfite and 1.5 g of 1,2,4-aminonaphthol sulfonic acid in 100 ml; solutions A and B mixed and diluted to 1 liter; mixed solution stable about 1 month) is added. The pH is adjusted to 3.0 ± 0.1, and the solution is stirred until the precipitate of thorium molybdate dissolves. The solution is diluted to 100 ml in a volumetric flask and mixed. The absorbance is measured in 5-cm cells at 840 mμ against water as a reference. The absorbance is corrected for a reagent blank. The standard curve is prepared with 0 to 160 μg of silicon carried through

the procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(c) *In Zirconium.* Only direct molybdenum blue procedures are described. Read and Martin [498] disolve the metal in nitric–hydrofluoric acid and use sulfite as the reducing agent. Read and Read [288] report a similar procedure for both zirconium and Zircaloy. Carlson and Banks [489] dissolve zirconium in sulfuric–hydrofluoric acid and use 1,2,4-aminonaphthol sulfonic acid–bisulfite. Goward and Wilson [499] have adapted this procedure to the analysis of zirconium and Zircaloy. A slightly modified procedure is reported by Goward, Wilson, and Kallman.[500]

Spectrophotometric Determination of Silicon in Zirconium and Zircaloy—Direct Molybdenum Blue. Procedure.[500] A 1-g sample is weighed into a 200-ml platinum beaker, and 20 ml of water and 0.5 ml of sulfuric acid (1+1) are added. The beaker is nearly covered with a platinum lid, and 2.0 ml of 48 per cent hydrofluoric acid is added dropwise. When the reaction subsides, 0.5 ml of 7 per cent (w/v) potassium chlorate solution (prepared fresh daily) is added, and the solution is allowed to stand 5 to 20 min until the black particles are all in solution.

For a reagent blank 1 g of zirconium or Zircaloy (whichever is being analyzed) is suspended in 10 ml of water in a platinum beaker, and 2.0 ml of 48 per cent hydrofluoric acid is added dropwise. To the reaction mixture is added 4.0 ml of concentrated sulfuric acid, and the solution is fumed until salts begin to separate. The solution is cooled; and 10 ml of water, 1.0 ml of concentrated sulfuric acid, and 2.0 ml of 48 per cent hydrofluoric acid are added. The solution is again fumed to salts. The beaker sides are washed down, and the solution is again fumed. Finally, 20 ml of water is added together with the same quantity of hydrofluoric acid as is used to dissolve the sample plus 0.5 ml of 7 per cent potassium chlorate solution.

To the sample and reagent blank solution is added 40 ml of saturated boric acid solution (52.5 g in 1 liter of solution). Reducing ions in both solutions are titrated to a faint pink color with *0.004M* potassium permanganate. To the solutions is added 4 ml of 10 per cent molybdic acid [25 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ dissolved in 200 ml; 20 ml of concentrated sulfuric acid added; solution diluted to 250 ml]. The pH is adjusted to 1.2 to 1.3 with ammonium hydroxide (tank ammonia bubbled into distilled water, held in polyethylene, until specific gravity is 0.92). After 8 to 12 min, 4 ml of 20 per cent tartaric acid is added. Immediately after the solution is mixed, 4 ml of reducing mixture (27 g of ammonium bisulfite, 2 g of sodium hydroxide, and 0.5 g of 1,2,4-aminonaphthol sulfonic acid in 250 ml of solution; prepared fresh every two weeks) is added, and the solution is transferred to a 100-ml volumetric flask and diluted to volume. After 20 min the absorbance at 815 mμ is measured in 1-cm cells against water as a reference. The sample absorbance is corrected for the reagent blank absorbance.

The standard curve is prepared by adding 0.5 ml of 7 per cent potassium chlorate solution and 40 ml of saturated boric acid solution to 0 to 200 μg of silicon in platinum beakers. The color development

is continued as described. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of silicon in titanium have been described in the literature (see Refs. 227, 231, 235, 278, 294, and 501–504).

(e) *In Niobium.* A procedure for the determination of silicon in niobium has been described by the British.[505]

11–2.30 Silver

(a) *In Uranium.* Although silver in uranium is generally determined spectrochemically, two chemical procedures have been described.

Fairly large quantities, >0.02 per cent, can be determined by titrating a uranyl nitrate solution, made ammoniacal after the addition of tartrate, with *p*-dimethylaminobenzylidinerhodanine.[506] Absorbance measurements with a green filter, maximum transmission at 525 mμ, are plotted against the volume of titrant. The end point is the intersection of the increasing absorbance curve with the maximum absorbance curve ("heterometric titration").

Eberle[507] has adapted the dithizone procedure of Friedeberg[508] to the determination of trace amounts of silver in beryllium and uranium. Silver and other metals are extracted from a nitric acid solution at pH 2.0 with dithizone in carbon tetrachloride. The silver is back-extracted with sodium chloride–hydrochloric acid and then re-extracted, after dilution of the solution, with dithizone in carbon tetrachloride. The silver dithizonate is measured spectrophotometrically. The procedure should also be useful in the analysis of thorium, zirconium, titanium, and other metals.

Spectrophotometric Determination of Silver in Uranium—Dithizone. Procedure.[507] A 1- to 10-g sample of uranium containing from 1 to 10 μg of silver is dissolved in a minimum of nitric acid, and the solution is evaporated to near dryness on a steam bath. The salts are dissolved in about 50 ml of water, and the pH is adjusted by means of a pH meter to 2.0 with dilute nitric acid or ammonium hydroxide. The solution is transferred to a 125-ml separatory funnel and extracted with 10-ml portions of 0.01 per cent dithizone (50 mg dissolved in 500 ml of carbon tetrachloride) until the last portion remains green after a 2-min shaking period. To the organic phase in another separatory funnel is added 3.0 ml of sodium chloride–hydrochloric acid solution (100 g of sodium chloride dissolved in water containing 1.28 ml of concentrated hydrochloric acid; solution diluted to 1 liter), and the contents are shaken for 2 min. The aqueous phase is transferred to another separatory funnel. The organic phase is back-extracted with another 3.0-ml portion of the sodium chloride–hydrochloric acid solution. The aqueous phases are combined and washed with 10 ml of chloroform.

To the chloride solution is added 60 ml of water. The solution is extracted with 20.0 ml of 0.0005 per cent dithizone (10.0 ml of 0.01 per

cent dithizone diluted to 200 ml with carbon tetrachloride). The carbon tetrachloride phase is filtered through a dry 9.0-cm Whatman No. 41 filter paper placed in the mouth of a 100-ml beaker. The absorbance is measured at 500 mμ in 5-cm cells against the 0.0005 per cent dithizone as a reference. The reagent blank is generally negligible.

The standard curve is prepared by adding 5 and 10 μg of silver, respectively, to 6.0 ml of the sodium chloride–hydrochloric acid solution, diluting each solution by the addition of 60 ml of water, extracting the silver with 20.0-ml portions of the 0.0005 per cent dithizone solution, and measuring the absorbance as above.

(b) *In Thorium.* Apart from flame photometric procedures described for the determination of silver in uranium oxide–thorium oxide mixtures [353] and thorium oxide,[216] no procedures are reported. However, the dithizone procedure of Friedeberg [508] described above under "Silver in Uranium" should be applicable.

(c) *In Zirconium.* An extractive titration procedure is reported by Chernikhov and Dobkina.[291] The metal is dissolved in hydrofluoric acid; the solution is evaporated to dryness after the addition of nitric acid. The residue is taken up in 10 ml of 0.5*M* nitric acid and extractively titrated with 0.002 per cent dithizone in carbon tetrachloride.

The Friedeberg [508] dithizone procedure described above under "Silver in Uranium" should be applicable.

(d) *In Titanium.* Procedures for the determination of silver in titanium have been described by Corbett [227] and by Codell et al.[235]

11–2.31 Sodium and Potassium in Uranium

Although the alkali metals are generally determined spectrographically or flame photometrically, chemical procedures are described for the determination of sodium and potassium.

The conventional triple-salt technique has been useful for the gravimetric determination of sodium.[509] Both magnesium and zinc uranyl acetate have been used as the precipitating reagent. A colorimetric triple-salt procedure has also been applied.[509] After removal of the uranium as the tetrafluoride by electrolytic reduction in the presence of fluoride, the fluoride and excess sulfate are fumed off. The triple zinc salt is then precipitated, dissolved in hot water, and the uranium–sulfosalicylic acid complex is produced and measured spectrophotometrically.

Precipitation of potassium as the chloroplatinate followed by reaction of the salt with iodide to liberate iodine [207] has been used for the colorimetric determination of potassium.[509] Uranium is first removed by a diethyl ether extraction and double ammonium hydroxide precipitation. Although a recovery of only 50 to 55 per cent is obtained, the recovery is fairly constant, and a factor can be applied to the result.

690–457 O—64——55

Another colorimetric procedure, developed for the analysis of plutonium, is applicable to the determination of potassium in uranium. After removal of the uranium by extraction of U(IV) cupferrate, the potassium is precipitated with silver cobaltinitrite. The precipitate is dissolved in sodium hydroxide solution, and the nitrite is diazotized and coupled with α-naphthylamine sulfanilic acid for the optical measurement.[509]

11–2.32 Strontium and Barium

(a) *In Uranium.* The spectrograph and flame photometer are relied upon exclusively for the determination of traces of strontium or barium in refined uranium materials. A carbonate separation has been used in the past prior to the determination.[247] Separation of the nitrates in fuming nitric acid solution has been useful in radiochemical analyses.[247]

(b) *In Zirconium.* Traces of barium in zirconium metal and salts have been determined gravimetrically.[510] Prior separation of the bulk of the zirconium as hydrated zirconyl chloride from hydrochloric acid (3+1) and removal of residual zirconium and iron by a cupferron–chloroform extraction are required. The barium is precipitated as sulfate with a large excess of ammonium sulfate at pH 1.0. The lower limit of determination is about 0.2 mg of barium. A sample weight of 10 g is generally used.

11–2.33 Sulfur

(a) *In Uranium.* Sulfur exists chiefly as sulfide in uranium metal and certain compounds. When these samples are dissolved in a nonoxidizing acid, hydrogen sulfide is evolved. This evolution of acid-soluble sulfide is the basis of a convenient separation procedure commonly used in the steel industry and applicable to the analysis of uranium metal. Oxygen compounds of sulfur in some samples must be reduced to sulfide prior to the distillation. With some uranium materials containing oxygen compounds of sulfur, the sulfur is converted to sulfate by fusing the sample with sodium peroxide or a mixture of sodium carbonate and potassium nitrate. The conventional gravimetric or turbidometric procedures that then can be applied to the determination of sulfate are covered in Rodden.[485] These procedures are generally not useful for the analysis of trace quantities.

In the analysis of uranium metal, the evolved hydrogen sulfide can be determined volumetrically. Although the lower limit of determination is generally about 0.1 mg of sulfur, with large samples and the proper scaling down of the reagents, this limit can be reduced [485] to about 10 μg. An iodometric procedure similar to that used in the steel industry is described.[302] Samples are dissolved in hydrochloric

acid (1+1) in a conventional ASTM sulfur apparatus, and the hydrogen sulfide is distilled into ammoniacal cadmium chloride. Starch solution containing potassium iodide is added to the distillate; the solution is made acidic with hydrochloric acid and then is titrated with standard iodate solution. The possible interference of selenium and arsenic in this type of analysis is discussed by Codell, Norwitz, and Clemency.[511] Apparently most of the sulfur present in the metal is acid-soluble, but no confirmatory data are available.

The iodometric procedure is applicable to sulfate sulfur existing in some materials after the reduction of the sulfate with a mixture of hydriodic and hypophosphorous acids and distillation of the sulfide.[485] Nitrate interferes and must be removed prior to the reduction by fuming with perchloric acid. The residual perchloric acid will not react explosively with the reducing mixture. (However, under no circumstances should the perchloric acid–reducing mixture be taken to fumes!)

In another iodometric procedure described for the analysis of both uranium and plutonium metal, the hydrogen sulfide is distilled into a calcium hypochlorite solution in which the sulfide is oxidized to sulfate. The excess hypochlorite is determined iodometrically.[485]

Traces of sulfur can be estimated [485] by the stain produced in a strip of paper or length of thread impregnated with lead acetate by evolved sulfide in a manner resembling the Gutzeit test for arsenic. Selenium interferes. Oxygen-containing sulfur compounds are reduced with aluminum. Acid-insoluble sulfides are made acid soluble by fusing the sample with an alkali or alkaline earth metal. The spectrophotometric determination by means of colloidal lead sulfide as recommended by Luke [512] should be useful but has not been applied.

A spectrophotometric procedure applied to the determination of traces of sulfur in uranium trioxide involves the fusion of the sample with vanadium pentoxide at 950°C to evolve sulfur trioxide.[513] The sulfur trioxide is reduced with copper turnings, and the resulting sulfur dioxide is absorbed in a sodium tetrachloromercurate solution. The color is produced by the reaction of the sulfite with pararosaniline and formaldehyde. The copper turnings also remove interfering nitrogen dioxide from any nitrate in the sample.

Spectrophotometric procedures capable of determining 1 to 100 ppm of sulfur in uranium metal are based upon the production of either methylene blue [485] or Lauth's violet [514] by the reaction of sulfide with *p*-dimethylaminoaniline or *p*-phenylenediamine, respectively, in the presence of an oxidizing agent such as ferric ion. Distillation of the sulfide is used. If nitrate is used for the sample dissolution, it must be destroyed with formic acid before the distillation. Oxygen-con-

taining sulfur compounds are reduced with hydriodic-hypophosphorous acid mixture. Selenium can interfere. The Lauth's violet procedure is described below.

Spectrophotometric Determination of Sulfur in Uranium—Distillation, Lauth's Violet. Special Apparatus. The simple all-glass distillation apparatus consists of a 250-ml flask, a trap containing 30 ml of water when half full, and a 50-ml glass-stoppered cylinder. The trap dips into a beaker of cold water. During distillation, a stream of nitrogen passes through the flask, the trap, and the cylinder receiver in that order.

Special Reagents. Sulfur-free Water. Water is made sulfur-free by passage through Amberlite IRA–410. This water is used for the preparation of all aqueous solutions.

Procedure.[514] The apparatus is assembled and purged with nitrogen. The flask is disconnected, and to it are added 10 ml of hydriodic–hypophosphorous acid mixture (100 ml of hydriodic acid, sp. gr. 1.7, added to 40 ml of 31 per cent hypophosphorous acid; mixture boiled for 15 min to remove sulfur) and 10 ml of concentrated hydrochloric acid. The mixture is boiled for 5 min and discarded. The flask is rinsed with sulfur-free water.

A 1-g sample of metal is placed in the flask, and 2 ml of concentrated nitric acid plus 8 ml of concentrated hydrochloric acid are added. When the sample has been dissolved, the solution is heated to boiling on a hot plate. To the boiling solution is added 4 ml of formic acid, 1 ml at a time. The nitrous fumes are boiled off before each addition. The solution is evaporated to dryness, 10 ml of concentrated hydrochloric acid is added, and the solution is cooled to room temperature.

To the cylinder receiver is added 25 ml of 4 per cent (w/v) zinc acetate solution, and to the trap is added 30 ml of sulfur-free water. To the sample solution in the flask is added 17 ml of hydriodic–hypophosphorous acid mixture. The apparatus is assembled, and nitrogen is passed through at a rate of about 4 bubbles per second.

The solution in the flask is boiled on a sand bath for 10 min. The cylinder is disconnected, the delivery tube from the trap is rinsed, and the rinsing is added to the cylinder.

To the cylinder are added 7.5 ml of hydrochloric acid (1+3), 1 ml of 1 per cent (w/v) *p*-phenylenediamine solution [1 g dissolved in 100 ml of hydrochloric acid (1+20)], and water to bring the volume to 45 ml. The solution is mixed well, and 1 ml of 2 per cent (w/v) ferric chloride solution [2 g of anhydrous salt dissolved in 100 ml of hydrochloric acid (1+1)] is added. The solution is mixed rapidly, diluted to 50 ml, and allowed to stand for 20 min. The absorbance is measured at 595 mμ in 1-cm cells against a reagent blank as a reference.

The standard curve is prepared by carrying 0 to 50 μg of sulfur through the procedure. The standard sulfur solution is conveniently prepared from ammonium alum.

(b) *In Thorium.* Sulfate sulfur in thorium nitrate is determined gravimetrically as barium sulfate after removal of the thorium and other cations with a cation resin, Zeo–Karb 225 (H).[515] If an oxalate

precipitation is used to remove the thorium before the barium sulfate precipitation, some sulfate is lost.[515]

Menis and coworkers [216] also remove the thorium and other cations by a cation resin, Dowex 50–X4, in the analysis of thorium oxide slurries. Sulfate in the effluent is then determined by one of three methods. (1) A turbidometric procedure can be used. (2) The sulfate can be titrated with barium chloride with tetrahydroxyquinone (THQ) as the indicator.[516] (3) The sulfate can be determined indirectly by adding an excess of a standard barium perchlorate solution and titrating the excess barium potentiometrically with ethylenediaminetetraacetic acid (EDTA). A mercury indicator electrode is used to detect the end point. Phosphate and fluoride interfere.

(c) *In Zirconium.* Traces of sulfur in zirconium have been determined by the combustion of the sample in a stream of dry purified oxygen and the absorption of the sulfur on silver wool.[517] A similar combustion procedure is reported by Rodden.[251]

(d) *In Titanium.* Procedures for the determination of sulfur in titanium have been described in the literature (see Refs. 235, 294, and 511).

11–2.34 Tantalum and Niobium

(a) *In Uranium.* The extraction of tantalum from hydrochloric, nitric, perchloric, or sulfuric acid solutions containing hydrofluoric acid by solvents such as methyl isobutyl ketone (hexone)[518, 519] and diisopropyl ketone [520] has been made the basis of a procedure for determining traces of tantalum in uranium.[521] In this procedure the tantalum is extracted from a 6*M* sulfuric acid solution containing 0.4*M* hydrofluoric acid with hexone and is determined spectrophotometrically by its reaction with hydroquinone in concentrated sulfuric acid to form the yellow tantalum–hydroquinone complex. Titanium, molybdenum, and niobium interfere, but the interference of the former two elements is eliminated by a double extraction of the tantalum. The interference of niobium remains in the procedure as written. However, if tantalum is extracted from a mixed acid medium composed of hydrochloric, nitric, and hydrofluoric acids,[519] this interference also can undoubtedly be eliminated. The procedure, described below, was originally devised for the analysis of uranium alloys. In the absence of niobium, down to 25 μg of tantalum can be determined.

A more recent procedure, developed for the analysis of zirconium and described in detail below, should be applicable to the analysis of uranium. The procedure is practically free of interference.

No procedures for the determination of traces of niobium in uranium are available. However, the separation reported by Stevenson and Hicks [520] perhaps can be made the basis of a satisfactory procedure.

In this separation the tantalum is first extracted with isopropyl ether from a mineral acid–hydrofluoric acid solution; then the niobium is extracted from the solution made substantially higher in total acidity and hydrofluoric acid concentration. Multiple extractions may be necessary.

Spectrographic examination of the chloroform–soluble cupferron group has been useful in the past for the determination of tantalum and niobium.[522]

Spectrophotometric Determination of Tantalum in Uranium–Hexone Extraction, Hydroquinone. Special Apparatus. The extractor consists of a 25- by 150-mm pyrex test tube and a motor-driven stirrer. The shaft of the stirrer is a 180-mm piece of 5-mm OD tubing joined to a 15-mm piece of the tubing on one end to form an elongated hollow T. A small hole, 2 to 3 mm in diameter, is blown in the shaft about 35 mm from the T end. In use, the T end of the shaft is near the bottom of the aqueous (lower) phase, and the hole in the shaft is in the organic (upper) phase.

Procedure.[521] A sample of metal or alloy weighing up to 3.5 g and containing at least 25 μg of tantalum is placed in a platinum dish. For each gram of sample are added 2 ml of water and 1 ml of concentrated sulfuric acid. The dish is covered, and 5 ml of concentrated nitric acid per gram of sample is added slowly. The dish is warmed under a heat lamp until the reaction stops. The cover is removed, and 0.5 ml of 48 per cent hydrofluoric acid per gram of sample is added. If uranium tetrafluoride forms at this point, 2 ml of concentrated nitric acid per gram of sample is added, and the dish is warmed until dissolution is complete. The solution is evaporated under the heat lamp to fumes of sulfur trioxide. More sulfuric acid is added, if needed, so that the total volume of sulfuric acid present is between 3.3 and 3.5 ml. The solution is then heated to strong fumes and cooled.

The solution is transferred to a 25- by 150-mm pyrex test tube. The platinum dish is washed three times with a total of 5 ml of water and once with 2 ml of 2*M* hydrofluoric acid. The water washes are added to the sulfuric acid solution, the solution is cooled, and then the hydrofluoric acid wash is added. To the solution is added 10.0 ml of hexone, and the mixture is equilibrated for 5 min with the hollow stirrer at a rapid rate without causing spray to be thrown up on the upper sides of the tube. The stirrer is washed with water, the mixture is allowed to stand for 5 min, and 8.0 ml of the organic phase is pipetted into a 30-ml platinum dish. After the addition of 3 drops of 5*N* sodium hydroxide, the solution is evaporated to dryness under a heat lamp. To the cooled residue are added 10 drops of water, 5 drops of concentrated hydrofluoric acid, and 2 to 3 ml of concentrated sulfuric acid dropwise. The solution is evaporated to fumes. If the solution at this point is discolored because of charring during the volatilization of the hexone, about 10 mg of ammonium persulfate is added and dissolved by swirling before heating to fumes. The addition of the ammonium persulfate and the heating to fumes are repeated until the solution is colorless.

The solution is fumed strongly for 3 to 5 min, and is transferred to a dry 10-ml volumetric flask. The dish is rinsed with dry concentrated sulfuric acid (concentrated sulfuric acid fumed strongly and transferred to a stoppered bottle that is stored in a desiccator) to give a total volume of not more than 7 ml. The solution is cooled, and 3.0 ml of 0.5*M* hydroquinone in dry concentrated sulfuric acid is added. The volume is adjusted to 10.0 ml with the dry acid, and the solution is mixed well. The absorbance is measured at 375 mμ in 1- to 5-cm cells against a reference prepared by diluting 3.0 ml of the hydroquinone solution to 10.0 ml with the dry concentrated acid.

A reagent blank is prepared by extracting a solution of 3.5 ml of concentrated sulfuric acid, 5 ml of water, and 2 ml of 2*M* hydrofluoric acid. Similar solutions containing known amounts of tantalum are carried through the procedure for the preparation of the standard curve. The same volume of organic phase is used with the reagent blank solution, the standard solutions, and the sample solution.

If the sample contains molybdenum or titanium, the residue remaining after the evaporation of the extract aliquot is dissolved in 3.5 ml of concentrated sulfuric acid, and the solution is evaporated to fumes. The extraction is then repeated before the procedure is continued as described.

(b) *In Zirconium.* Two similar procedures have been recently described for the determination of tantalum in zirconium. In one [523] tantalum is extracted from a hydrochloric–hydrofluoric acid solution with methyl isobutyl ketone (hexone) and is determined, after removal of the organic matter, with 2,3,7-trihydroxy-9-phenyl-6-fluorone (phenylfluorone) [524] in the presence of ethylenediaminetetraacetic acid (EDTA). The procedure, described below, is also applicable to the analysis of Zircaloy. In the other [525] a nitric–hydrofluoric acid medium is used with a 1 : 1 acetone–isobutanol mixture as the extracting agent. The chromogenic reagent is 9-(p-dimethylaminophenyl)-2,6,7-trihydroxy-3-fluorone.

Niobium in zirconium and Zircaloy can be determined [526] by utilizing the color given by Nb(III) with thiocyanate in strong hydrochloric acid solution.[207] Platinum, dissolved from beakers used, interferes, but the error is compensated by the blank determination. Tungsten over 50 ppm gives a positive error. Uranium, iron, molybdenum, vanadium, and titanium in small amounts do not interfere.

Spectrophotometric Determination of Tantalum in Zirconium and Zircaloy-Hexone Extraction, Phenylfluorone. Procedure.[523] The calibration curve is prepared by pipetting 0 to 1.20 ml of a standard tantalum solution containing 100 μg per milliliter into 30-ml platinum dishes. Each solution is evaporated to dryness in a 90°C water bath. After the addition of 1 ml of hydrofluoric acid (1+99) to the residue, the dish is warmed to dissolve the tantalum. The solution is cooled, 5 ml of 10 per cent (w/v) EDTA (disodium salt) solution is added, and the solution is transferred to a 50-ml volumetric flask containing 10 ml of pH 4.5 buffer (500 g of ammonium acetate dissolved in 500 ml of water;

700 ml of acetic acid plus 2 g of benzoic acid dissolved in 20 ml of methanol added to ammonium acetate; solution diluted to 2 liters; 10 g of pure gelatin dissolved in 1 liter of water at 90°C; both solutions mixed, cooled, and the pH adjusted to 4.5). Then 10 ml of phenylfluorone solution (0.50 g dissolved in 50 ml of methanol and 1 ml of concentrated hydrochloric acid; solution diluted to 500 ml with methanol) is added. The solution is mixed and allowed to stand for 30 min. The solution is diluted to volume with acetic acid (1+9) and mixed. The absorbance is measured within 5 min at 530 mμ in 1-cm cells against water as a reference. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

In the analysis of samples, a 1-g quantity of zirconium or Zircaloy is suspended in 10 ml of water and is dissolved by the addition of 2 ml of 48 per cent hydrofluoric acid and 5 drops of 30 per cent hydrogen peroxide. The solution is evaporated to dryness in a boiling water bath. The salts are dissolved in 10 ml of acid mixture (20 ml of 48 per cent hydrofluoric acid, 20 ml of concentrated hydrochloric acid, and 360 ml of water), and the solution is transferred to a 100-ml separatory funnel with an additional 10 ml of acid mixture.

The tantalum is extracted with two 5-ml portions of hexone for 30 sec each time. The combined hexone extract is washed for 20 sec with 5 ml of the acid mixture. The organic phase is evaporated to dryness in a boiling-water bath under an air jet stream. Any organic matter is oxidized by treatment with nitric and perchloric acid. The residue is treated with 2 ml of 48 per cent hydrofluoric acid, and the solution is evaporated just to dryness in a boiling-water bath. The steps described above for the calibration-curve preparation are now applied to the residue. A reagent blank is carried through the procedure.

Spectrophotometric Determination of Niobium in Zirconium and Zircaloy—Thiocyanate. Procedure.[526] Crystal-bar zirconium containing less than 2 ppm of niobium is used for the preparation of the standard curve. Samples of 0.25 g in platinum dishes are dissolved in 10 ml of water, 1 ml of 48 per cent hydrofluoric acid, and 3 drops of 30 per cent hydrogen peroxide. To these solutions are added, respectively, 0.0 (blank), 1.0, 2.0, and 3.0 ml of a standard niobium solution containing 10 μg per milliliter. To each solution is added 1 ml of sulfuric acid (1+1). The solution in each dish is heated to strong fumes of sulfur trioxide. The dish is cooled, the sides are washed down with water, and the solution is again heated to fumes. The solution is cooled, and 5 ml of concentrated hydrochloric acid and 5 ml of water are added. The dish is warmed and swirled until a clear solution is obtained. The solution is cooled to 10°C in an ice bath, and 4 ml of stannous chloride solution (15 g of dihydrate dissolved in 50 ml of concentrated hydrochloric acid; solution diluted to 100 ml) is added. After the solution has been stirred, 5 ml of 30 per cent (w/v) potassium thiocyanate solution is added. The solution is mixed and within 5 min is extracted with 10 ml of diethyl ether for 90 sec. The extract is diluted to 25 ml with diethyl ether. The absorbance is measured in stoppered 1-cm cells at 385 mμ against an ether reference. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

A sample is analyzed in the same manner. The absorbance is corrected for a reagent blank carried through the same procedure.

(c) *In Titanium.* Procedures for the determination of niobium (see Refs. 235 and 527–532) and tantalum (see Refs. 227 and 530–533) have been described in the literature.

(d) *In Niobium.* Procedures for the determination of tantalum in niobium have been described in the literature (see Refs. 519, 525, 534, and 535).

11–2.35 Tellurium in Uranium

The spectograph is generally used for the determination of traces of tellurium. However, concentrations down to 2 ppm in uranium metal can be determined [485] turbidimetrically by: reduction of the tellurium and added carrier selenium in a nitric–hydrochloric–phosphoric acid solution of uranium with sodium hypophosphite; dissolution of the separated elemental tellurium and selenium in a bromine–hydrochloric acid solution and evaporation of the solution to dryness to remove the selenium; and dissolution of the tellurium in dilute phosphoric acid and reduction again to the metal in the presence of gum arabic. The turbidity of the colloidal solution is measured in a filter photometer with a dark-blue filter. A recovery of only 50 to 80 per cent of the tellurium is obtained.

11–2.36 Thorium

(a) *In Uranium.* Traces of thorium in uranium metal and compounds are determined spectrophotometrically with 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid (thoron, thorin, thoronol, naphtharson, APANS).[536, 537] The red complex shows essentially a constant absorbance [537, 538] when produced over the pH range of 0.2 to 1.4. Many elements including uranium(IV), zirconium, titanium, tin, niobium, bismuth, and scandium interfere seriously. Moderate amounts of iron(III), rare earths, uranium(VI), and tungsten can also interfere. Traces of fluoride and appreciable quantities of phosphate, sulfate, and other anions cannot be tolerated (see Refs. 536, 537, 539, and 540). In the analysis of uranium, these interferences necessitate a separation procedure before the color reaction is applied.

Thorium in relatively impure uranium solutions can be precipitated as the fluoride with lanthanum as a carrier.[541] The fluoride precipitate is dissolved in perchloric acid, the solution is fumed to remove fluoride, and the thorin complex is produced for the optical measurement. Thorium in the same type of sample has been separated by ion-exchange techniques before the spectrophotometric determination.[542] In one procedure the sample in 9*M* hydrochloric acid is

passed through a column of anion resin Dowex–1. Thorium passes through the column; U(VI), Fe(III), and other elements forming chloro complexes are retained. In another procedure the sample in 1*M* sulfuric acid is passed through a column of cation resin Amberlite IR–120. Cations such as uranium(VI), cobalt, chromium(VI), copper, iron(III), molybdenum(IV), nickel, vanadium(IV), and titanium(IV), retained by the resin, are eluted with 2*M* hydrochloric acid. Thorium is then removed with 3*M* sulfuric acid. These procedures have not been applied to the analysis of purified uranium materials although they are apparently capable of determining microgram quantities of thorium. Laux and Brown [540] have evaluated the cation-exchange procedure with solutions of uranium-ore concentrates. Recovery of tracer quantities of ionium, Th^{230}, was complete as shown by activity measurements.

Smith [543] determines 50 to 300 ppm of thorium in 0.5-g samples of uranium by precipitating the uranium as peroxide at pH 2.0 in the presence of ethylenediaminetetraacetic acid (EDTA). After destruction of the EDTA with nitric and perchloric acid, Fe(III) is reduced with hydroxylamine, and the thorium-thorin complex is formed. Since some thorium is carried down by the peroxide and some uranium is found in the filtrate, the preparation of the standard curve must include the precipitation step. Interfering elements are assumed to be absent. Smaller quantities can be determined by the use of larger samples. It would appear necessary to study the interferences for the accurate determination of these smaller quantities.

A procedure involving both an iodate and an oxalate precipitation of thorium with suitable carriers is described in Rodden.[300] The iodate separation is carried out on a 1.6*M* nitric acid solution of uranium with 150 mg of mercurous ion carrier. The filtered iodates are dissolved in 6*M* hydrochloric acid, and an oxalate precipitation with 170 mg of carrier calcium ion at pH 5 is made. The ignited oxalate precipitate is dissolved in hydrochloric acid for the color development. Any Fe(III) surviving the double precipitation can be reduced with ascorbic acid. The lower limit of determination is about 5 ppm on a 1-g sample basis. Larger samples can be used.

2-Thenoyltrifluoroacetone (TTA) is used by Fulda [544] to separate thorium from uranium before the spectrophotometric determination. A summary of the extractability of other ions by TTA and a theoretical treatment of the chelate system are given by Morrison and Freiser.[545] Fulda extracts 0.5-g samples of uranium in 0.1*M* nitric acid with 0.5*M* TTA in xylene. Coextracted U(VI) is removed by washing the organic phase with 0.1*M* nitric acid. Thorium is then removed with 2.0*M* nitric acid for the color reaction. Laux and Brown [540] have made a comprehensive study of the TTA extraction–thorin procedure.

Essentially complete recovery of tracer ionium, Th^{230}, is obtained in the TTA extraction. The chief interferences found in the over-all procedure are tin, bismuth, and zirconium. If over 5 μg of zirconium, 25 μg of tin, and 50 μg of bismuth are present in the sample, a preliminary acid sulfide precipitation and color development in the presence of mesotartaric acid [539] is recommended. These metals, however, are generally not found in purified uranium materials in the quantities mentioned.

Spectrophotometric Determination of Thorium in Uranium—TTA Extraction, Thorin. Procedure.[544] A 10-ml volume of a nitric acid solution containing up to 100 μg of thorium and 500 mg of uranium is adjusted to pH 1.0±0.1 with nitric acid or sodium hydroxide solution. The solution is extracted with 2 ml of 0.5*M* TTA in xylene for 5 min. The organic phase is washed twice with 10-ml portions of 0.1*M* nitric acid for 2 min each time. The aqueous phases are discarded. The organic phase is washed twice, first with 3.0 ml and then with 5.0 ml of 2.0*M* nitric acid for 1 min each time. The aqueous phases are collected in a 50-ml volumetric flask.

To the solution is added 5 ml of 0.1 per cent thorin solution, and the solution is diluted to volume. The absorbance is measured in 5-cm cells at 545 mμ against a reference prepared by adding 15 ml of 1.0*M* nitric acid to 5 ml of 0.1 per cent thorin solution and diluting the mixture to 50.0 ml. The absorbance is corrected for a reagent blank. The standard curve is prepared by carrying 0 to 100 μg of thorium in 10 ml of dilute nitric acid through the entire procedure. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(b) *In Zirconium.* As discussed in Sec. 11–2.36(a), zirconium interferes seriously with the spectrophotometric determination of thorium with thorin. However, Fletcher, Grimaldi, and Jenkins [539] have shown that mesotartaric acid is a satisfactory masking agent for as much as 8 mg of zirconium in 25 ml of solution. By developing the color in a mesotartaric acid–thorin system, down to 500 ppm of thorium in zircon can be determined directly after a suitable dilution of the sample solution. Quantities of thorium down to 100 ppm in zircon are first separated by an iodate precipitation with mixed Fe(III)–Hg(II) carrier from a nitric acid solution containing hydrogen peroxide, *d*-tartaric acid, and 8-quinolinol (oxine).[546] The hydrogen peroxide minimizes the precipitation of any titanium, niobium, and tantalum; the *d*-tartaric acid inhibits the precipitation of zirconium, tungsten, scandium, and bismuth. Oxine prevents the catalytic decomposition of hydrogen peroxide. The final color development is carried out in the presence of mesotartaric acid. Hydroxylamine hydrochloride plus cupric chloride catalyst prevents interference from Fe(III). This procedure probably can be adapted to the determination of smaller amounts of thorium in zirconium metal.

Horton and Moak [547] determine microgram quantities of thorium in Zircaloy–2 by X-ray fluorescence after isolation of the thorium on an ion-exchange membrane, Amberplex C–1. The procedure is also applicable to zirconium metal and to Zircaloy–1 and Zircaloy–3. Samples of 1 g are dissolved in mixed acid, fluoboric, sulfuric, and hydrochloric acid; citric acid is added; and the pH is adjusted to 1.8. A ½-in disk of membrane is stirred in the solution for 24 hr. The dried membrane is then placed in an X-ray fluorescence spectrometer, and the main thorium line $L\alpha_1$ is excited. Horton and Moak also determine traces of thorium in Zircaloy–2 by an isotope dilution–mass spectrometer technique with tracer ionium, Th^{230}. After equilibration in the solution, an ion-exchange membrane is washed with 0.05*M* citrate at pH 4.78 to remove the retained thorium. The citrate is destroyed with nitric acid, and the Th^{230} to Th^{232} ratio is determined to obtain the Th^{232}.

11–2.37 Tin

(a) *In Uranium.* Apparently no spectrophotometric procedures for the determination of traces of tin in uranium are available at the present time. However, the chromogenic reagent toluene-3,4-dithiol (dithiol) [207] should be applicable if a separation of the tin as the volatile tetrabromide is made after the removal of arsenic, antimony, and other elements as volatile chlorides.[548] If a dispersant, Santomerse S (Monsanto Chemical Co.), is added, the red complex in the final solution can be measured with transmitted light instead of with reflected light as was formerly necessary. Menis, Manning, and Ball [549] investigated the distillation separation of tin from uranyl sulfate solutions and found that 100 to 500 μg could be recovered satisfactorily. Below 50 μg the recovery was erratic and high, presumably due to the high tin blank in the hydrogen peroxide used to destroy bromide. Farnsworth and Pekola,[548] on the other hand, report quantitative recoveries down to the 6-μg level.

Dithiol has been applied to the spectrophotometric determination of macro amounts of tin in uranium–Zircaloy alloys.[550] The tin is first extracted as the diethyldithiocarbamate, followed by destruction of the organic matter and color development in the presence of Santomerse S. Marley and Articolo [550] note that only the "old" Santomerse S is effective and suggest that the older product rather than the new be requested when the material is ordered.

Menis, Manning, and Ball [549] prefer to separate traces of tin from uranyl sulfate solutions by precipitation with ammonium hydroxide from a basic carbonate solution with aluminum as a carrier. The tin is determined polarographically in a hydrochloric acid–ethyl alcohol medium. Down to 5 μg of tin in the presence of not more than 200 mg

of uranium can be determined. If more than 200 mg of uranium is present, a necessary second precipitation results in losses of tin. Lead interferes.

Polarographic Determination of Tin in Uranium—Hydroxide Precipitation. Procedure.[549] An aliquot of uranyl sulfate solution containing at least 5 μg of tin and not more than 200 mg of uranium is placed in a conical centrifuge tube. To the tube are added 1 to 2 ml of aluminum nitrate solution containing 5 mg of aluminum per milliliter and 2 drops of methyl red solution (0.1 g dissolved in 60 ml of ethyl alcohol; solution diluted to 100 ml with water). The solution is neutralized with ammonium hyroxide, and then is reacidified with a few drops of 7*N* nitric acid. To the tube is now added 40 ml of basic carbonate reagent (25 g of ammonium carbonate dissolved in 500 ml of water; 70 ml of concentrated ammonium hyroxide added; solution diluted to 1 liter). After the solution is well mixed, it is centrifuged for 5 min. The supernatant liquid is decanted, and the precipitate is washed twice with 5-ml portions of basic carbonate reagent. After each wash the mixture is centrifuged. To the precipitate is added 3 ml of concentrated hydrochloric acid, and the mixture is gently heated until the precipitate dissolves. The solution is cooled, 2 ml of 95 per cent ethyl alcohol is added, and the solution is diluted to 10.0 ml.

The solution is transferred to a polarographic cell and deaerated. The polarogram is recorded from −0.4 to −0.7 volt vs. a saturated calomel electrode (S.C.E.). The diffusion current of the Sn(II) to Sn(0) reduction at −0.55 volt vs. S.C.E. is measured.

(b) *In Zirconium.* As with uranium there has been little interest up to the present time in the development of a chemical method for traces of tin in zirconium. The determination of relatively large amounts of tin in Zircaloys and other zirconium alloys, however, is often necessary. Although the determination of these alloying quantities is beyond the scope of this chapter, a brief survey of the available procedures may be helpful.

Volumetric procedures adapted from methods found in standard texts have been used. Reduction to tin(II) is carried out by metallic lead,[288] antimony,[551] iron in the presence of antimony(III),[288] aluminum,[552] and aluminum plus titanium(III).[553] Standard iodate–iodine solution is generally the titrant.

Polarographic procedures can be applied directly after dissolution[554, 555] or after separation of the tin by steam distillation with hydrobromic acid.[556] One direct procedure utilizes the reduction of tin (II) at −0.25 volt vs. S.C.E. in a hydrochloric–sulfuric–fluoboric acid mixture.[554] In another direct procedure[555] the reduction wave at −0.25 volt vs. the mercury-pool electrode is measured in a bromide medium. With the distillation separation procedure,[556] the polarographic measurements are made in a similar medium.

Spectrophotometric procedures with dithiol, discussed above under "Tin in Uranium," require an ion-exchange separation of the tin.[550]

A solution of Zircaloy in 3*N* hydrochloric acid is added to a column of anion resin, Dowex–2, and the column is washed with 3*N* hydrochloric acid to remove zirconium and other elements. The tin is eluted with 3.6*N* sulfuric acid. The color with dithiol is developed in the presence of the dispersant Santomerse S so that transmitted light can be used for the absorbance measurements. In the case of uranium–zirconium alloys,[550] a prior separation of the tin and other elements is made by extraction of the diethyldithiocarbamates with chloroform before color development.

(c) *In Titanium.* Procedures for the determination of tin in titanium have been described in the literature (see Refs. 226, 227, 231, 235, 239, 333, 401, and 557).

11–2.38 Titanium

(a) *In Uranium.* Both hydrogen peroxide and the more sensitive thymol are used in spectrophotometric procedures developed for the analysis of uranium. A preliminary separation step is required with both reagents.

A red-orange color is produced [207] when hydrogen peroxide is added to an acid solution containing Ti(IV). Vanadium(V), molybdenum (VI), and chromium(VI) give colored products under similar conditions and must be removed. Uranium(VI), iron(III), nickel, and other ions interfere because of their colors. After a cupferron extraction and a subsequent sodium hydroxide precipitation applied to the extracted metals with an iron carrier if necessary, a precipitate is obtained that consists primarily of titanium, iron, and traces of uranium and other colored ions.[379] The effect of these colored ions can be practically eliminated by measuring the absorbance of the peroxidized titanium against a reference in which the titanium color is not produced.[207, 379] Fluoride and phosphate bleach the color of the pertitanic acid. Fluoride is easily removed by fuming; phosphate interferes only slightly [207] if the absorbance is measured at 400 mμ.

Titanium can also be separated from uranium by hydrogen peroxide prior to color development with the same reagent. An optimum pH of 3 to 4 for the precipitation of the uranium peroxide is given in Rodden.[379] A pH of 2.5 and a digestion period of 3 hr have been recommended for the separation.[558]

Both the cupferron [559, 560] and the peroxide [558] separations are applicable if thymol [561] is used as the chromogenic reagent. This reagent is at least 10 times more sensitive than hydrogen peroxide for titanium. When a prior cupferron extraction is applied, only iron interferes by its color and by the precipitation of Fe(III) sulfate in the concentrated sulfuric acid solution employed for the color development. Either hydroxylamine or phosphoric acid can be used to minimize

the interference. Traces of vanadium, tungsten, or uranium do not interfere. Nitrates and nitrites must be removed by fuming. When the peroxide precipitation of uranium is used, only the peroxide in the filtrate must be removed by fuming before the color is developed in concentrated sulfuric acid. Both procedures have a lower limit of determination of about 1 ppm with 5-g samples.

Spectrophotometric Determination of Titanium in Uranium–Cupferron Extraction, Thymol. Special Apparatus. All beakers used in the preparation of the thymol reagent and in the calibration must be fumed. with sulfuric acid prior to use to avoid high blanks.

Special Reagents. Thymol Solution. A solution of 5 g of thymol dissolved in 5 ml of glacial acetic acid is poured, with constant stirring, into 95 ml of concentrated sulfuric acid. For use as required, 10 ml of the solution is diluted to 100 ml with concentrated sulfuric acid.

Purified Cupferron Solution. To a filtered solution of 5 g of cupferron in 100 ml of water is added 50 ml of sulfuric acid (1+1), and the mixture is filtered immediately on a Buchner funnel. The precipitate is washed quickly with 40 ml of water, and the precipitate is transferred at once to a beaker containing 3 ml of concentrated ammonium hydroxide in 50 ml of water. The mixture is stirred and filtered. The solution is diluted to 100 ml, and 1 drop of 30 per cent hydrogen peroxide is added. The solution is extracted with 10 ml of chloroform, and the organic phase is discarded. When this cupferron solution is titrated in sulfuric acid (1+1) with 0.5*N* potassium permanganate, 5 ml should require 10 ml of permanganate solution.

Procedure.[560] A 5-g sample containing less than 20 ppm of titanium is dissolved in 20 ml of nitric acid (1+1). The solution is boiled for a few minutes, cooled, diluted to 50 ml; then it is transferred to a 250-ml separatory funnel. Concentrated ammonium hydroxide is added dropwise until a permanent precipitate forms. The precipitate is redissolved by the dropwise addition of concentrated hydrochloric acid, then 5 ml in excess is added. The solution is diluted to 100 ml.

To the separatory funnel is added 5 ml of cupferron solution. The solution is extracted with 10-ml portions of chloroform until the last extract is colorless. If the initial extracts are deep brown in color, denoting a large amount of iron, an additional 5 ml of cupferron is added after the second extract. The extracts are filtered through dry Whatman No. 41 paper into a 150-ml flask. The organic phase is evaporated to dryness, 3 ml of concentrated sulfuric acid is added, and the flask is heated to copious fumes of sulfur trioxide. Concentrated nitric acid is added dropwise until the organic matter is destroyed. The solution is fumed for 30 min and cooled. To the solution is added 25 ml of water, and the solution is evaporated to fumes. When the solution has cooled, 20 ml of water and 3 ml of phosphoric acid solution (50 ml of syrupy phosphoric acid diluted to 150 ml) are added, and the solution is again evaporated to fumes. The solution is cooled to room temperature.

To the solution is now added 5 ml of the diluted thymol reagent, and the mixture is transferred to a dry 25-ml stoppered cylinder. The flask is rinsed with concentrated sulfuric acid. The solution is diluted to 25 ml with concentrated sulfuric acid.

The absorbance is measured at 440 mμ in 2-cm cells against concentrated sulfuric acid. The absorbance must be corrected for a reagent blank carried through the entire procedure. The standard curve is prepared by adding from 0 to 100 μg of titanium to 3 ml of concentrated sulfuric acid, evaporating to fumes, cooling, adding 5 ml of the diluted thymol reagent, and diluting to 25 ml with concentrated sulfuric acid. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(b) *In Thorium.* A direct polarographic procedure based upon the use of a perchloric acid medium containing 0.6*M* citrate at pH 5.7 has been applied to the determination of greater than 100 ppm of titanium in thorium oxide slurries.[562, 563]

Direct hydrogen peroxide procedures are available for amounts greater than 10 ppm. The color of the peroxidized titanium can be developed in solutions prepared by dissolving the metal in nitric acid plus a trace of fluosilicic acid.[214] In the analysis of thorium oxide slurries,[216] a perchloric acid solution containing phosphoric acid to complex Fe(III) is recommended. In this procedure interfering quantities of molybdenum are removed either by extraction with α-benzoinoxime in chloroform or by extraction with methyl isobutyl ketone (hexone) from a chloride solution. A direct peroxide procedure has also been applied to the analysis of thorium oxide–uranium oxide slurries.[311] Interference from molybdenum and vanadium is eliminated by measuring the absorbance at 330 and 460 mμ, respectively, and applying the calculated corrections.

8-Quinolinol (oxine) has been studied for the determination of greater than 20 ppm of titanium.[216, 564, 565] Titanium in a solution of thorium complexed with a high concentration, 6*M*, of acetate ion is extracted at pH 4.5 to 5 with oxine in chloroform.[217] Various interferences are eliminated by washing the extract with alkaline cyanide[564] or by a mercury-cathode electrolysis before the extraction.[565] In a novel procedure[216] the extract is treated with hydrogen peroxide; the titanium–oxine complex color is enhanced, and the absorption maximum is shifted to a longer wave length. The colors of the oxine complexes of other ions commonly interfering are not altered by this treatment. Therefore, the interference due to aluminum, iron, chromium, manganese, nickel, zinc, and zirconium is circumvented.

A sensitive procedure[216] capable of determining 2 to 10 ppm of titanium utilizes 1,2-dihydroxybenzene-3,5-disulfonate (tiron), discussed briefly below under "Titanium in Zirconium." The yellow color of the titanium–tiron complex is developed at pH 4 in a 2*M* acetate solution which is 0.05*M* in ethylenediaminetetraacetate (EDTA). The EDTA complexes both thorium and iron. In the

analysis of thorium oxide slurries, molybdenum interferes and must be removed by extraction with hexone;[566] uranium must be removed by retention on a column of anion-exchange resin, Dowex–1.[567] Large amounts of chromium are removed by volatilization as chromyl chloride prior to the extraction or ion-exchange separation.

(c) *In Zirconium.* Direct hydrogen peroxide procedures have been applied to the determination of titanium in zirconium and Zircaloys. Fluoride, used in the sample dissolution, is either fumed off [288, 291, 568] or complexed with boric acid.[569] A portion of the sample solution is used as a reference in the optical measurements to eliminate the background color of other impurities. Corrections for the interference of molybdenum and vanadium can be made by the following expression: [569]

$$\text{Actual Ti}(\mu g) = \text{apparent Ti}(\mu g) - 0.200\ \text{V}(\mu g) - 0.087\ \text{Mo}(\mu g)$$

Beaumont [396] determines both titanium and iron in zirconium solutions by the disodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron) procedure of Yoe and Armstrong.[395] In a fluoride solution at pH 4.7 containing boric acid and acetate buffer, Fe(III) forms a blue complex, and titanium a yellow complex with the reagent. The color of the titanium complex does not interfere with the measurement of the iron color; however, the blue color must be destroyed by reducing the Fe(III) to Fe(II) with sodium dithionite before the absorbance of the titanium color is measured. The reagent is seven times as sensitive as peroxide for titanium, but only a quarter as sensitive as *o*-phenanthroline for iron. Of the elements interfering with the titanium determination [silver, bismuth, mercury(II), molybdate, osmate, and copper(II)], only copper(II) is normally found in significant amounts of zirconium. Copper can be removed by a prior dithizone extraction, or a correction for the amount present can be applied.

A useful procedure [570] for the determination of traces of titanium, involving the reaction of titanium(IV) with sulfosalicylic acid in concentrated sulfuric acid to give a stable intense yellow color, has been applied to the analysis of zirconium and Zircaloys by Reed.[571] Interference from iron and vanadium is negligible if the sample contains less than 0.2 per cent iron and 100 ppm of vanadium. Fluoride must be fumed off. Background color due to traces of colored ions is compensated by the use of a sample solution reference in the absorbance measurements. The procedure, as described below, is suitable for the determination of from 10 to 100 ppm with a 1-g sample.

Spectrophotometric Determination of Titanium in Zirconium and Zircaloy—5-Sulfosalicylic Acid. Procedure.[571] A 2.5-g sample is placed in a platinum dish, and 20 ml of sulfuric acid (1+1) is added.

The sample is dissolved by the dropwise addition of 2 ml of 48 per cent hydrofluoric acid plus 5 to 10 drops of concentrated nitric acid. When dissolution has been completed, 25 ml of concentrated sulfuric acid is added, the lid and sides of the dish are washed down, and the solution is evaporated to fumes. The dish is cooled, washed down again, and warmed gently to dissolve any hydrolyzed salts; then the solution is again fumed. The solution is cooled and transferred to a 50-ml volumetric flask; the dish is rinsed with concentrated sulfuric acid in the transfer. The solution is diluted to volume with concentrated sulfuric acid.

A 20-ml aliquot is placed in each of two 50-ml volumetric flasks. One aliquot is diluted to volume with concentrated sulfuric acid for use as a reference solution. To the other aliquot is added 10 ml of 5-sulfosalicylic acid solution (25.0 g of reagent dissolved in 200 ml of concentrated sulfuric acid with the aid of gentle heating: solution diluted to 250 ml with concentrated sulfuric acid). The solution is diluted to volume with concentrated acid. After 1 hr the absorbance is measured in 5-cm cells at 450 mμ against the reference solution. The absorbance is corrected for a reagent blank carried through the procedure.

The standard curve is prepared by adding 25 ml of concentrated sulfuric acid to 0 to 100 μg of titanium in a platinum dish. The solution is evaporated to fumes. When cool, the solution is transferred to a dry 50-ml volumetric flask by the use of concentrated sulfuric acid. After the addition of 10 ml of sulfosalicylic acid solution, the solution is diluted to volume with concentrated acid. After 1 hr the absorbance of each solution is measured against concentrated sulfuric acid as a reference. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Niobium.* A procedure for the determination of titanium in niobium has been described by Dickinson and Ryan.[572]

11–2.39 Tungsten

(a) *In Uranium.* Apparently no further work has been done on the determination of tungsten in uranium since that reported in Rodden.[326] In the procedure described traces of tungsten are determined spectrophotometrically by utilizing the blue-green color of the tungsten complex with toluene-3,4-dithiol (dithiol). Both tungsten and molybdenum are isolated from the uranium and other elements by a prior precipitation with α-benzoinoxime. Molybdenum is removed before the final color development by extraction of its thiocyanate complex. The dithiol reaction is discussed briefly below under the analysis of zirconium.

Determination of Tungsten in Uranium—α-Benzoinoxime Precipitation, Dithiol. Procedure.[326] A suitably sized sample is dissolved in a minimum quantity of concentrated nitric acid plus 2 to 3 ml of 48 per cent hydrofluoric acid. After dissolution, 5 ml of concentrated sulfuric acid is added; the solution is evaporated to fumes, cooled, and diluted to about 100 ml.

To the solution is added with stirring 15 ml of 2 per cent α-benzoinoxime solution (2 g in 100 ml of ethyl alcohol), followed by sufficient bromine water to color the solution, and then an additional 10 ml of the α-benzoinoxime solution. The solution is cooled to about 10°C for 20 min. A small amount of filter pulp is added, and the solution is filtered through Whatman No. 40 paper. The paper is washed with dilute sulfuric acid containing a small amount of α-benzoinoxime and then with water. The paper is ignited at the lowest possible temperature. The residue is fused with 1 g of fusion mixture (1 part sodium carbonate to 2 parts potassium carbonate), and the cooled melt is leached with water. Any insoluble material is filtered off.

About 6 drops of 50 per cent thioglycolic acid followed by 1 ml of 20 per cent potassium thiocyanate solution are added to the solution. For each 30 ml of solution, 7 ml of concentrated sulfuric acid is added. The solution is cooled, and the molybdenum(V)–thiocyanate is extracted with two 25-ml portions of *n*-butyl acetate. The organic phase is discarded.

About 10 ml of concentrated nitric acid is added to the aqueous phase, and the solution is evaporated to fumes. The sides of the beaker are washed with water, and the solution is again evaporated to fumes. The solution is cooled, diluted to about 50 ml, made just ammoniacal, and cooled again. To the solution is added 0.5 ml of 0.2 per cent dithiol solution (0.2 g in 100 ml of 1 per cent sodium hydroxide solution) followed by 5*N* sulfuric acid until a distinct turbidity appears. An excess of 5 drops of acid is added, and the solution is allowed to stand for 20 min. The tungsten complex is extracted with 5-ml portions of *n*-butyl acetate; the extracts are filtered through dry paper into a graduated cylinder of suitable size. The volume is adjusted with *n*-butyl acetate, and the absorbance is measured at 630 mμ against a water reference. The absorbance is corrected for a reagent blank. A standard curve is prepared with quantities of tungsten carried through the entire procedure.

(b) *In Zirconium.* The colors given by thiocyanate [207] or toluene-3,4-dithiol (dithiol)[207] with reduced tungsten are generally used for the spectrophotometric determination of tungsten in zirconium and zirconium alloys. The red color of tungsten(VI)–hydroquinone in concentrated sulfuric acid [207] has also been applied.

In the thiocyanate procedures the reducing agents are most commonly stannous chloride [288, 573, 574] or titanous chloride.[291, 575] A critical investigation of the formation of the tungsten(V)–thiocyanate complex is reported by Freund, Wright, and Brookshier [574] and by Crouthamel and Johnson.[439] The yellow complex produced in strong hydrochloric acid is generally measured directly, but, for greater sensitivity and freedom from the effect of the common colored ions, the color may be extracted before measurement.[207, 291, 439] Extraction, however, may increase the interference of such ions as Ti(IV), Nb(V), Co(II) and V(III), which require a nonaqueous medium for color development.[439] Although many organic solvents do not extract the

tungsten complex quantitatively,[575] isopropyl ether or a 1:1 mixture of isoamyl alcohol and chloroform apparently is suitable.[207, 576] Conflicting statements regarding the extracting ability of diethyl ether have been made.[439, 575]

With direct measurement of the color, colored ions such as chromium, nickel, and vanadium interfere, but, with a proper reference solution for the absorbance measurement, this effect is overcome. In the presence of copper, cuprous thiocyanate may precipitate, but the precipitate occludes little tungsten. Molybdenum over 0.05 per cent interferes. The procedure has a lower limit of about 25 ppm on a 0.5-g sample basis.

Reduction with tin amalgam in the presence of stannous chloride is also recommended.[288, 576] In this case the tungsten is said to reduce to the trivalent state. With this technique the interference of molybdenum is relatively small but that of vanadium and niobium is rather serious.[207]

The dithiol procedure depends on the formation of a blue-green complex of tungsten with dithiol and extraction of the complex with an organic solvent such as isoamyl acetate, amyl acetate, or carbon tetrachloride.[207] Although more lengthy than the direct thiocyanate procedure, this procedure is more sensitive since concentrations down to 0.001 per cent can be determined. Molybdenum forms a green extractable complex with dithiol and consequently interferes seriously.

Two methods are used to remove the molybdenum prior to the formation and extraction of the tungsten complex. Greenberg [577] has adapted the technique of Bagshawe and Truman [442] and Short [449] of extracting with amyl acetate the molybdenum–dithiol complex from a cold dilute hydrochloric acid solution prior to the extraction of the tungsten compound formed in a hot solution of increased acidity. Carbon tetrachloride has been used with this technique as the extracting agent.[447] Wood and Clark [575] find selective extraction [442, 447, 449] to be somewhat erratic and prefer to precipitate the molybdenum as sulfide prior to extraction of the tungsten-dithiol compound with isoamyl acetate.

The composition of the dithiol complex is not clear; Wood and Clark [575] state that the presence of iron is necessary to obtain quantitative production of the color. The reactive valence state [577] is apparently W(V). The stannous chloride or titanous chloride reducing agent required to obtain the W(V) also serves to decrease the interference of iron and other metals.[207, 442]

Spectrophotometric Determination of Tungsten in Zirconium and Zircaloy—Direct Thiocyanate. Procedure.[578] A 0.5-g sample is weighed into an unscratched pyrex 150-ml beaker. The sample is covered with water; 1 ml of 48 per cent hydrofluoric acid is added, and the beaker is

covered with a watch glass. When the reaction subsides, 0.5 ml of concentrated nitric acid is added, and the watch glass is rinsed. To the beaker is carefully added 5 ml of concentrated sulfuric acid, and the solution is evaporated to fumes. The solution is cooled, the beaker sides are washed down, and the solution is again fumed until it becomes turbid. The solution is cooled, and 2.5 ml of water is added. The solution is gently warmed until any turbidity disappears.

The solution is transferred to a 25-ml volumetric flask. The beaker is rinsed with two 2.5-ml portions of concentrated hydrochloric acid and 2.5 ml of 1*M* stannous chloride solution [113 g of dihydrate in 100 ml of concentrated hydrochloric acid; solution diluted to 500 ml with hydrochloric acid (1+3) and a few pieces of tin added; solution prepared fresh weekly]. The solution is mixed and allowed to stand for 2 to 5 min. The flask is immersed in a boiling-water bath for exactly 10 min. The solution is cooled to below room temperature by immersing the flask in an ice bath, and 2.5 ml of 2*M* potassium thiocyanate (194 g in 1 liter of solution) is added. The solution is diluted almost to volume, cooled again, and finally diluted to volume.

After 15 min the absorbance is measured at 400 mμ in 1- to 5-cm cells against water. If a precipitate of cuprous thiocyanate forms owing to the presence of greater than 200 ppm of copper after the addition of the thiocyanate, the solution is filtered before the absorbance is measured.

Another 0.5-g sample is carried through the same procedure except that the thiocyanate is omitted. The absorbance of this sample "blank" against water is subtracted from the absorbance of the sample. In most cases the sample blank can be omitted. With Zircaloy-2 the sample blank corresponds to 2 μg of tungsten on a 0.5-g sample. Correction should also be made for a reagent blank.

The standard curve is prepared by carrying aliquots of a standard tungsten solution, conveniently prepared by dissolving sodium tungstate dihydrate in water, containing from 0 to 200 μg of tungsten, through the entire procedure.

(c) *In Titanium.* Procedures for the determination of tungsten in titanium have been described in the literature (see Refs. 227, 231, 235, 316, 449, 450, 575, and 577–579).

(d) *In Niobium.* A procedure for the determinaton of tungsten in niobium has been described by Reed et al.[452]

11–2.40 Uranium

(a) *In Thorium.* Traces of uranium in thorium can be determined fluorometrically. Although thorium quenches the fluorescence of uranium, a direct semiquantitative procedure involving the fluorescence in glassy phosphoric acid has been used.[580] Other procedures, based upon the fluorescence in a flux of sodium fluoride, mixtures of alkali fluorides, or mixtures of alkali carbonates and fluorides,[581, 582] require prior separation of the uranium. The fluorometric procedures that are applied after separation are described in Chap. 1, Sec. 1–3.4.

Various separation procedures are reported. The thorium can be removed by extracting a nitrate solution at pH 1 with 2-thenoyltri-

fluoroacetone (TTA) in chloroform.[214] Cellulose column procedures are reported.[583-587] Separation of the thorium by oxalate precipitation has been used.[330, 588] The uranium can be extracted with tributyl phosphate (TBP) from a 6*M* hydrochloric acid solution,[589] or by methyl isobutyl ketone (hexone) from a nitrate solution salted with aluminum nitrate.[214]

Spectrophotometric procedures[581] can be applied after the separations described above if the quantity of uranium present is sufficiently large. The spectrophotometric determinations are discussed in detail in Chap. 1, Sec. 1–3.3. Thus the alkaline peroxide procedure is applied after the cellulose column separation.[585] The thiocyanate procedure has been used after a diethyl ether extraction of the uranium.[214] A procedure involving the extraction of the uranium thiocyanate complex with dibutoxytetraethylene glycol (pentaether) and subsequent spectrophotometric determination has been reported.[590] Thiocyanate is also used in the analysis of thorium oxide slurries after the extraction of the molybdenum with α-benzoinoxime.[216]

A useful procedure reported is based upon the extraction of uranium with tributyl phosphate (TBP) and subsequent spectrophotometric determination with 8-hydroxyquinoline (oxine).[591] This procedure, applicable to the analysis of thorium, bismuth, and low-grade ores, is described in detail in Chap. 1, Sec. 1–3.3(c)(1).

In another spectrophotometric procedure described,[592] the 1-(2-pyridylazo)-2-naphthol complex of uranium is produced at pH 10 in the presence of potassium cyanide and ethylenediaminetetraacetate (EDTA), and the complex is extracted with *o*-dichlorobenzene.[593] The absorbance of the extract is measured at 570 mμ.

(b) *In Zirconium.* Traces of uranium in zirconium and Zircaloy are determined fluorometrically.[594] A prior separation of the uranium is made by a diethyl ether extraction.[594] An ethyl acetate extraction in the presence of disodium hydrogen phosphate to hold back zirconium has been applied to the analysis of zirconium oxide.[595] For a complete discussion of the extraction and fluorometric determination of uranium, see Chap. 1, Sec. 1–3.4.

Fluorometric Determination of Uranium in Zirconium and Zircaloy–Diethyl Ether Extraction. Special Apparatus. Galvanek–Morrison Fluorometer (Jarrell–Ash Company). Platinum dishes, formed from ¾ in. by 10 mil blank with Jarrell–Ash die.

Procedure.[594] A calibration curve is prepared by adding 0 to 5 ml of a standard solution containing 1.0 μg of uranium per milliliter to 4-oz polyethylene bottles containing 1 g of uranium-free (<0.1 ppm) zirconium. To each bottle are added 10 ml of water and about 30 drops of 48 per cent hydrofluoric acid, 5 drops at a time, to dissolve the sample. After the sample has been dissolved, 0.5 ml of concentrated nitric acid and 5 g of solid aluminum nitrate nonahydrate are

added. The bottle is shaken until the salt dissolves to complex fluoride ion, and 20 g of ammonium nitrate and 10 ml of diethyl ether are added. The bottle is capped tightly and shaken for 5 min on a mechanical shaker. The solution is transferred to a 60-ml separatory funnel without rinsing.

The aqueous layer is discarded, and the ether layer is drained into a 50-ml beaker containing 3 ml of water. The ether is evaporated, and the aqueous layer is transferred to a 10-ml volumetric flask, cooled, and diluted to volume. An aliquot of 0.25 ml from each solution is pipetted into a platinum dish and evaporated to dryness under moderate heat from an infrared lamp. The dish is heated to momentary redness over a Meker burner. A compressed pellet of fusion mixture (98 per cent sodium fluoride–2 per cent lithium fluoride) weighing 0.3 g is added to the dish. The pellet is fused exactly 3 min over a gas burner. The button is removed and cooled, and its fluorescence is measured. A blank reading on a pellet is obtained and subtracted from the readings of each standard.

A 1.0-g sample is weighed into a polyethylene bottle containing 10 ml of water. The sample is dissolved by adding 30 drops of 48 per cent hydrofluoric acid, 5 drops at a time. The procedure is continued as described above. A reagent blank and a control standard are carried through the entire procedure.

11–2.41 Vanadium

(a) *In Uranium.* Quantities down to 0.02 per cent of vanadium in uranium have been determined coulometrically at constant current.[596] Added ferric ion serves as a "carrier" to assist in the reduction of the metavanadate to vanadyl ion. The end point is observed amperometrically. Interferences were not studied.

Spectrophotometric procedures are by far the most useful. Quantities of vanadium down to about 0.004 per cent can be determined directly with hydrogen peroxide.[522] Titanium(IV), molybdenum (VI), and chromium(VI) in moderately strong acid solution give colors [207] along with vanadium(V). The titanium color can be bleached with fluoride.[207, 522] The molybdenum interference is generally not serious because the color reaction is not sensitive and molybdenum is rarely present in significant amounts. The color given by chromium fades rapidly.[207] Colored ions such as chromium, nickel, cobalt, and iron will cause errors if present in appreciable amounts, but this effect can be decreased by using a portion of the sample solution as a reference for the absorbance measurements. Fluoride or phosphate decreases the iron interference. A wave length of 530 mμ [522] or 520 mμ [597] is used instead of the maximum at 450 mμ to avoid the interference of uranium. It is recommended that a vanadium-free uranium solution be used for the reagent blank and standard curve preparation because the red-brown color of the peroxide product is slow in forming and is rather unstable in the presence of uranium.[597] Peroxide is

recommended for the analysis of uranium-vanadium alloys containing from 0.05 to 0.30 per cent vanadium.[597]

Trace amounts of vanadium in uranium are best determined after a separation of the vanadium and other metals by extraction of the cupferrates with chloroform from dilute acid solution.[522] Sample dissolution in the presence of fluorides should be carried out under reflux to avoid loss of volatile vanadium oxyfluoride.[598] The optimum pH for extracting vanadium(V) cupferrate from perchloric acid solutions of uranium is 1.2 to 1.6.[598] Traces of uranium and elements extracting along with the vanadium, such as iron and copper, may interfere in the subsequent colorimetric determination. These elements can be removed by either a sodium hydroxide leach of the residue obtained after destruction of the cupferrates with nitric and perchloric acid or preferably by a sodium hydroxide precipitation carried out on a solution of the residue.[598] A sodium hydroxide fusion is sometimes used to remove iron and other interfering elements and to destroy the organic matter after the cupferron extraction.[599]

The final determination [599] can be based upon the formation of the yellow phosphotungstovanadic acid by the addition of phosphoric acid and tungstate to the acid V(V) solution.[207] Optical measurements made at 370 mμ yield more reproducible results [599] than those made at the maximum at 350 mμ. Generally, no interferences are encountered if the cupferron separation and subsequent hydroxide precipitation are carried out. If only traces of iron, copper, and cerium are present in the sample, the hydroxide precipitation can be omitted.[600] The solution prepared from the cupferron extract should contain at least 10 μg of vanadium for the color development.

The spectrophotometric determination can be carried out with 8-quinolinol (oxine). In the presence of oxine and ethyl alcohol, V(V) forms a red complex that can be extracted with chloroform at pH 4±0.5 and measured [522] at 475 mμ. Again, if this procedure is applied after the cupferron separation and subsequent iron removal, no interferences are met. The lower limit of determination is about 10 μg of vanadium.

With both procedures depending on cupferron separation as described above, the accurate determination of less than 10 μg of vanadium apparently is difficult. Recoveries of less than 20 μg of vanadium in a cupferron extraction are said to be generally incomplete; blanks as high as 8 μg are common. A more reliable separation procedure appears to be the extraction of the uranium with tributyl phosphate.[601] The final determination by oxine is carred out [602] by extracting the magenta-colored oxinate with chloroform in the absence of ethyl alcohol at pH 4.0. Iron(III) oxinate also extracts and interferes with the color measurement, but this difficulty is easily avoided by washing

the extract with an ammoniacal buffer at pH 9.4. The iron remains in the organic phase, and the vanadium, transferred to the aqueous phase, is then re-extracted into chloroform. The procedure, originally devised for the analysis of hexafluoride but applicable to metal, is described below. The procedure is lengthy but is said to be reliable for the determination of 1 to 10 ppm. Reagent blanks generally are less than 1 μg.

Spectrophotometric Determination of Vanadium in Uranium—Tributyl Phosphate Extraction, Oxine. Procedure.[601] A 1- to 5-g sample is dissolved in nitric acid (1+1). The solution is evaporated to dryness and taken up in the minimum quantity of 5*M* nitric acid. The solution is extracted three times with an equal volume of tributyl phosphate (TBP)–carbon tetrachloride [(3+7) washed first with 0.1*N* sodium hydroxide, then with water until all the washings are neutral] and twice with half volumes of carbon tetrachloride. The organic phases are discarded.

The aqueous phase is evaporated to dryness; 1 ml of 70 per cent perchloric acid is added, and the solution is again evaporated to dryness. The residue is dissolved in 2 to 3 drops of concentrated nitric acid followed by about 20 ml of water. The pH is adjusted to 4.0±0.2 with dilute ammonium hydroxide. The solution is extracted for 5 min each with two 10-ml portions of 1 per cent (w/v) oxine in chloroform (the preservative ethyl alcohol removed by washing with six separate portions of water, each portion a quarter of the volume of the chloroform), then 2 min each with three 5-ml portions of 1 per cent oxine. The organic extracts are collected in a separatory funnel containing 50 ml of ammoniacal buffer solution (6.4 ml of concentrated nitric acid plus 13.3 ml of concentrated ammonium hydroxide in 500 ml of solution adjusted to pH 9.4). The last oxine–chloroform extract should be colorless.

The chloroform extract–ammoniacal buffer mixture is equilibrated for 5 min. The chloroform phase is discarded. The aqueous phase is washed with 5-ml portions of chloroform until the washings are colorless. The solution is warmed to evaporate droplets of chloroform, the solution is cooled, and the pH is adjusted to 4.0±0.2 with dilute nitric acid.

The vanadium is re-extracted by shaking for 5 min with five 5-ml portions of 0.1 per cent oxine in chloroform. The extracts are collected in a 25-ml cylinder and brought to volume with chloroform.

The absorbance is measured at 550 mμ in 5-cm cells against a reagent blank carried through the procedure. Standard vanadium solutions carried though the entire procedure (including the tributyl phosphate–carbon tetrachloride extraction) are used to prepare the standard curve.

(b) *In Zirconium.* Vanadium in zirconium metal can be determined by the phosphotungstovanadic acid procedure described above.[291] A prior separation of the vanadium is first made by extraction of the V(V) diethyldithiocarbamate from a fluoride solution at pH 1, and removal of the vanadium from the extract by washing with nitric acid (1+1) containing hydrogen peroxide.

The oxidation of vanadium in sulfuric acid solution by potassium chlorate and other oxidants to a yellow product, presumably a polyvanadate, has been made the basis of a simple but reliable spectrophotometric procedure for the determination of as little as 5 ppm in zirconium or Zircaloy.[288] Interference from alloying or impurity elements such as iron, chromium, and nickel is eliminated by measuring the absorbance of the color against a sample solution in which the vanadium color is not developed.[603] The standard solutions for the preparation of the standard curve generally contain vanadium-free zirconium, but subsequent work has shown that vanadium solutions alone can be used.[603]

Spectrophotometric Determination of Vanadium in Zirconium and Zircaloy—Potassium Chlorate Oxidation. Procedure.[603] A 1-g sample in a platinum beaker is dissolved by adding about 5 ml of water, a few drops of concentrated nitric acid, and 2 to 3 ml of 48 per cent hydrofluoric acid dropwise. To the solution is added 50.0 ml of concentrated sulfuric acid. The solution is heated to fumes and cooled. The solution is transferred, with washing, to a 300-ml Erlenmeyer flask and again brought to fumes on a hot plate. The solution is now fumed over a free flame, vigorously but briefly, to avoid a significant volume change. The solution is cooled in a cold-water bath. To the cold solution is added 0.5 g of potassium chlorate crystals through a powder funnel reaching almost to the surface of the solution. (Crystals depositing on the walls of the flask cause an extraneous color later when the solution is transferred to the optical cell.) The solution is again heated to fumes on the hot plate. When the solution has cooled, the absorbance is measured in 10-cm cells at 410 mμ approximately 30 min after the addition of the potassium chlorate. A sample solution carried through the procedure but omitting the addition of the potassium chlorate serves as a reference solution.

The standard curve is prepared by adding 0 to 100 μg of vanadium to 50.0-ml portions of concentrated sulfuric acid in 300-ml Erlenmeyer flasks. The flasks are treated as above, starting with the vigorous fuming before the potassium chlorate addition. The absorbance of each standard is measured against the 0-μg standard as a reference.

(c) *In Titanium.* Procedures for the determination of vanadium in titanium have been described in the literature (see Refs. 226, 231, 234, 235, 294, 316, 332, 333, and 604).

11–2.42 Zinc

(a) *In Uranium.* The determination of traces of zinc in uranium can be carried out polarographically after separation of the zinc and other metals by a mercury-cathode electrolysis[281–283] or by extraction with dithizone[284] or diethyldithiocarbamate (DDTC).[346] The mercury-cathode separation, discussed briefly in Sec. 11–2.7(a), is time consuming, erratic, and hazardous. The dithizone separation, also discussed in Sec. 11–2.7(a) and described in detail in Chap. 4, "Beryllium," Sec. 4–4.11, is more satisfactory. Zinc, cadmium, copper,

lead, nickel, and cobalt can be determined at one time. The DDTC extraction has been applied to the analysis of uranyl sulfate solutions containing corrosion products.

Dithizone spectrophotometric procedures for the determination of zinc in uranium involve various techniques to remove or prevent the interference of other metals reacting with dithizone. In one procedure [285] similar to that developed by Cowling and Miller,[605] the uranium solution at pH 8.3 to 8.5 containing citrate is extracted with dithizone in carbon tetrachloride. The extracted dithizonates are contacted with 0.02*N* hydrochloric acid which decomposes the lead, zinc, cadmium, and thallium complexes. A second extraction is then made on the acid wash to which diethyldithiocarbamate and sufficient ammonium hydroxide to pH 8.5 to 9.0 are added. Under these conditions only the zinc dithizonate extracts since the other metals are complexed strongly by the carbamate. [207, 605] Large amounts of cadmium may interfere, but, if the quantity of cadmium is less than one-half that of zinc, as is generally the case in the analysis of uranium, the interference is negligible. No interference is shown by 100-μg quantities of copper(II), lead, mercury(II), bismuth, cobalt, tin(II), and nickel.[605] The reaction of zinc with dithizone in the presence of DDTC is not strictly quantitative, but under constant conditions the recoveries are reproducible.

Diethyldithiocarbamate can be utilized in a different manner to isolate the zinc.[285] If the carbamates are extracted from a citrate solution at pH 8.8 to 9.0 and then are shaken with a strongly basic solution containing more citrate and DDTC, the zinc complex is decomposed and is transferred to the aqueous phase. After destruction of the free carbamate with bromine in acid solution, the pH is readjusted to about 8.5, and the zinc is extracted with dithizone for the absorbance measurement.

More recent procedures [207, 606, 607] make use of the fact that excess dithizone and small amounts of many metal dithizonates are decomposed by a dilute sodium sulfide solution, whereas zinc dithizonate is stable and nickel dithizonate is only slightly decomposed. Nickel is easily removed by prior extraction of its dimethylglyoxime complex from an ammoniacal citrate solution. Apparently no other metals reacting with dithizone interfere. Recoveries of 1 to 20 μg of zinc added to synthetic uranium solutions containing representative amounts of nickel, iron, cobalt, chromium, copper, silicon, lead, manganese, and aluminum are within 1 μg of the added quantities.

Spectrophotometric Determination of Zinc in Uranium—Dithizone. Special Reagents. Carbon Tetrachloride. A cold solution of 30 g of potassium hydroxide dissolved in 20 ml of water is diluted to 180 ml with methyl alcohol, and 5 g of paraformaldehyde and 20 g of lead

acetate are added. To this freshly prepared reagent is added 1 liter of carbon tetrachloride. After 8 to 10 hr, 200 ml of water is added, and the mixture is shaken well. The organic phase is separated and filtered through Whatman No. 41 paper. The carbon tetrachloride is then washed with 100 ml of 4 per cent sodium hydroxide solution and twice with 100-ml portions of water. The solvent is finally filtered again through Whatman No. 41 paper.

Dithizone, 0.01 Per Cent. Although most of the commercial dithizone available is probably sufficiently pure for use, a purification step is described similar to that in Sandell.[207] A 0.01 per cent solution in purified carbon tetrachloride is prepared daily by dilution of a 0.05 per cent stock solution stored at a temperature not exceeding 20°C for no longer than three weeks.

Procedure.[607] To a 1-g sample of uranium in a quartz beaker is added 10 ml of nitric acid (1+1) (prepared from acid redistilled, diluted, and stored in polyethylene). After the sample has been dissolved, the solution is evaporated just to dryness. The residue is dissolved in 40 ml of water, and 5 ml of 40 per cent ammonium citrate solution (168 g of citric acid dissolved in 200 ml of water; the pH adjusted to 8.5 with concentrated ammonium hydroxide, and the solution cooled and diluted to 500 ml; solution extracted with 10-ml portions of 0.05 per cent dithizone until final portion remains green; solution acidified with hydrochloric acid and washed with chloroform until the washings are colorless; solution stored in polyethylene) is added. The pH is adjusted to about 8.5 with ammonium hydroxide, and the solution is transferred to a separatory funnel. To the funnel is added 1 ml of 1 per cent dimethylglyoxime solution (1 g dissolved in 100 ml of ethyl alcohol). The solution is extracted with three 10-ml portions of chloroform [purified by washing a 500-ml quantity first with 100 ml of hydrochloric acid (1+4) and then three times each with 250 ml of water] followed by a 5-ml portion of carbon tetrachloride.

The pH is checked to make sure the solution is still alkaline. More ammonium hydroxide is added if necessary to reach a pH of about 8.5. The solution is extracted with 10-ml portions of 0.01 per cent dithizone until the final extract is green. The extracts are combined and washed with 20 ml of water.

The organic phase is washed with successive 40-ml portions of 0.025 per cent sodium sulfide solution (2 g dissolved in 200 ml distilled water; solution prepared fresh weekly and stored in polyethylene; 25 ml of this stock solution diluted to 1 liter; this 0.025 per cent solution prepared fresh daily) until the last extract is colorless. Usually four to five washes are required. The organic phase is filtered through Whatman No. 41 paper and diluted to 50 ml with carbon tetrachloride.

The absorbance is measured in 1-cm cells at 535 mμ against chloroform. Correction is made for a reagent blank carried through the procedure. The standard curve is prepared with solutions made by adding 0 to 30 μg of zinc to water, diluting to 50 ml, adding 5 ml of ammonium citrate solution and ammonium hydroxide to pH 8.5. The solutions are extracted and washed as described above. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(b) *In Thorium.* The polarograph has been useful in the determination of traces of zinc in thorium. Patterson and Banks[608] de-

scribe a direct procedure in which thorium in a hydrochloric acid solution is complexed with sulfosalicylate at pH 8.5, and the diffusion current of the zinc reduction at a half-wave potential of −1.05 volts vs. a saturated calomel electrode (S.C.E.) is recorded. For large amounts of zinc in thorium alloys, an electrolytic procedure involving deposition from citrate solution is recommended.[608]

Other polarographic procedures are based upon a prior extraction of the zinc. The dithizone extraction–polarographic procedure discussed in Sec. 11–2.7(a) and described in detail in Chap. 4, Sec. 4–4.11, is very satisfactory for the determination of traces of zinc and other metals.[284] Thorium is complexed with citrate or tartrate before the exhaustive extractions at pH 7.5 and 9.0. An extraction at a single pH of 9.5 has been used to determine zinc and lead by a similar procedure.[412] The zinc is determined in a 0.5*N* hydrochloric acid strip of the dithizone extract in a supporting electrolyte 0.1*N* in ammonium acetate and 0.025*N* in potassium thiocyanate. The half-wave potential of zinc in this medium is −1.0 volt vs. S.C.E. A diethyldithiocarbamate–chloroform extraction from a carbonate solution at pH 8 is also used.[216] The zinc is re-extracted from the chloroform phase with 0.01*M* hydrochloric acid for the polarography . The half-wave potential is −1.0 volt vs. S.C.E.

A dithizone spectrophotometric procedure has been found convenient.[214] This procedure is based upon the extraction of zinc dithizonate in the presence of thiosulfate to prevent the formation of the dithizonates of copper, mercury, silver, gold, bismuth, lead, and cadmium. The final extract is washed with a dilute sodium sulfide solution to destroy excess dithizone and all dithizonates except that of zinc.[207] The procedure is described below under zirconium. Thorium metal or oxide is dissolved in hot nitric acid containing fluoride ion and is complexed with citrate, 15 ml of 40 per cent (w/v) ammomium citrate per gram of thorium, for the initial extraction.

(c) *In Zirconium.* The dithizone extraction–polarographic procedure,[251] discussed under Sec. 11–2.7(c) and described in detail in Chap. 4, Sec. 4–4.11, is applicable to the determination of zinc and other metals in zirconium. A less satisfactory direct procedure [284] giving the sum of the zinc and cobalt in zirconium is also described briefly in Sec. 11–2.7(c).

Two spectrophotometric procedures with dithizone are available for the analysis of zirconium metal and Zircaloys. Both utilize the complexing action of thiosulfate at pH 5 to prevent the formation of the dithizonates of many metals ordinarily reacting except those of palladium, tin(II), and zinc.[207] In one procedure [288] the dithizone extract, made at about pH 8.5 and containing the zinc and other

metals, is washed with 0.01*N* hydrochloric acid to destroy the dithizonates of lead, zinc, cadmium, and thallium and to transfer these metals to the acid phase. Another extraction from a slightly acid solution containing thiosulfate yields the zinc dithizonate.

The other procedure [288] involves an extraction at pH 5.0 to 5.5 in the presence of thiosulfate, washing of the extract with dilute acid, re-extraction at pH 5.0 to 5.5 in the presence of thiosulfate, and the added precaution of washing the final extract with dilute sodium sulfide solution. The sulfide solution destroys all dithizonates except those of zinc and nickel, and also excess dithizone.[207] Nickel is removed in the previous extraction and washing steps.

Spectrophotometric Determination of Zinc in Zirconium and Zircaloy–Dithizone. Special Reagents. All the reagents possible are purified by extraction with dithizone according to standard practice to keep the blank as low as possible.

Procedure.[288] A 1- to 2-g sample containing up to 25 μg of zinc is suspended in 15 ml of sulfuric acid (1+2) in a platinum dish and is dissolved by the dropwise addition of 48 per cent hydrofluoric acid. The solution is evaporated to fumes, cooled, and diluted to about 50 ml.

To the solution are added 10 ml of 40 per cent (w/v) ammonium citrate, 1 ml of 20 per cent (w/v) hydroxylamine hydrochloride solution, and 1 ml of 12.5 per cent (w/v) sodium thiosulfate solution. The pH is adjusted to 5.0 to 5.5 with ammonium hydroxide. The solution is extracted with dithizone solution (10 to 20 mg per liter of carbon tetrachloride) in 5-ml portions. When the last portion remains green after 2 min of shaking, the combined extracts are washed with 50 ml of 0.02*N* hydrochloric acid. The organic phase is discarded.

To the acid phase are added 1 ml of the hydroxylamine hydrochloride solution and 1 ml of the thiosulfate solution. The pH is adjusted to 5.0 to 5.5, and the solution is re-extracted with 5-ml portions of the dithizone solution until the last portion remains green. The combined extracts are diluted with chloroform to 50 ml, and the solution is washed with 50-ml portions of 0.4 per cent (w/v) sodium sulfide solution until the last portion remains colorless. An emulsion forming at this point may be broken with about 200 mg of dry powdered potassium chloride.

The zinc dithizonate solution is filtered through a dry filter paper, and the absorbance is measured in 1-cm cells at 535 mμ against carbon tetrachloride as a reference. The absorbance is corrected for a reagent blank carried through the entire procedure. The standard curve is prepared by adding 0 to 50 μg of zinc to 15 ml of sulfuric acid (1+2). diluting each solution to about 50 ml, and following the procedure outlined above. The absorbance of each standard is corrected for the absorbance of the 0-μg standard.

(d) *In Titanium.* Procedures for the determination of zinc in titanium have been described in the literature (see Refs. 239, 316, and 429).

11–2.43 Zirconium

(a) *In Uranium.* Quantities of zirconium greater than 100 μg can be determined by X-ray fluorescence after extraction of the uranium by tributyl phosphate.[327]

Because of the lack of specific chromogenic reagents for zirconium, there are no entirely satisfactory spectrophotometric procedures available for the determination of traces of this element in uranium. Four reagents have been used. Of these, *p*-(*p*-dimethylaminophenylazo) benzenearsonic acid (pararsonic acid) and alizarin (or Alizarin Red S) are perhaps the most useful at the present time. The sensitive [609] reagent 3,5,7,3′,4′-pentahydroxyflavone (quercetin) and the very sensitive [610] fluorometric reagent 3,5,7,2′,4′-pentahydroxyflavone (morin) apparently have not been applied to the analysis of uranium.

Horton [611] recommends the use of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid (thorin).[537] Chromium (III) and (VI), molybdate, iron(III), tin(II) and (IV), thorium, titanium (III) and (IV), and uranium (IV) and (VI) all can interfere in one way or another. The interference of Cr(VI) and Fe(III) can be eliminated by reduction with hydroxylamine. Fluoride and phosphate interfere seriously. An ion-exchange separation of uranium from zirconium prior to the determination by thorin is also described by Horton.[612] A 5*M* hydrochloric acid solution of U(VI) is passed through a column of Dowex A–1 in the chloride form. Uranium is held on the column; zirconium passes through.

Chloranilic acid [613] is used by Menis.[614] Uranium, however, also forms a chloranilic acid complex with similar light absorption characteristics. The absorbances of the zirconium and uranium complexes are additive; the zirconium concentration can therefore be determined by subtracting the absorbance due to uranium from the total. The amount of uranium that can be tolerated is fairly small: 6 mg per milliliter of final solution. Other cations interfere: iron(III), tin (II) and (IV), and thorium. Reduction with hydrazine removes the Fe(III) interference. Fluoride interferes badly and must be removed by fuming the solution with perchloric acid.

1,2-Dihydroxyanthraquinone (alizarin) forms a lake with zirconium stable at relatively high acidities and suitable for its determination in the presence of uranium.[207, 379] Phosphate, sulfate, fluoride, molybdate, tungstate, and organic hydroxy acids interfere. Large amounts of iron(III), chromium, cobalt, cadmium, copper, lead, and aluminum may also interfere. Uranium in a 100-fold excess may cause small positive errors. King and Owens [615] use Alizarin Red S for the analysis of uranium–zirconium alloys. Fluoride and phosphate are removed by volatilization with perchloric acid after treatment with

hydrofluoric acid; the phosphate is eliminated as phosphorus tri- and pentafluoride. Organic matter is destroyed with nitric acid. Sulfate is eliminated with calcium chloride.

A direct Alizarin Red S procedure is also reported by Patterson.[616] The lake is developed in a 1 per cent hydrochloric acid solution after dissolving the sample in aqua regia and fuming the solution to dryness with sulfuric acid. In the analysis of solutions containing over 75 μg of zirconium and up to 1 g of uranium per 100 ml, only barium, niobium, phosphate, and thorium are said to interfere. Precautions must be taken to avoid hydrolytic loss of zirconium by boiling the solution made up to 10 per cent hydrochloric acid the same day it is to be analyzed.

Smaller amounts of zirconium in the presence of uranium are determined by Laux and Brown [617] by first extracting the uranium from 4*M* hydrochloric acid solution with triisooctyl amine in xylene and then applying the Alizarin Red S procedure [615] mentioned above to the aqueous phase.

p-(*p*-Dimethylaminophenylazo) benzenearsonic acid (pararsonic acid) precipitates microamounts of zirconium from acid solution. If the complex is filtered and decomposed with ammonium hydroxide, the yellow color of the released reagent can be measured to determine the zirconium.[379, 618] The red color obtained by either acidifying the yellow solution of reagent [618] or by decomposing the insoluble zirconium complex with an acid–hydrofluoric acid mixture [619, 620] can also be used. The red color is more sensitive. Interfering substances include fluoride, phosphate, and sulfate. Large amounts of nitric acid, thorium, and plutonium may also interfere. The plutonium can be made innocuous by reduction with hydroxylamine. In the presence of interferences, a preliminary cupferron precipitation of the zirconium with Fe(III) as a carrier is useful.[379, 618]

Pararsonic acid is also used in a turbidimetric procedure.[379] A 10-g sample of metal is dissolved in hydrochloric acid followed by nitric acid, and the solution is evaporated to dryness several times with hydrochloric acid. The salts are taken up in dilute hydrochloric acid, and a cupferron–chloroform extraction is made. The extract is evaporated to dryness, and the residue is fused with pyrosulfate. The cooled melt is taken up in water, and the solution is filtered and made up to 10 ml. Aliquots of this solution are then treated with pararsonic acid, and the precipitates are measured turbidimetrically. Standards are prepared in the same manner. Niobium and tantalum are harmless, but 300 μg of tin or 25 μg of titanium interfere. The procedure is useful in the 1- to 12-ppm range.

The spectrophotometric pararsonic procedure of Russell [619] is described below. This procedure was primarily designed to determine

zirconium in solutions containing nitric acid, uranyl nitrate, and fission products. The level of radioactivity of the solutions limited the sample size to that containing 1 to 10 μg of zirconium and 400 mg of uranium. Presumably, larger samples can be taken in the analysis of less radioactive solutions of uranium. If one is to obtain reproducible results, it has been found necessary to precipitate the zirconium complex at 60 to 70°C in the presence of excess pararsonic acid and to digest the precipitate overnight. It has also been found important in the filtration to use pulverized filter paper for quantitative retention.

Spectrophotometric Determination of Zirconium in Uranium—Pararsonic Acid. Procedure.[619] Uranium metal is dissolved in nitric acid so that the final solution is 0.2*M* or less in nitric acid. The solution preferably should be made up so that 1 ml contains 1 to 10 μg of zirconium and 400 mg or less of uranium.

To 4 ml of 1.2*M* hydrochloric acid in a 15-ml beaker is added 1 ml or less of the sample solution. To the solution is added 1 ml of 0.2 per cent pararsonic acid (0.2 g dissolved in a mixture of 90 ml of 95 per cent ethyl alcohol plus 10 ml of 2*M* hydrochloric acid; solution filtered; stable at least three months). The solution is heated to 60 to 70°C for 15 min. The red color should turn to brown; if it becomes yellow instead, more reagent is added dropwise until the brown color appears. The solution is then digested overnight at room temperature.

A wad of Whatman No. 42 filter paper is placed in the cone of a funnel fitted with a Whatman No. 42 paper. The paper is washed with warm, 60 to 70°C, 1.2*M* hydrochloric acid; sufficient acid is left in the funnel after the last wash to cover the mat. The solution is filtered. The beaker is washed with warm, 60 to 70°C, 1.2*M* hydrochloric acid, and the washings are added to the funnel. The funnel and precipitate are washed with warm 1.2*M* hydrochloric acid until the washings are colorless.

A 25-ml volumetric flask is placed under the funnel. The funnel is washed with 2 ml of 5*M* hydrofluoric acid and 5 ml of warm 0.4*M* oxalic acid. The washing step is repeated. The funnel is finally washed with small portions of warm 0.4*M* oxalic acid until no more color is removed from the funnel. The solution is diluted to volume. The absorbance is measured at 490 mμ in 5-cm cells against water. (The sample cell should be emptied and rinsed immediately.) The absorbance is corrected for a reagent blank.

The standard curve is prepared by analyzing 1 to 10 μg of zirconium by the identical procedure.

(b) *In Thorium.* Rubin and House[218] extract microgram quantities of zirconium from gram amounts of thorium in 2*M* nitric acid with 0.5*M* 2-thenoyltrifluoroacetone (TTA) in carbon tetrachloride. The extracted zirconium is determined spectrophotometrically with quercetin[609] or chloranilic acid.[614] A similar extraction separation is reported by Menis and coworkers.[216] The extraction is made from 6*M* hydrochloric acid with TTA in chloro-

form. Traces of iron and occluded elements are removed from the organic phase by washing with 10*M* hydrochloric acid. The extract is evaporated to dryness, and the organic matter is destroyed by wet oxidation. The zirconium is then determined spectrophotometrically in the 5- to 50-μg range with quercetin [609] or fluorometrically in the 0.25- to 2-μg range with morin.[610]

An ion-exchange separation of zirconium and thorium followed by the determination with chloranilic acid [614] is reported by Layton.[621] Thorium in 10*N* hydrochloric acid is passed through a column of Dowex–1 in the chloride form. The thorium is eluted with 12*N* hydrochloric acid, and the zirconium is then removed with 6*N* sulfuric acid.

Two alizarin sulfonic acid procedures are available. Silverman and Hawley [622] determine from 10 to 700 μg directly in the presence of 200 mg of thorium. Small amounts of iron and other metals normally present are said not to interfere. DeGroot [623] makes a prior separation of the zirconium with cupferron and a bismuth carrier.

(c) *In Titanium.* Procedures for the determination of zirconium in titanium have been described in the literature (see Refs. 235, 624, and 625).

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CHAPTER 12

SPECTROCHEMICAL METHODS

By Harold R. Mullin* and Clara Gale Goldbeck*

The determination of trace amounts of impurities in materials used in the nuclear energy field is of prime importance both from the standpoint of neutron absorption and from their effect on the metallurgical properties of materials. The following discussion is divided into spectrochemical methods and chemical methods of separation that are sometimes necessary prior to a spectrochemical determination. In addition, consideration is given to the spectrochemical determination of isotopes.

12–1 SPECTROCHEMICAL METHODS

By Harold R. Mullin

During the period of preparation of this book and this chapter on spectrochemical methods, a book entitled *The Emission Spectrographic Analysis of Atomic Materials* was published in the U.S.S.R. The book was edited by A. N. Zaidel', with additional authorship of N. I. Kaliteevskii, L. V. Lipis, and M. P. Chaika and was published by the State Government Publishing House for Physical-Mathematical Literature, Moscow. In this chapter no attempt will be made to include the detail that is found in Zaidel's publication; instead an attempt will be made to show the relationship and extent of spectrochemical analysis to the over all problem of analysis of essential reactor materials.

In spectrochemical procedures the amount of sample required for an analysis is small; however, considerable information about the impurity composition of the material can be obtained from the sample spectrum. This information is limited only by the spectral sensitivity of the separate elements and by the ingenuity of the spectrographer in determining conditions for handling the sample in order to realize the full sensitivity of the spectrograph. Since the first application of spectral analysis by simple burning of the material in a flame or d-c arc, changes in procedures and apparatus have been appreciable. No attempt will be made in this chapter to discuss either the advantages or disadvantages of the various types of excitation conditions available to the spectrographer or any of the theory relative to qualitative and quantitative spectrochemical analysis since these are extensively

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covered in text books on spectrochemical analysis, such as *Practical Spectroscopy*, by G. R. Harrison, R. C. Lord, and J. R. Loofbourow, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1948, *Principles and Practice of Spectrochemical Analysis*, by N. H. Nachtrieb, McGraw–Hill Book Company, Inc., New York, 1950, or the more-recent *Spectrochemical Analysis*, 2d ed., by L. H. Ahrens and S. R. Taylor, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1961. Discussion will be limited to the spectrographic analysis of the various reactor materials and the specialized techniques used for the determination of the impurities according to the excitation method used. In this discussion it will be assumed that all spectrographs are equal in response and that the main differences in the procedures are in the form and preparation of the sample and in the type of source used for the sample excitation.

The sample to be analyzed may be regarded as consisting of the following: (1) one or more major constituents, which together constitute the sample matrix and have a direct influence on the excitation conditions in the source, and (2) from 1- to 70-odd atomic constituents or impurity elements which are to be spectrochemically determined and are present in such small concentrations that their presence will not significantly affect the excitation conditions. The sample may exist as a metal, liquid, or chemical compound. When samples are being prepared for spectrographic examination, it is important to minimize the sample handling, both to simplify the operations and to avoid possible sources of contamination. If the material to be analyzed is metallic and can be obtained in small uniform rods or bars, it may be analyzed directly as a self-electrode. However, some metallic samples, especially metals of the refractory type that do not make good melts, present a problem of nonhomogeneity of material and cannot be used as self-electrodes. (Excitation of a nonhomogeneous metal sample in an arc or spark discharge will give preferential volatilization for many of the impurities. Crystals or compounds of metals that have low ionization potentials when segregated in the matrix are more readily burned and thus give erroneous impressions of the concentration of impurities present.) If the metal sample exists in a powdered form, it may be pressed into a shape for use as a self-electrode or be burned either directly in a d-c arc discharge or handled in the same manner as oxide samples. Any metal sample that cannot be used as a self-electrode or which is suspected to be nonhomogeneous in composition must be handled in some other manner. The sample may either be dissolved and the resulting solution analyzed according to one of the special techniques for liquids, or it may be converted to a usable compound and analyzed as such. The oxide is the compound form most generally used.

The nonmetallic sample, such as a refractory oxide, is treated in several ways in spectrochemical analysis. The sample is ground to a fine powder, placed in a cupped electrode, and then excited, generally with a d-c arc discharge. For some samples it is necessary to mix a buffering material with the sample to help stabilize the discharge conditions by producing a controllable and reproducible arc matrix. A briquette sample may be made by mixing the powdered material with several times its weight of a conducting powder, such as graphite or metal powder, and pressing the mixture into a pellet or briquette. This briquette is then used as one electrode in the electrode system, and the sample can be excited in the same manner as for any metallic sample.

In quantitative spectrographic analysis the determination of the different impurities is relative to certain standards used as controls and run at the same time and with the same source conditions. Simple estimations of element concentrations can be made from an examination of the spectral-line blackening and a knowledge of the general sensitivity of the element in question. The accuracy and precision of results are improved by creating a definite matrix for the sample and by stabilizing and controlling all suspected variables in the excitation discharge through the use of homologous line pairs and internal intensity standards. Unfortunately, such a simple approach to the analysis of reactor materials is not possible in all cases. The refractory nature of many of the reactor metals and the variations in the metallurgical and physical composition of these materials make it essential that the comparison standards used in spectrochemical analysis be as similar to the samples as possible or that the sample be converted into a form that is comparable to the standards.

If the sample under investigation has a simple spectrum and it is desired to check the sample qualitatively for a large number of constituents, the spectrographic approach is, generally, by excitation of the sample with the d-c arc. If results with greater precision are desired, high-voltage spark discharges are used as a source. However, direct excitation of the sample cannot always be applied to materials with complex spectra, and many of the ores and concentrates of the reactor materials are of a refractory nature and have a complex spectra. For these materials direct burning of the sample in a d-c arc in many cases gives erratic and nonuniform exposures. Buffers, such as graphite, lithium or sodium carbonate, and some of the ammonium salts, can be mixed with the sample. These buffers help stabilize the arc discharge so that the burning of the sample is more reproducible and complete.

The electric arc is the most extensively used excitation source for the spectrochemical analysis of reactor materials. The arc produces

intense spectral lines of high sensitivity for the detection of almost all elements. The sensitivity obtained by the d-c arc can be improved by use of the "Glimmschicht" or cathode-layer method. In this method the positive ions formed in the d-c arc migrate in the electric field about the arc and become enriched near the cathode and build up a concentration gradient there which enhances light emission. The lower electrode, containing the sample, is made the cathode, and the region of the arc just above the cathode, which is the point of higher excitation, is focused on the slit of the spectrograph. This arrangement increases the sensitivity of detection of trace impurities by at least a factor of 10. Since good reproducibility is difficult to achieve, this method has not been generally adopted for routine analyses.

Another problem associated with a complete examination of the d-c arc spectrum of many reactor metal concentrates is the difficulty of determining some elements because of interference due to the cyanogen bands. In air these bands are quite strong in any exposure using graphite electrodes. The formation of cyanogen bands can be controlled either by using metallic electrodes as support electrodes to remove the source of carbon or by placing an inert atmosphere around the electrodes to remove the source of nitrogen.

Oxides of a number of reactor materials are quite refractory and hard to vaporize reproducibly in a d-c arc discharge; however, a reasonably controlled vaporization of the sample oxide can be achieved by the conducting-briquette excitation technique. In this method conductivity is imparted directly to the refractory oxide sample, which is in the form of conducting briquettes made from mixtures of dry, finely ground sample and powdered flake graphite. High-voltage spark discharges between a counter electrode and the briquette are generally used, but any of the standard controlled a-c or interrupted discharges should be applicable. With the conducting briquettes there is little or no selective volatilization of sample components or suppression of the complex spectrum of the sample matrix; so the matrix spectral lines may unavoidably interfere with many of the impurity spectral lines. The matrix will, however, give numerous lines suitable for internal standard reference lines. The conducting-briquette technique does not have the sensitivity of detection of some of the other procedures for impurity analysis; however, the increased precision, because of spark excitation, may offset this disadvantage. Furthermore, with this procedure the preparation of the oxide sample is not as critical a factor as is the case in other procedures; because of this it is not necessary that the standards and samples be treated in exactly the same manner.

A specialized type of arc discharge is obtained by use of a hollow-cathode source. Hollow-cathode sources can increase the sensitivity of

detection of certain impurities such as the halogens over that obtained with conventional d-c arc techniques. The hollow-cathode source differs from the d-c arc principally in the manner in which the sample enters the arc column. In the d-c arc the sample is vaporized thermally, whereas in the hollow-cathode source the mechanism is one of cathode sputtering by positive ions' impinging on the cathode (sample) surface. An integral component of the source is a carrier gas, usually helium or argon, introduced in the correct amount to create the optimum number of positive ions; the gas pressure must be confined to a unique and relatively narrow range, commonly a few millimeters. The hollow-cathode source affords more selective control of excitation energy with extremely stable discharges. It has been applied to some specific problems in the spectrochemical analysis of nuclear materials, e.g., the determination of halogens, and has been used as a source of the narrow spectral lines needed in spectroisotopic determinations.

Because the spectra of most reactor materials are quite complex, consisting of thousands of lines of comparatively uniform intensity, the determination of a large number of impurities in trace concentrations, many in the fractional parts per million range, is quite difficult. In the search for more sensitive detection methods, a number of procedures have been developed in spectrochemical analysis which are dependent upon the separation of the trace impurities from the matrix material. These procedures can be classed as either physical or chemical. One method of a physical-separation procedure depends upon the distillation of the volatile trace impurities from the matrix during the exposure cycle; another calls for the evaporation or distillation of the impurities from the matrix with a condensation of the impurities on a separate electrode prior to the exposure cycle. The chemical procedures for the separation of impurities are many and varied; they are covered in sec. 12–2.

A procedure that is widely used for trace-element determinations in refractory materials has been designated the "carrier-distillation" procedure. As the name implies, this procedure is a fractional distillation of the volatile impurity elements from the more refractory oxide matrix aided by a carrier material of intermediate volatility. Simple fractional distillation of the impurities from a sample of reactor material such as uranium or thorium by direct ignition of the sample charge is unsatisfactory. For this approach higher amperage d-c arcs are needed to distill all the impurities into the arc stream, and, with the arc temperatures thus obtained, complete suppression of the matrix spectrum is not possible. The addition of a small amount of a selected volatile "carrier" material improves the distillation of the impurities under carefully controlled arc conditions. There are certain limitations on the choice of a carrier, but it can be expected

that several materials will provide satisfactory results. Ammonium salts are too volatile, break down in the heat of the arc, and during the arcing cycle may physically carry particles of the matrix material into the arc stream. Alkali salts tend to suppress many of the impurity elements probably because of the low ionization potential of the alkali metal in the arc. In general, the carrier should be of intermediate volatility among the group of elements to be determined, free of those elements, stable, inert, nonhygroscopic, and easily incorporated into the sample. The compounds gallium oxide and silver chloride have been among those most commonly used.

In the carrier-distillation procedure the arc excitation of the sample is characterized by a cycle of burning that is quite reproducible for the purer grades of reactor material. The arc burns somewhat erratically for 6 to 8 sec owing mainly to the burning of the supporting electrode. At the end of this period, the arc changes in color from indigo, the color of the graphite arc, to a color characteristic of the carrier material and burns quietly and steadily for approximately 25 sec. At the end of this time, the arc changes again back to the unsteady discharge of the initial period. Most of the impurity elements are distilled into the arc during the steady-burn portion of the arc cycle; however, such highly volatile impurities as cadmium and mercury begin to volatilize ahead of the steady period whereas such elements as iron and aluminum still persist in the arc at the end of the steady-burning period. The procedure has good reproducibility and sensitivity for most elements.

A procedure known as the evaporation method for the physical separation of trace impurities from refractory reactor materials has been developed in the U.S.S.R. Evaporation may be carried out in either air or vacuum. In this procedure the distillation of the impurities and the spectrographic excitation of them are separate steps, and, as a consequence, optimum excitation conditions for greater sensitivity can be used. The sample is placed in a graphite crucible, which is heated by an electrical current to the temperature of evaporation of the impurities from the sample. The distilled impurities are condensed on the surface of a cooled metallic or graphite electrode located near the orifice of the crucible. At the end of the distillation process, the electrode with the condensate is used as one electrode in the arc or spark discharge, and the spectrum of the discharge is registered in the normal manner. With the evaporation procedure it is possible to use larger samples. The quantity of evaporated and condensed impurities increases proportionally with increases in the weight of the samples up to approximately 200 mg. For samples larger than 200 mg the evaporization rate slows down. Choice of the right temperature for heating the crucible can ensure a system

of evaporation in which only those impurities that have a volatility somewhat greater than the major constituent of the sample are evaporated. The condensate layer, consisting of only the impurities, is normally very thin and can be completely burned by either the arc or the spark in a few seconds. This type of sample allows the selection of the most effective source conditions for the analysis of interest. Furthermore, this technique may not require as many types of comparison standards as other procedures. Since little or no matrix material will vaporize over to the sample electrodes, there should be no difference in the impurities condensed on the electrode whether they are obtained from uranium, thorium, or aluminum. Any differences in the evaporation step, however, would be apparent and must be considered. Since the recoveries for all volatile impurities were not found to be 100 per cent, it is still necessary to prepare standard electrodes by the distillation of synthetic samples rather than by direct evaporation of trace metals on a comparison electrode. Although the evaporation technique is perhaps more sensitive for the different impurity elements than the carrier-distillation method, unless such absolute sensitivities are needed, the involved procedure of sample preparation would make this method less convenient than the carrier-distillation method.

An excitation source used extensively for the determination of the alkalis and alkaline earths is flame spectroscopy. For interested investigators in the field of flame spectroscopy, an excellent treatise is *Flame Photometry* by F. Burriel-Marti and J. Ramirez-Muñoz, Elsevier Publishing Company, New York, 1957. The principle of the method is based primarily on atomizing a portion of a solution containing the sample into a flame where the sample atoms are excited and the characteristic spectral patterns are formed. Through control of the flame temperature, the number of elements excited can be regulated. The standard gas-air flame will excite only the alkalis and alkaline earths; the oxyhydrogen or even the hotter oxycyanogen flame is capable of exciting over forty elements. Flame spectroscopy is dependent upon the sample being in solution although there have been attempts to atomize extremely fine particles of the sample directly into the flame. The solution used in the analysis can be either a solution of the original sample or a solution obtained following a chemical separation with the final solution containing the element in question. In flame spectroscopy there are a number of variables: type of solution, whether aqueous or organic; acidity of the sample: type of acid present; viscosity of the solution; and possible effect of other ions present. It is important that standards be prepared in exactly the same way and be in the same type of solution as the sample to be examined.

No attempt has been made in this chapter to include the descriptions of such other techniques for sample handling as the use of plasma jets, Stallwood jet, or vacuum cups in emission spectrochemical procedures, or some of the new flame photometric sources, such as fluorine-hydrogen or the incandescent oxyacetylene flames. Workers in the field of reactor metal analyses have undoubtedly used these various methods in attempting to improve the analysis of reactor materials. However, no reports are currently available describing results with these particular procedures.

In all spectrochemical analysis electronic read-out systems have been added to increase the speed of analysis. Direct-reading instruments are now quite prevalent in the metal industry where they are used in quality control. These systems can be applied to any procedure that is to be handled in a routine manner. They are now in use in uranium-materials production as control instruments where the method of excitation is the carrier-distillation procedure using the d-c arc. The precision of photoelectric measurement is a factor of 3 greater than the precision of photographic measurement in almost all cases. In those procedures where it is possible to excite metal samples with spark discharges, the improvement in the precision is extremely good. Direct-reading techniques give a further advantage to metal analysis. Because of the speed with which an analysis can be made and the small amount of metal involved, segregation studies of metal ingots can be made readily. Each direct-reading instrument is custom designed for a particular analysis, and it is difficult to vary procedures or the material analyzed. This limits the general utility of the instrument.

No discussion on spectrochemical analysis would be complete without some mention of emission spectrographic standards. Spectrographic analysis, basically a comparative method, requires standard samples matching the analytical samples closely in composition, form, and physical condition. Over a period of years, numerous samples suitable for comparison purposes have been made available to the emission spectroscopist. These include the metallic samples in solid or chip form; such nonmetallic standards as ores, minerals, and special compounds especially prepared for use in chemical analysis; and synthetic mixtures to approximate regular samples in composition.

A comparison standard is only as good as the knowledge and care that went into its preparation and analysis. Since spectrochemical results are ultimately judged against chemical values, the spectrochemical comparison standards should be accurately analyzed. In the metallurgical industry there are a number of standards available for comparison purposes. These standards exist in either rod or disk form to match the shape and size in which the sample is

generally prepared or as chips to match the samples that do not cast into homogenous samples. Many of these metallic standards with certified levels of impurity concentrations are available from the National Bureau of Standards or other agencies.

The production of metals and compounds of interest in the nuclear energy field developed faster than a corresponding standards program. The development and ultimate use of the nuclear materials require knowledge of the composition of the material in regard to a large number of elements present and to the concentration of these elements, many in trace amounts. Without adequate knowledge of the composition of the base material, the preparation of reliable metallic comparison standards is difficult if not impossible. There have been attempts to prepare metallic standards of reactor materials suitable for use as spectrochemical comparison standards, but only with certain alloys and with beryllium metal have they proven useful.

Since reactor materials are generally analyzed spectrographically as the refractory oxide and not as the metal, the preparation of synthetic nonmetallic standards is required. A synthetic nonmetallic standard is prepared by mixing known amounts of various substances of known purity either together or as trace components in a pure matrix material so that the final mixture will have definite amounts of the various elements present. The main requirement for nonmetallic standards is that the standards match the expected samples in both chemical composition and chemical form insofar as possible. Equivalence of the concentration of various elements sought is not enough in the preparation of the standard. Since reactor materials are analyzed in the form of the oxide, it is safe to assume that synthetic standards prepared from mixed oxides are acceptable. The validity of this assumption and the resulting reliability of the standard should be checked by comparison with accurate chemical analysis. There are frequently occasions when a sample converted to the oxide in a different manner than the preparation of the standard will vary in density or some other physical property. In these instances the results can be in error.

It is not possible to stress too strongly the care required in the preparation of adequate comparison standards or the need of matching the particular material when endeavoring to make precise spectrochemical analysis of reactor materials.

In the following sections certain procedures that have been found to be successful in the spectrochemical analysis of reactor materials will be highlighted. Additional work is included in the reference section; Table 12.13 lists the references according to the element to which they apply.

12–1.1 Determination of Uranium

(a) *Uranium in Ores.* The high sensitivity of the d-c arc and the ease in making this type analysis naturally lead to this method being tried for the determination of uranium in ores, concentrates, and even biological materials. Kaufman and Perkins [1] made a direct burn of a 10-mg sample. They reported a sensitivity limit of 0.05 per cent U_3O_8; however, the accuracy of this method is not good because of numerous interferences. Several workers [2, 3] used the cathode-layer technique to improve the determination. Mercader and Benavente [2] added molybdenum as an internal standard and, after correcting for spectral background, determined uranium in ores at a concentration of 0.77 per cent with a mean deviation of 8 per cent. Steadman [4] and Strasheim [5] succeeded in increasing the sensitivity for uranium in biological materials by adding buffers or enhancing agents to the samples. Steadman used rubidium chloride, and Strasheim used lead chloride.

In Steadman's procedure the uranium is separated from any extraneous material by an ether separation. The uranium extract is placed on a graphite electrode along with 10 mg of rubidium chloride, and the sample is burned in a d-c arc. The sensitivity of the procedure is 0.02 μg of uranium in the arc. In the Strasheim procedure the uranium extract is evaporated onto powdered graphite, which is used to stabilize the d-c arc. The sensitivity of the Strasheim method for the detection of uranium is reported to be 0.006 per cent U_3O_8 in a sample of 40 mg.

Morozova [6] has presented a procedure for the determination of uranium in ores. Feldman [7] has described Morozova's procedure quite well. Copper electrodes are used to avoid the background effect caused by the graphite electrodes. The sample is mixed with nine times its weight of copper powder plus 4 per cent ammonium molybdate; it is then pressed into a pellet under a pressure of 10,000 kg/sq cm. The added molybdenum is used as an internal standard in the spectrochemical analysis. The pellet is placed in a water-cooled holder and prearced for 20 sec; then an exposure of 40 sec is made using a 6-amp a-c arc. The source used is a Sventitskii ignited low-voltage a-c arc, which is comparable to the various intermittent low-voltage arcs available in this country. When greater sensitivity is desired, the sample is pelletized without the copper powder and placed in a shallow copper dish, which serves as the lower electrode. The spectral lines used in the analysis are U(II) 4090.14 A/Mo 4086.025 A. Standards are prepared by diluting U_3O_8 with SiO_2 and adding the molybdate salt and copper as specified. The procedure is used for samples of ore with 0.1 to 1.0 per cent U_3O_8.

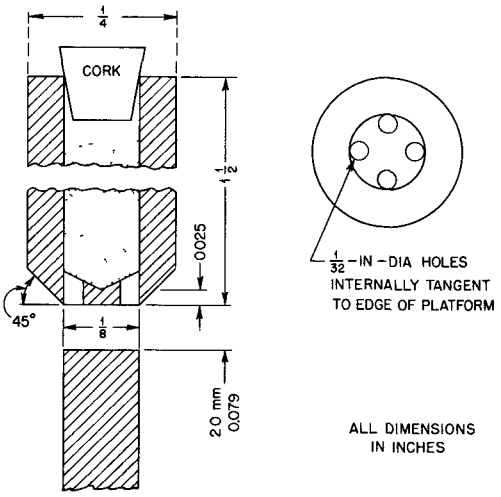


Fig. 12.1—Filled sifter electrode and counter in position for exposure (cutaway and bottom views). Material is graphite. (From Feldman and Ellenburg, *Anal. Chem.*, Ref. 71.)

Czakow [11] reported the determination of uranium using the same source as Morozova, but the sample was contained in a sifter type electrode. The dry ore was mixed with graphite and placed in a three-piece copper electrode similar in design to the Feldman–Ellenburg sifter electrode shown (Fig. 12.1). The sifter holes were adjusted so that the finely ground mixture would pass into the arc column throughout the 30- to 45-sec exposure period. The sample was excited with a Sventitskii low-voltage 6-amp a-c arc. The discharge took place in an oxygen-argon atmosphere to suppress the cyanogen bands. The procedure was used for concentrations from 0.001 to 0.1 per cent uranium and gave a 2.8 per cent precision at the 95 per cent confidence level.

(b) *Uranium in Alloys.* In addition to the determination of uranium as a minor constituent in ores, it also is desirable to determine the uranium content in alloys where it would be classed as a major constituent. Gordon [12] and his coworkers developed a procedure for the determination of uranium in the 2.0 to 6.0 per cent range in uranium-zirconium fuel plates. The procedure used was the point-to-plane technique with a high-frequency spark discharge. The electrodes for the system are a machined flat section of the uranium-zirconium alloy and ¼-in.-diameter graphite electrode machined to a 45° cone tip to be used as a counter electrode. The discharge is a high-voltage spark with 15-sec preexposure and 45-sec exposure of the discharge. This procedure may be limited in its usefulness because the sample

size must always be considered. Small samples subject to localized uneven heat losses during excitation may result in erratic results.

12–1.2 Impurities in Uranium and Its Compounds

(a) *Direct Excitation.* The spectrum of uranium is quite complex, and many line interferences are noted in direct spectrographic impurity measurements. There have been a number of procedures reported in which the author sought to determine either several impurity elements at high levels of concentration or only one or two elements of lower concentration in select areas where the spectral interference would be low. Burkhart [13] reported a procedure for the determination of aluminum, calcium, chromium, iron, molybdenum, nickel, silicon, tin, titanium, and vanadium in concentration ranges up to 0.5 to 1 per cent for the individual elements. In this procedure a rotating step sector was used to reduce the overall intensity of the spectrum of the matrix and also to establish a considerable concentration range for the impurity determinations. A d-c arc was used to produce the desired sensitivities.

Franklin and Woodman [14] and Birks [15] made determinations in the parts per million range by limiting their determinations to select elements and by carrying out the measurements under conditions in which the uranium spectrum gave little interference.

Walsh [16] successfully analyzed uranium metal directly for copper, iron, manganese, nickel, and silicon by using a very arc-like spark discharge. These elements appear as minor constituents (i.e., they are in the concentration range of tenths or hundredths of one per cent) in the uranium metal. The source conditions are as follows: During one half-cycle of the power supply, a condenser of 240 μfd is charged with a peak charging voltage of 310 volts; during the next half-cycle, the triggering circuit passes a spark across the analytical gap, discharging the condenser through an inductance of 0.5 mh, a resistance of 12 ohms, and the analytical gap. Higher values for the capacitance and the resistance will increase the time constant of the discharge to such an extent that the discharge may not be extinguished before the next charging period begins. This procedure uses a machined metal electrode as the lower electrode and opposes it with a pointed graphite electrode. There would probably be some improvement in the analysis if the opposing electrodes were of the same material. The complex spectra obtained from these samples limits the number of elements and range of concentration that can be determined. The standard deviation for the determination of silicon, manganese, copper, and nickel was less than 10 per cent, but for iron the value was approximately 20 per cent.

(b) *Flame Photometry.* The determination of impurities by flame spectroscopy is generally limited to the alkali and alkaline-earth elements. When the particular impurities (sodium, potassium, etc.) are to be determined as part of a number of impurity elements, it may be easier to make the determination on the same sample by emission spectroscopy and not have to make the special sample solutions that are necessary for flame spectroscopy. When the analysis is to be for only one or two impurity elements, especially the alkali metals, it may be easier in regard to sample handling to do the analysis by flame spectroscopy.

The Springfield Works laboratory of the United Kingdom Atomic Energy Authority has routine procedures for the determination of several impurities in uranium material.[17, 18]

> *Procedure.* Five grams of sample as uranium is dissolved in (1+1) nitric acid and evaporated to dryness. If the sample is heterogeneous, the sample weight is increased to 20 g. The uranyl nitrate is dissolved in water, and an aliquot is taken and further diluted so that the final solution concentration equals 1 g of uranium per 100 ml. The sample is placed in the spray chamber of the Lundegarth apparatus, which is used as the source for a medium-dispersion quartz spectrograph. The air pressure for the atomizer is set at 30 psi, and the acetylene gas pressure is set at 65 cm of water. During the burning of the acetylene gas, the sample is allowed to flush the spray chamber for 15 sec before a 30-sec exposure is made to the spectrograph. The lines 4226.7 A for calcium and 5890.0 A for sodium are measured. The spectral background measured at a distance of 1 mm from each line is used as the internal standard. The procedure is used for the determination of calcium at concentrations of 50 to 2,000 ppm and for sodium at concentrations of 20 to 10,000 ppm with a precision of ±10 per cent.

Kramer and Pinto [19] extended the flame photometric procedure to the determination of sodium in uranium ores. The lower limit of sensitivity was 0.001 per cent. In this procedure no prior chemical separation is required for the impurities that might cause individual interferences when present in large amounts. Compensation for these possible interferences is made by preparing a special buffering solution containing a number of these other substances and adding a finite volume of this solution to both the standards and sample solutions. When this is done, small variations in the concentrations of the major elements within the samples themselves have little or no effect on the sodium emission. The composition of the buffering solution is shown in Table 12.1. The instrument used in this analysis was a Beckman DU spectrophotometer with the flame attachment. The source was an oxyhydrogen flame with an operating hydrogen pressure of 4 psi and an oxygen pressure of 10 psi.

Although the flame photometer has its best application in the determination of the alkali metals, its use is not limited to the determina-

Table 12.1—COMPOSITION OF BUFFERING SOLUTION FOR THE DETERMINATION OF SODIUM

Element	Concentration in final standard solution, ppm	Element	Concentration in final standard solution, ppm
U	425	Mg	200
V	10	Al	100
Ca	20	K	200
Fe	20	Mn	10
SO_4^{-2}	3.3	B	10
PO_4^{-3}	200	Cu	10

tion of the alkalis. With the use of sensitive photomultiplier tubes for signal detection and either oxygen-hydrogen, oxygen-ethane, or even oxygen-cyanogen burners for higher energy flames, the elements that require greater excitation energies can now be determined. The procedures are relatively simple in that the elements in question are separated and taken up in aqueous solutions, which are then atomized in the flame photometer. Menis [20] and his coworkers reported a procedure for the determination of lanthanum in solutions from a variety of materials. No chemical separation is necessary since there is little interference from any foreign ions at the region 743 mμ where the measurements are made. The intensity of the lanthanum emission was increased when the solution used in the analysis was a water-methanol mixture (1+1) instead of a plain aqueous solution.

Possidoni de Albinati [21] made flame photometric determinations of lanthanum, iron, and magnesium after chemical separations from uranium nitrate solutions.

In this procedure a 10-g sample of uranium is converted to the nitrate, and the aqueous solution is evaporated almost to dryness. The sample is then taken into solution with 4*M* nitric acid and extracted with 5-ml portions of peroxide-free ether until the ether phase is colorless. The aqueous phase containing the iron, lanthanum, and magnesium is evaporated almost to dryness. This residue is dissolved in 5- to 7-ml of 6*N* hydrochloric acid, and the ferric chloride is removed by an ether extraction. The two portions are evaporated to dryness to remove all traces of ether, and the residue is dissolved in water and made to a 25-ml volume. The samples are then burned in the flame attachment for the Beckman DU spectrophotometer using either an oxygen-hydrogen or oxygen-ethane flame. The lanthanum is measured at 440 mμ, magnesium at 371 mμ, and iron at 372 mμ.

(c) *Physical Separation of Impurities.* (1) *Carrier-distillation Method.* Scribner and Mullin [22] developed a spectrographic procedure

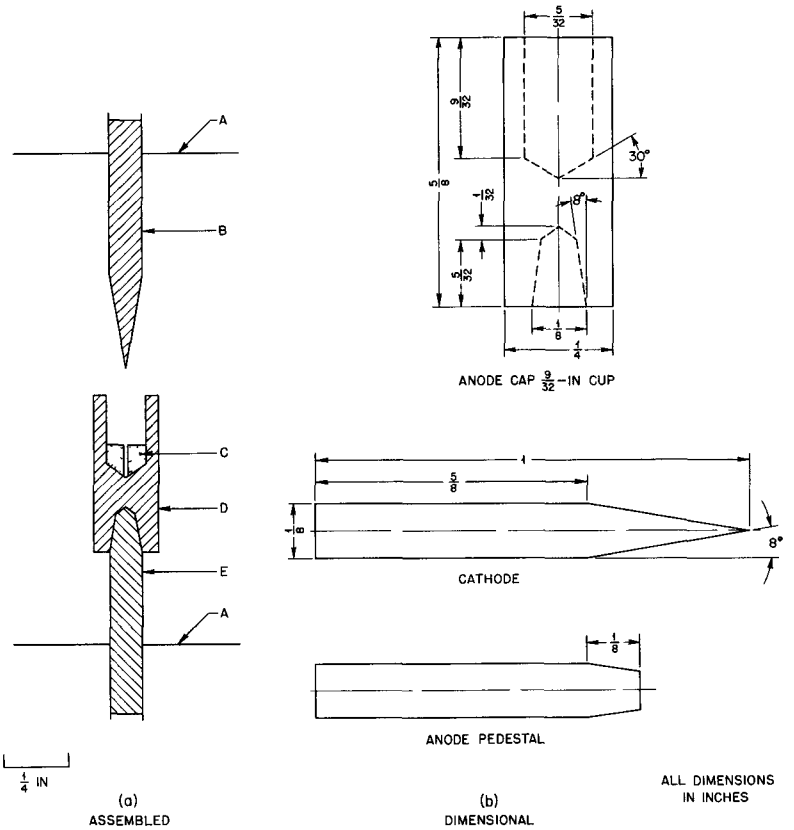


Fig. 12.2—Pedestal electrode. A, holder. B, cathode. C, sample charge. D, anode. E, pedestal. (From Scribner and Mullin, *J. Research Nat. Bur. Standards*, Ref. 22.)

that has been extensively used in the analysis of refractory materials and is identified as the carrier-distillation technique. The original work was applied to the analysis of uranium compounds and included the spectrographic determination of 33 volatile impurity elements at concentrations as low as a fraction of a part per million for many of the elements.

In this procedure the uranium material is first converted to the refractory oxide U_3O_8. To a portion of this material, 2 wt.% gallium oxide is added and is well mixed with the U_3O_8 by grinding. One hundred milligrams of the mixture is weighed into the anode cap electrode (Fig. 12.2), and a needle hole is punched through the charge into the graphite to serve as a vent hole for the escape of the gases formed during the arcing of the sample. The electrodes, spaced with a 4-mm arc gap, are placed in a support stand using a pedestal elec-

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trode as the support for the anode cap. The spectral excitation source is a 10-amp d-c arc. The electrode clamps must be water cooled, otherwise the heating of the electrode charge becomes very erratic and nonreproducible and a poor exposure cycle frequently results. The pedestal electrode extends ½ in. from the lower electrode clamp. The spacing of the electrodes should be consistent to give reproducible burns of the sample electrodes. After a 5-sec prearc period, the spectrum is recorded for 30 sec; this period includes all of the smooth-burning time of the carrier-distillation cycle. The spectrum is then examined for the sensitive lines of the elements of interest. If a slight increase in sensitivity for boron, cadmium, arsenic, and other volatile elements is desired, the prearc period is omitted; however, this will generally add background to the remainder of the spectrum and may interfere with the determination of the other elements.

The reproducibility of spectra with this procedure is quite good, and a precision of about 10 per cent can be obtained for many impurities by photometric measurement of samples and standards on the same plate. The less volatile elements, such as iron, manganese, and nickel, are much more sensitive to fluctuations in the discharge and yield less reproducible results. Scribner and Mullin showed that greatly improved precision can be obtained for these elements by adding an internal standard element, such as chromium, which responds similarly to the arc fluctuations. The chromium is incorporated into the sample by adding it as chromic oxide to the gallium oxide carrier. The amount added to the gallium oxide is 1 wt.% chromium.

A considerable amount of additional study has been carried out on the carrier-distillation procedure both in regard to the type of carrier used and to the different elements used as internal standards. Silver chloride, recommended by Harrison [24] as a carrier, has proven quite popular. The use of this carrier does seem to increase the sensitivities of detection for some elements to a slight extent. Carriers containing fluorides are effective in increasing the sensitivity of detection of boron.[26, 27] Serin and Franklin [28] found that the use of sodium fluoride as a carrier increased the sensitivity of lithium detection, and Leslie and Kiehl [29] were successful in extending the sensitivity for molybdenum detection from the usual 1 to 3 ppm down to 0.1 ppm by using copper sulfide as the carrier.

The particular element used as an internal standard in spectrographic analysis is dependent upon the elements determined. Ramsay [31] used cobalt at a level of 250 ppm in the uranium oxide as a spectrographic internal standard to determine iron. The use of cobalt as an internal standard gave results with a coefficient of variation of

0.9 per cent as against 15 per cent without it and a bias of plus 6 per cent in comparison to 44 per cent obtained formerly. At the New Brunswick Laboratory, it was found that the use of either cobalt or vanadium as an internal standard element was satisfactory. The cobalt or vanadium is added to the gallium oxide during its preparation as 1 per cent of the total weight of gallium oxide. This gives the internal standard element a concentration range of 200 ppm in the sample, and the spectral lines obtained have a suitable density for measuring.

Some investigators working for the United Kingdom Atomic Energy Authority [82] have extended the carrier-distillation procedure to include the removal of the impurities from one refractory matrix and the transfer of these impurities by adsorption to another matrix. The concentrations are determined from a carrier-distillation spectrographic analysis of the second matrix. A procedure of this nature was developed for the special determination of cadmium. This technique can also be applied for other elements. A 5-g sample of uranium is dissolved in nitric acid, and, after the removal of excess acid, citrate is added and the pH is adjusted to the end point of phenolphthalein. The cadmium impurity is extracted as the dithizonate into carbon tetrachloride. The extract is passed through an alumina column on top of which the cadmium is retained. The portion of the alumina containing the cadmium is mixed with a carrier containing arsenic, which is incorporated as an internal standard, and examined spectrographically using the carrier-distillation technique. The concentration of cadmium is determined from the intensity of the cadmium 2288.0 A line in comparison to the arsenic 2288.1 A line. The method is suitable for the analysis of uranium with cadmium content ranging between 0.015 and 0.15 ppm.

The sensitivity obtained from spectrographic examination by the carrier-distillation method is rather fixed for each type of material. The exposure cycle is internal and comes directly from the sample material and carrier used. It is not possible to increase the time of exposure to increase sensitivity as is done in other methods, and increases in sample size or amperage of the arc does not necessarily increase the quantity of the element detected by comparable amounts. Since the type of matrix substantially affects the behavior of the impurities in the carrier-distillation procedure, Marinković [183] changed the matrix from U_3O_8 to uranium dioxide by hydrogen reduction prior to the arcing of the sample. This sample procedure gave enhanced line intensities, and it improved the detection limits for the impurities by a factor of 2.5 to 8 depending upon the element.

(2) *Evaporation–distillation Method.* Another method for determining the impurities in refractory materials is to physically remove

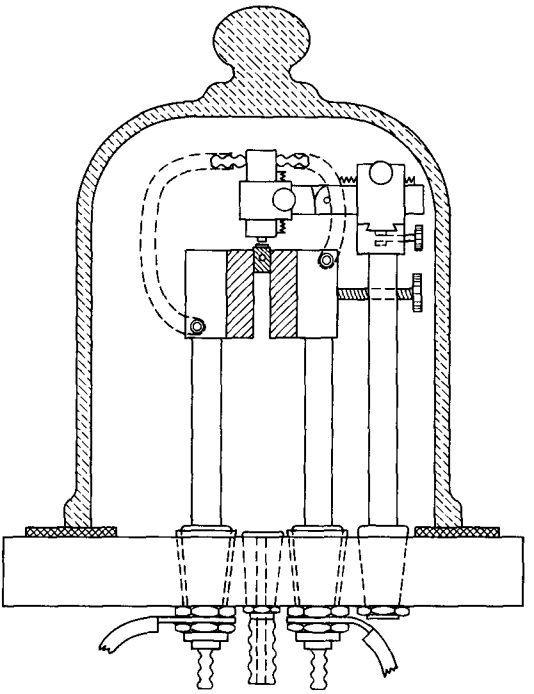


Fig. 12.3—Schematic drawing of a vacuum evaporator.

those impurities from the sample matrix and to subject only the separated concentrate of impurities to spectrochemical analysis. Mandel'shtam, Semenov, and Turovtseva [33] introduced a procedure based on distilling the impurities from uranium, condensing the impurities on a cooled graphite electrode, and then exciting the separated impurities in either an arc or a spark discharge. Zaidel' [34, 35] and his coworkers reported a very similar method. In their procedure the impurities are evaporated from the sample under a vacuum. The degree of condensation of impurities on the condensing electrode, both in air at atmospheric pressure and in a vacuum (10^{-2} mm), for sample heating temperatures of 800 to 2000° C was studied for uranium oxide, plutonium dioxide, thorium oxide, beryllium oxide, zirconium oxide, lanthanum oxide, and aluminum oxide.

Procedure. The evaporation of impurities from the sample is carried out as follows. A 10- to 50-mg sample (sample weight depends upon matrix material used and sensitivity of detection desired) is placed in a graphite crucible about the size of the carrier-distillation electrode. The crucible is then placed in an oven and heated to approximately 600°C to remove water and gases. The crucible is then placed in the evaporation apparatus, and the vacuum is turned on. Figure 12.3 shows an overall view of the apparatus for the distillation of the impurities under re-

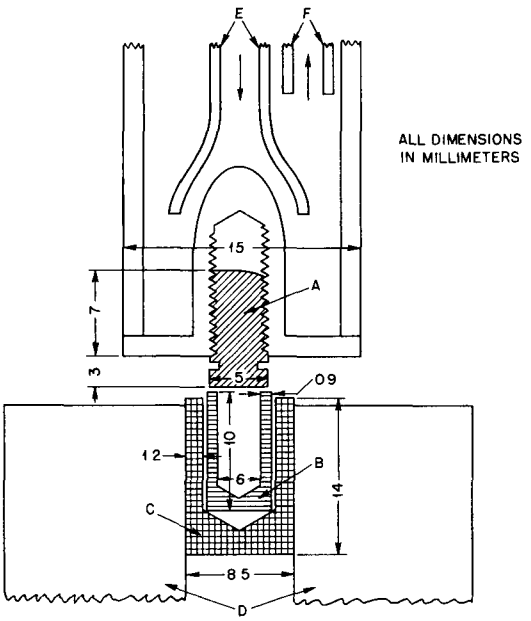


Fig. 12.4—The evaporation setup. A, cooled capsule. B, inner graphite beaker containing test sample. C, outer graphite beaker (oven). D, contact graphite clamps. E, lead-in tube for water. F, exit tube for water.

duced pressure. Figure 12.4 shows a close-up of the electrode assembly and the electrode furnace for the distillation of the impurities. When the required vacuum (0.01 mm of mercury) is reached, the current is switched on, and the crucible electrode is heated to 1400 to 2000°C. The preferred temperature is 1600°C. At a higher temperature there is the possibility that some of the more volatile impurities, such as antimony, bismuth, or cadmium, might be reevaporated from the condenser electrode because of the closeness of the hot crucible. The test sample is heated for 1 to 2 min at this temperature for complete removal of the volatile components. After the distillation step the electrode with the condensed impurities is used as one electrode in the analytical arc gap. The discharge can be either an arc or spark, whichever procedure would give the optimum sensitivity for the particular determination desired. Usually the source is similar to an IG–2 spark generator under the following conditions: capacitance, 0.01 mfd; inductance, 0.15 mh; and current, 2 amp.

The methods previously described under physical separation of impurities are necessarily applicable to the determination of only some elements, and none can be used for the nonvolatile impurities, such as the rare-earth elements, platinum metals, or the other refractory elements. For these elements to be determined spectrographically, it is necessary to first make certain chemical separations either to con-

centrate the desired elements to detectable levels or to remove the interfering matrix material. The chemical procedures are described in Sec. 12–2. The resulting product available for spectrographic examination following the chemical treatment can be either a solid or a liquid sample. The solid sample can be analyzed by any of the conventional procedures. The liquid sample can be analyzed spectrographically by conventional solution procedures or by either evaporating the solution to dryness to obtain a solid matrix or absorbing the solution in another matrix and analyzing this matrix by regular spectrochemical procedures. The excitation of the electrodes in all solution procedures is generally with a high-voltage spark discharge. The several techniques differ from each other in the manner of getting the sample solution into the spark gap. The different procedures for handling the solutions are identified as the porous cup, the rotating disk, and the copper spark; in the latter the solution is dried to a film on copper electrodes. The atomization of a solution into a flame in flame spectrophotometry is also an application of the spectrochemical analysis of solutions.

In summary, chemical separations of the components of the sample are made for the following reasons: (1) It is possible to extract the impurities from a large sample and thereby increase the ultimate sensitivity of detection of the element of interest by making more of that element available for determination. (2) The matrix of the spectrochemical sample can be closely controlled by extracting the impurities from a reactor material with a complex spectrum and depositing the impurities thus extracted on a matrix material with a relatively simple spectrum. (3) Sampling, which is frequently a problem in trace analysis, can be reasonably eliminated when solutions are a step in the spectrochemical analysis. (4) It is not necessary to limit the separation to the specific group involved; further separations can be made to remove all but one or two impurities; then determine these spectrographically.

(d) *Chemical Separation of Impurities.* For some problems it may not be possible or practical to develop direct spectrochemical procedures for the determination of the desired impurities, and preliminary chemical separations may be necessary. Any of the more selective separation procedures may be used, i.e., solvent extraction of compounds or organic complexes, electrolytic deposition to a mercury cathode, adsorption with an ion-exchange column, or precipitation with a suitable carrier to collect the minor constituent. Many of the individual chemical procedures will be found in Sec. 12–2. In this section a part of the spectrographic procedures dealing with either the solid or liquid residues from the samples will be considered.

As in other spectrochemical procedures, the solid sample residue may be either burned directly by arc or spark excitation or mixed with buffers or other materials to establish a new sample matrix and then burned according to procedures common to these materials. For liquid samples the spectrochemical analysis of a solution is usually made by a residue method, such as the copper-spark technique, by an impregnation method, such as the porous-cup technique, by a continuous-feed method, such as the rotating-disk technique, or directly in an instrument such as a flame photometer.

Although these procedures will be discussed in a section concerned with the determination of impurities in uranium, it is not the intent to imply that these procedures are limited to uranium analysis. Chemical separations have been used for all reactor materials, and, after the final separation has been completed, the spectrographic treatment is very similar in all cases.

(1) *Copper-spark Technique.* The copper-spark technique is not particularly new; the method had been used in the past for many determinations. However, Fred [37] and coworkers extended the procedure to include so many elements determined on a routine basis that the procedure has been associated with them. Fred and coworkers originally applied the procedure to plutonium analysis; however, it was also used extensively in uranium analysis. The procedure can be applied to a test solution prepared by any chemical-separation technique followed by evaporation of the resulting solution on copper electrodes. The spectra obtained from the copper-spark exposure are then examined. The method is also satisfactory for the determination of impurities in acids and other liquids for which the bulk of the sample can be removed by evaporation. It can be used to determine minor impurities in any solid sample soluble in acid; the sensitivity of the method for impurities is limited by the amount of spectral interference from the main constituent and by the fact that only a small weight of sample can be utilized.

The electrodes are formed from 0.25-in.-diameter copper rods; the ends are machined flat and the surface of the sides is removed for a distance of about 0.5-in. back from the ends. No other cleaning except a preliminary nitric acid wash is necessary. Since the acidic sample solution has a tendency to run over the side of the electrode, the electrode is first treated by dipping it in a petroleum-ether solution of Apiezon N grease (1 g per liter). The sample, in the form of 0.1 ml of 1 per cent hydrochloric acid solution, is deposited in equal portions on the ends of two electrodes and is evaporated to dryness. Care in evaporation should be observed to avoid boiling and spattering of the sample solution. The exposure conditions are not

critical. Any convenient spark source and spectograph can be used; the exposure times are usually 30 sec or less because a sample is rapidly consumed. The reported sensitivities of the method for various elements are shown in Table 12.2.

(2) *Porous-cup Technique.* Some procedures for the analysis of solutions are limited in usefulness because the solutions contain high concentrations of salts that clog atomizers or leave fluffy or deli-

Table 12.2—SENSITIVITIES WITH COPPER-SPARK AND POROUS-CUP TECHNIQUES

Element	Sample		Element	Sample	
	Copper spark, mμg	Porous cup, μg/ml		Copper spark, mμg	Porous cup, μg/ml
Ag	----	0.1	Mg	1	0.001
Al	10	0.2	Mn	2	0.1
As	500	50	Mo	5	0.5
Au	20	10	Na	10	----
B	----	0.5	Nd	20	----
Ba	10	----	Ni	10	1
Be	0.2	0.005	P	2000	50
Bi	20	5	Pb	5	5
Ca	10	----	Pd	50	0.5
Cb	20	1	Pr	20	----
Cd	200	10	Pt	2	10
Ce	50	----	Rb	20	----
Co	50	2	Re	200	5
Cr	5	0.1	Ru	----	50
Cs	50	----	Sb	500	5
Cu	----	0.05	Sc	0.5	0.1
Dy	50	----	Si	10	----
Er	50	----	Sm	20	----
Eu	2	----	Sn	----	2
Fe	50	0.3	Sr	50	----
Ga	100	10	Ta	100	2
Gd	10	----	Te	50	50
Ge	----	10	Th	20	25
Hf	50	2	Ti	10	0.05
Hg	500	10	U	100	----
Ho	20	----	V	5	0.3
In	100	10	W	50	10
Ir	500	----	Y	1	0.01
K	10	----	Yb	10	----
La	5	0.5	Zn	200	10
Li	0.2	0.1	Zr	10	0.2
Lu	200	----			

quescent residues when evaporated. Feldman [38] has reported a procedure for the spectrochemical analysis of solutions that does not have these particular objections. All aqueous, acidic, neutral, or weakly alkaline solutions that wet graphite can be analyzed by the porous-cup technique. Some solutions of pH 9 and above do not wet graphite sufficiently to give the desired wick action. In recent work Feldman reports that carbon, particularly National Carbon Company grade L 1135P carbon, is much superior to graphite for making porous cups.

The upper-cup electrode consists of a 0.25- by 1.5-in. cylindrical graphite rod with a 0.125-in. hole drilled along its axis from one end to within 1.1 ± 0.2 mm of the other end. A greater floor thickness than this may prevent the passage of some solutions; a lesser thickness increases the danger of puncture during the sparking cycle. This electrode, with the open end up, serves as the upper electrode in the electrode system. The lower electrode is a solid 0.125-in. graphite rod. The upper electrode is filled by inserting a long-nosed pipet containing 0.2 to 0.3 ml of the solution to be analyzed into the cavity until the tip touches the bottom; the solution is then expelled as the pipet is withdrawn. Using a 2-mm arc gap the electrodes are excited for 5 to 10 sec with a high-voltage spark. This discharge heats the electrodes slightly and helps the liquid to soak through the bottom of the porous cup and to reach the sparking surface. After about a 15-sec rest period the sparking is resumed.

Approximate sensitivities of this method for various elements are shown in Table 12.2.

(3) *Rotating-disk Electrode Procedure.* A rotating-disk electrode is a convenient method for analyzing solutions and is used in many reactor-material laboratories where solutions are spectrographically analyzed. Pierucci and Barbanti-Silva [39] studied this technique extensively. The procedure has the advantage over spray methods of being free of errors caused by the formation of dried salts. Although porous-cup electrodes can be used with some oils and viscous solutions, the rotating disk is better in that these particular solutions can be more readily handled.

Owing to the relatively high resistance of the solution, this procedure does not function well with d-c arcs. Excitation can be either by condensed spark or by spark-ignited interrupted-arc discharge. The condensed spark will give better precision, but the interrupted arc will give greater sensitivity.

The necessary equipment for this procedure is commercially available and consists of a disk of graphite ½ in. in diameter and ⅛ in. thick with a central hole to fit onto a horizontally mounted spindle, which is rotated at about 5 to 6 rpm. This serves as the lower electrode.

The lower rim of the disk is arranged to dip into the sample solution contained in a shallow boat. A tapered graphite electrode is positioned above the disk so that an electric discharge passing between the electrodes is continuously fed with solution.

The speed of the rotating disk, the type of discharge, particularly in respect to current and resultant heating of the electrode and solution, and the concentration of solution are all interdependent variables and should be studied with some care to determine the optimum conditions.

12–1.3 Determination of Plutonium

Plutonium is one of the elements unknown prior to the development of the atomic energy program. Plutonium, like uranium, has a complex spectrum. When plutonium is excited in a direct-burn discharge, the sensitive lines of a number of elements are completely masked, and the determination of trace impurities is made difficult. Plutonium is not a desirable material to analyze spectrographically. In addition to having a complex spectrum, plutonium is also a strong alpha emitter and is quite toxic. Because of its toxic nature, extensive alpha hood trains and elaborate personnel safeguards are required during the sample-preparation and arcing processes. Plutonium, as such, is generally determined by chemical or radiochemical procedures; however, Birks [40] determined plutonium as the major constituent in a mixture by the iron-flux technique.

Procedure. The sample is diluted (1+10) with a flux composed of ferric sulfate and ammonium sulfate. The mixture is pressed into a pellet and burned in a 7-amp d-c arc using a copper electrode as the support electrode and a copper counter electrode. The ratio of the intensity of the 2904.3 A spectral line for plutonium to the 2901.4 A line for iron is used to determine the concentration of plutonium. The concentration range covered is 0.5 to 100 per cent plutonium oxide. The procedure has a coefficient of variation of 6.6 per cent at the 50 per cent concentration level. Other elements that exist as major impurities in plutonium can also be determined from this direct burn by the iron-flux method.

12–1.4 Impurities in Plutonium and Its Compounds

(a) *Direct Excitation.* Zotov and Fowler [41] reported a procedure for the direct determination of a number of impurities in plutonium. This procedure is based on a method similar to the copper-spark procedure reported under uranium. Graphite electrodes waterproofed with a solution of Apiezon N grease are used as support electrodes. The sample is added to the electrode as the nitrate in $2N$ hydrochloric acid solution. This procedure lacks the desired sensitivity for the determination of many impurities at trace levels in plutonium; how-

ever, the sample is readily prepared and, at higher levels of impurities, would be satisfactory. The spark discharge is made in an oxygen atmosphere that decreases the spectral background due to cyanogen and thus does improve the sensitivity of detection for many spectral lines. Zaidel'[42] and coworkers reported a similar procedure using a chloride solution evaporated in a vacuum on copper electrodes. For this work an argon atmosphere was used instead of oxygen. They reported an increase in the spectral sensitivity of a factor of 10 over Zotov's work.

(b) *Formation of a Volatile Matrix.* Another direct spectrographic method for the determination of trace amounts of impurities in plutonium was developed by Johnson and Vejvoda.[43] This procedure lacks the sensitivity of some of the other procedures, such as the carrier-distillation method or the ion-exchange–copper-spark technique; however, the method requires less handling of the samples and consequently results in greater speed in analysis. The method is somewhat similar to the carrier-distillation procedure in that a volatile matrix is used which has a definite quenching effect on the plutonium spectrum. The procedure is accurate to ±20 per cent of the amount present for the particular elements densitometered. The detection sensitivity for the 34 elements determined by this procedure is shown in Table 12.3.

Procedure. The sample is dissolved in nitric acid, and 500 μg of plutonium is placed on 800 μg of sodium fluoride previously placed in a cupped, waterproofed graphite electrode. The cup is a 1-mm-deep hemispherical depression in a ¼-in. graphite electrode (United Carbon Products type 4925). The graphite electrode is waterproofed with an ethereal solution of Apiezon N grease. The counter electrode in the system is a ⅛-in.-diameter pointed graphite rod. The electrodes are excited with a 2400-volt 4.5-amp a-c arc for a 4-sec exposure following a 4-sec preburn.

(c) *Physical Separation of Impurities.* Because of the refractory nature of plutonium oxide and the complexity of its spectrum, impurity spectral analysis is generally made with the same procedures used for uranium analysis. The carrier-distillation procedure described in the uranium section has been applied almost identically to the spectroanalysis of plutonium. The original carrier-distillation spectrochemical procedure for impurties in plutonium was even based on comparison with standards made of a uranium oxide matrix. Kofoed[44] studied the effect of the sample matrix on the determination of impurities in plutonium and found that to make a spectrochemical analysis of plutonium by the carrier-distillation procedure it is quite necessary that the sample be compared against plutonium oxide standards and not uranium oxide standards. Many elements give different spectrographic response when excited from a uranium oxide

Table 12.3—WAVE LENGTHS OF SPECTRAL LINES AND LIMITS OF DETECTION FOR IMPURITIES IN PLUTONIUM OXIDE WITH SODIUM FLUORIDE CARRIER

Element	Wave length, A	Limit of detection, ppm	Element	Wave length, A	Limit of detection, ppm
Ag	3280. 68	10	In	3256. 09	100
Al	3082. 16	25	La	4333. 74	2000
As	2349. 84	2000	Mg	2795. 53	25
Au	2427. 95	200	Mn	2801. 06	25
B	2497. 73	25	Mo	3132. 59	25
Ba	4554. 03	25	Nb	3094. 18	2000
Be	2348. 61	4	Ni	3002. 49	25
Bi	3067. 72	100	Pb	2833. 06	50
Ca	3933. 67	25	Pd	3242. 70	200
Cd	2288. 02	100	Sb	2598. 06	1000
Ce	3942. 75	10000	Sn	2839. 99	25
Co	3405. 12	1000	Th	3208. 03	10000
Cr	3024. 35	25	Ti	3199. 92	200
Cu	3273. 96	25	V	3185. 40	40
Fe	2599. 57	50	W	4294. 61	2000
Ga	2874. 24	100	Zn	3282. 33	100
Ge	3039. 06	200	Zr	3391. 98	2000

matrix than from a plutonium oxide matrix. Furthermore, the density of the oxide must be the same for both sample and standards for best results, and this is a condition difficult to obtain for plutonium and uranium oxides. Table 12.4 taken from Kofoed's work shows a comparison of the detection sensitivities of a number of elements in plutonium when compared to uranium oxide standards and also plutonium oxide standards.

12–1.5 Determination of Thorium

Thorium is listed as a refractory metal and as such has a complex spectrum with many spectral lines of approximately the same intensity. In this respect thorium is comparable to uranium, and similar techniques can be used for both the spectral determination of thorium and also the spectral determination of the impurities in thorium.

(a) *Direct Excitation.* On the direct determination of thorium in its ores, the estimated sensitivity is approximately 1 per cent. Dutra and Murata [45] have proposed a procedure for determining thorium directly in its ores, especially monazite, in the range of 3 to 20 per cent thoria. The coefficient of variation was 4 per cent with a maximum error of ±10 per cent of the thoria content. The method developed uses zirconium as the internal standard element. Although monazite

Table 12.4—SPECTRAL SENSITIVITIES IN PLUTONIUM OXIDE COMPARED TO URANIUM OXIDE

Element	U_3O_8 std., ppm	PuO_2 std., ppm	Element	U_3O_8 std., ppm	PuO_2 std., ppm
Ag	1	1	Mg	10	20
As	20	20	Mn	5	5
B	1	1	Mo	10	10
Be	1	1	Na	1	1
Bi	5	2	Ni	10	20
Cd	10	20	P	100	20
Cr	1	1	Pb	10	2
Cu	1	1	Sb	20	20
Fe	50	50	Sn	10	2
Ge	5	2	Te	2	2
K	5	5	V	10	50
Li	1	1	Zn	50	20

ore itself is generally free of zirconium, the ore should be checked beforehand because some monazite concentrates may contain zirconium, and its presence at concentrations greater than 1 per cent in the original samples would constitute an interference. In these cases it would be necessary to first remove most of the zirconium from the samples.

Procedure. The monazite sample is diluted (1+15) with a pegmatite base (60 parts quartz, 40 parts microcline, and 1 part ferric oxide) containing 0.538 per cent zirconium oxide. The zirconium oxide content of the mixture is 0.500 per cent. The diluted sample is mixed with graphite in the ratio of 2 parts sample to 1 part graphite. Approximately 25 mg of sample mixture is placed in a 3.3-mm-diameter by 6-mm-deep cup in an undercut 6-mm graphite electrode that is made the anode of a 15.5- to 17.5-amp d-c arc. The arc is maintained until the sample is completely burned. The spectral line used is Th(II) 2870.41 A, and the internal standard line is Zr(II) 2844.58 A. Comparison synthetic standards are prepared by mixing graduated amounts of thorium oxide in a pegmatite base and then adding zirconium oxide as 0.500 per cent of the mixture.

(b) *Examination of Chemical Concentrates.* In addition to the methods used for the direct determination of thorium, procedures based on a preliminary chemical separation of the thorium have also been employed. Waring and Mela [46] separated the thorium along with the rare-earth materials in the sample and then determined the thorium in the rare-earth mixture. The rare earths and thorium are concentrated by a double oxalate precipitation using calcium as a carrier. The rare-earth and thorium mixture is freed from calcium by an

ammonium hydroxide precipitation with a fixed amount of aluminum as a carrier. The aluminum also serves as an internal standard in the spectrographic analysis. The precipitated hydroxides are ignited to the oxides, and 10 mg of the oxide is mixed with 20 mg of graphite and placed in the cup of a graphite electrode and made the anode of a 12-amp d-c arc. The precision of the determination by this method is approximately 10 per cent.

12–1.6 Impurities in Thorium and Its Compounds

(a) *Direct Excitation.* Since thorium oxide is a very refractory compound, reproducible d-c arc discharges that would permit the determination of trace impurities in the sample cannot readily be produced. Fassel and DeKalb [48] reported a conducting-briquette technique for the determination of the impurities in thorium metal. This procedure does not require any prior separation of the impurities, either physical or chemical, for the analysis. In this method conductivity is imparted directly to the sample by forming conducting briquettes from mixtures of finely divided thorium oxide and powdered flake graphite. The pellets are excited by a high-energy unidirectional overdamped condenser discharge; however, other types of controlled alternating or interrupted discharge should be applicable. With this type of excitation technique, there is no suppression of the thorium spectrum; so numerous cases of spectral-line interference will be encountered.

Procedure. The thorium metal is ignited to the oxide at 750°C for 3 to 4 hr. The ignited oxide is finely ground in a tungsten carbide mortar, and then it is well mixed with an equal weight of flake graphite (National Carbon Company SP–2). Six hundred milligrams of the sample–graphite mixture is pressed into a ¼-in.-diameter pellet under a total load of 7000 lb. Heating the briquette at 300 to 400°C for 10 min prior to excitation makes the briquet more resistant to fracture during the excitation cycle. The pellet is made the lower electrode in the discharge system, and a ⅛-in.-diameter flat-end graphite rod is used as the counter electrode. The sample is excited in the spark discharge for 60 sec. The spectrum from the sample is examined for the elements listed in Table 12.5. The table also includes selected internal standard lines and the concentration range of the impurities.

(b) *Physical Separation of Impurities.* Since there is so much similarity in the analytical emission spectroscopy of thorium and uranium, it is only natural that the same procedures that have proved successful in uranium analysis should be used in thorium analysis. The carrier-distillation technique has been used extensively by the various workers engaged in the analysis of thorium. All impurity elements do not show the same sensitivity of detection for thorium-base materials as are reported for uranium-base materials. Care must

Table 12.5—LINE PAIRS USED IN THE CONDUCTING-BRIQUETTE PROCEDURE

Element	Line pair, A	Concentration range, ppm
Al	Al 3961.53 / Th 3923.81*	10–600
Be	Be 3130.42 / Th 3141.85	10–500
Ca	Ca 3933.67 / Th 3895.42	20–600
Fe	Fe 2599.39 / Th 2603.57*	20–600
Mg	Mg 2802.69 / Th 2816.08	20–600
Ni	Ni 3012.00 / Th 2993.07*	20–600
Si	Si 2516.12 / Th 2534.61*	30–600
Zr	Zr 3496.21 / Th 3489.83	100–1200
Zr	Zr 3496.21 / Th 3491.58	250–4000

*These thorium lines were identified by the authors.

be used in the selection of comparison standards; and, if at all possible, standards prepared from similar types of material should be used. The evaporation method of Mandel'shtam [33] and Zaidel' [34] has also been extended to include the analysis of impurities in thorium. This procedure, of course, is less critical of the source of the standards. In the evaporation procedure the standards used for uranium impurity analysis could also be used in the thorium analysis.

12–1.7 Determination of Beryllium

Beryllium as a reactor material is quite important because of its value as a light-weight structural material and because of its nuclear property of being a good neutron reflector. Beryllium is toxic and must be handled very carefully during its fabrication and during analysis. Special precautions must be taken at each step to protect not only those working with the material but also those inside and outside the building. Necessary precautions require the use of hoods and glove boxes for the sample preparation.

Because of the toxicity of the beryllium materials, almost all the development work for the determination of beryllium by spectrochemical procedures has been limited to the determination of beryllium in air. This aspect of analysis of nuclear materials is not being covered in this chapter. For those who would be particularly interested in this problem, several references are included in the bibliography (see Refs. 49 through 52).

12–1.8 Impurities in Beryllium and Its Compounds

(a) *Direct Examination: Buffered Sample.* The carrier-distillation technique is the method generally used in the spectroanalysis of refractory materials, and it has been successfully used for the determination of many elements in beryllium oxide.[53–55] However, it is not applicable to the determination of important impurities such as aluminum, calcium, silicon, and other elements whose oxides are too refractory to be vaporized satisfactorily during the carrier-distillation cycle. Smith and Fassel [56] reported a procedure for the determination of aluminum, calcium, chromium, iron, magnesium, manganese, and silicon in beryllium metal and its compounds in which the sample as beryllium oxide is mixed with a mixture of graphite and barium hydroxide containing some tin oxide. The mixture is burned directly in a d-c arc. The graphite-barium hydroxide buffer stabilizes the arc discharge so that reproducibility of the determination is obtained. The tin salt is included strictly as an internal standard element for the densitometric determination of the impurities.

Procedure. Beryllium metal is converted to the oxide by cautiously dissolving the metal in purified dilute hydrochloric acid, adding an excess of purified ammonia, evaporating the slurry to dryness, and igniting it at 700°C for 1 hr. The oxide sample is ground with the proper amount of a previously prepared graphite mixture. The graphite mixture is of such composition that the final composition of the electrode charge is: beryllium oxide, 55.7 per cent; graphite, 33.3 per cent; barium hydroxide, 10.0 per cent; and tin oxide, 1.0 per cent. An electrode charge of 15 mg of the mixture is placed in a 2- by 5-mm cup in the end of a ¼-in. graphite electrode. The counter electrode is a ⅛-in. pointed graphite rod. The sample is excited for 20 sec with a 16-amp 250-volt d-c discharge. The spectrum is examined for the elements and the concentrations shown in Table 12.6.

Powdered beryllium metal can be used in place of the beryllium oxide in the Smith–Fassel procedure. The fine-grain berryllium metal in a sieve size of 100 to 325 mesh should be mixed fresh with the graphite–barium hydroxide mixture. If the powdered metal and graphite–barium hydroxide mixture is permitted to stand for a period of time after mixing, the material has a tendency to separate again, and this results in poor spectral exposures. The standards for

Table 12.6—LINE PAIRS USED IN THE GRAPHITE-BARIUM HYDROXIDE BUFFER TECHNIQUE FOR ANALYSIS OF BERYLLIUM

Element	Line pair, A	Concentration range, ppm
Al	Al 3961.53 / Ba 3993.40	50–2500
Ca	Ca 3179.33 / Sn 3141.81	100–5000
Cr	Cr 2843.25 / Sn 2913.54	50–1000
Fe	Fe 2966.90 / Sn 3032.78	90–500
Fe	Fe 2813.29 / Sn 2913.54	500–5000
Mg	Mg 2781.42 / Sn 2913.44	100–5000
Mn	Mn 2949.21 / Sn 2913.54	50–1000
Mn	Mg 2801.64 / Sn 2913.54	5–60
Si	Si 2881.58 / Sn 2850.62	50–5000

the spectral comparison should also be as powdered metal because there is considerable difference in the exposures obtained from the two types of samples, oxide and metal.

The precision obtainable by the procedure is not so good as that for some of the other procedures for several reasons. The standards, graphite, and barium hydroxide mixtures have to be prepared fairly frequently. Owing to the large factor of beryllium oxide to beryllium metal, there is a very small amount of beryllium metal actually taken for the analysis, and this presents a sampling problem. Also, grain-size testing with other sample powders [57] showed that care had to be taken that the particle size of the sample that went into the electrode cup was truly representative of the size of particle in the original sample. Some impurities appeared to exist in greater amounts in the sample fines than in the sample as a whole. This possibility has been checked on some sieved beryllium-metal samples, and it was found that powdered berryllium metal that passed a 325-mesh sieve had an apparent impurity analysis much greater than that of the same with mesh sizes of 100 to 325.

690-457 O—64——60

(b) *Physical Separation of Impurities. Carrier Distillation.* The carrier-distillation technique has been applied [53-55] to the spectrographic analysis of beryllium oxide. The amount of carrier material used in the beryllium analysis is 5 or 6 per cent instead of the 2 per cent used in the uranium procedure. This procedure is not very satisfactory for the determination of such impurities as aluminum, calcium, and silicon, whose oxides are too refractory to be vaporized satisfactorily during the distillation step. It is also doubtful that comparable excitation of the sample mixture can be achieved with both low- and high-fired matrices. Because of the lack of agreement between different oxides, comparable standards are of prime importance. Sensitivities of the method [55] for important elements with 6 per cent silver chloride as the carrier material are shown in Table 12.7.

Table 12.7—SPECTROGRAPHIC DETECTION LIMITS FOR TRACE IMPURITIES IN BERYLLIUM OXIDE WITH SILVER CHLORIDE AS CARRIER

Element	Wave length, A	Limit of detection, p.p.m.	Element	Wave length, A	Limit of detection, p.p.m.
Al	3082. 2	1	Ge	3039. 1	10
As	2780. 2	100	Hg	2536. 5	100
Au	2427. 9	1	In	3256. 1	1
B	2496. 8	1	Mg	2795. 5	10
Ba	4554. 0	30	Mn	2576. 1	1
Bi	3067. 7	10	Mo	3170. 3	10
Ca	3158. 9	50	Ni	3414. 8	1
Cd	2288. 2	1	Pb	2833. 1	1
Co	2407. 3	1	Rh	3396. 9	3
Cr	2835. 6	1	Si	2506. 9	10
Cu	3247. 5	10	Sn	2840. 0	10
Fe	2483. 3	1	Ti	3349. 0	3
Ga	2943. 6	10	V	3183. 4	10

12–1.9 Determination of Zirconium-Hafnium Ratios

The metallurgical development of zirconium as a reactor material has presented the analytical chemist with a new problem. Hafnium is invariably associated with zirconium and, owing to its high neutron cross section, must be separated from the zirconium if the zirconium is to be used for nuclear purposes.

Before the zirconium can be used in reactor production, it is necessary that the concentration of the residual hafnium be determined with great accuracy. A knowledge of the hafnium content of zirconium is

important even in the range of a hundred parts per million or less. In view of the chemical similarity of hafnium and zirconium, the chemical determination of hafnium presents a serious analytical problem.

Most general procedures for the determination of hafnium cover only specific ranges of hafnium concentrations; however, there should be no reason why they could not be equally effective throughout the whole range of analytical interest if the investigator were willing to determine other suitable spectral line pairs. Most of the procedures have several points in common; e.g., the sample must be converted to the oxide and the oxide sample must be mixed with a buffering material to produce satisfactory, reproducible arc excitation. The buffering material may be graphite or graphite containing equal amounts of either barium fluoride or sodium pyrophosphate. High-amperage d-c arcs are needed to adequately excite the hafnium and zirconium material. Various d-c discharges from 15 to 30 amps have been reported. An intermittent arc, or impulse arc, has also been used with varying success. When spark discharges are used, the sample can be in the form of a conducting pressed pellet, or it can be held to the flat ends of electrodes with a resin.

Many investigators have reported on the determination of hafnium in zirconium oxide. Many of these procedures have been limited in their analytical range owing to the limited range of interest of the various zirconium producers; however, the spectrographic methods can reasonably be extended to any concentration range with the same relative accuracy and precision as found at the lower levels of concentration.

(a) *Analysis of Pressed Pellets.* Fassel and Anderson [58] in 1950 and Rossi [59] in 1959 covered the determination of hafnium in zirconium from 0.01 to 100 per cent. The procedure suggested by Fassel and Anderson uses an overdamped-condenser discharge to a conducting pellet prepared from a mixture of zirconium oxide and powdered flake graphite.

Procedure. The sample is converted to the oxide and mixed with pelleting-grade pure graphite powder in the ratio of 1 part oxide to 4 parts graphite. A 500-mg portion of the mixture is pressed into a ¼-in.-diameter pellet. The pellet is used as the lower electrode; a ⅛-in. pointed graphite is used as the opposing electrode. The electrode system is sparked for 40 sec with an overdamped-condenser discharge as obtained from a commercial Multisource source unit with the controls set at: capacitance, 14 mfd; inductance, 480 mh; resistance, 65 ohms; phase angle, 30°. Since this work covers the full range of concentrations, it is quite obvious that an analysis for different concentrations cannot be accomplished with a single pair of spectral lines. The authors chose a number of spectral line pairs to cover the complete ana-

Table 12.8—LINE PAIRS USED IN ANALYSIS OF HAFNIUM–ZIRCONIUM MIXTURES

Wave length, A	Concentration range, % Hf
Hf(II)2861.696 / Zr(II)2856.055	0. 1– 6. 4
Hf(II)2861.696 / Zr(II)2839.339	6. 4–20
Hf(II)2975.882 / Zr(II)3003.736	20 –44
Hf(II)3109.117 / Zr(II)3164.310	31 –58
Hf(II)3000.096 / Zr(II)3003.736	54 –78
Hf(II)3000.096 / Zr(II)3028.040	72 –89
Hf(II)2857.650 / Zr(II)2844.579	89 –99. 5

lytical range. They chose line pairs that had an intensity ratio that approached unity at the middle of the analytical curve. This was done to increase the accuracy of the determination by eliminating some of the error of determination contributed by the photography and photometry of the system. The line pairs used and the concentration range are shown in Table 12.8.

The precision of this method as stated by the authors varies from 0.9 to 2.0 per cent standard deviation. The accuracy of any spectrochemical procedure depends upon how well the results check with values obtained by accepted chemical analysis. In hafnium and zirconium analysis, this is not readily accomplished; however, the accuracy achieved is as good as that achieved in the preparation of the synthetic standards.

(b) *Porous-cup Technique.* Feldman [60] applied the porous-cup procedure to the determination of hafnium. This procedure has an advantage in that it is much easier to obtain the sample in the same form as the synthetic standards and it uses a uniform controlled-spark excitation. The sample is brought into solution with 10 per cent sulfuric acid and made to such volume that the final concentration is 5 mg of zirconium per milliliter. A high-voltage spark is used to excite the sample passing through the porous cup with an exposure time of 180 sec. The spectral lines used for the measurement of hafnium are Hf(II)2641.406 A/Zr(II)2761.911 A. The accuracy of

this procedure for the determination of hafnium when compared to independent determinations made by capture cross section for thermal neutrons or activation analysis is very good.

12–1.10 Impurities in Zirconium and Its Compounds

In a study of the spectroanalytical problems associated with hafnium, zirconium, or the different zirconium alloys, it is not necessary to differentiate between the materials because their chemical similarity is so great that all analysis is effectively performed on the same matrix. Zirconium oxide, in common with most of the reactor materials, is refractory and therefore can be analyzed for many trace impurities by procedures similar to those used for other refractory oxides.

(a) *Direct Excitation.* (1) *Conducting Briquette.* Spark discharges to metal electrodes or conducting briquettes formed from the oxide of the sample should give more uniform and more reproducible discharges than other direct-burn discharges. Fassel [66] and coworkers have shown that highly refractory nonmetallic samples, such as zirconium oxide, can be volatilized in a uniform, controlled, and reproducible manner by the conducting-briquette excitation technique. In contrast to the d–c arc exposures, there is negligible selective volatilization; this makes it possible for zirconium spectral lines to serve as internal standard lines for both volatile and refractory impurities. The type of discharge used by Fassel was an unidirectional high-energy overdamped-condenser discharge, with the following parameters: capacitance, 50 mfd; inductance, 400 mh; resistance, 15 ohms.

In the conducting-briquette procedure, the zirconium sample is converted to the oxide and mixed with powdered flake graphite in the ratio of 1 part zirconium oxide and 2 parts graphite and then pressed into a briquette. The briquette is ignited at 400°C for 5 min prior to excitation. The sample is excited for 90 sec with the above-described discharge. The spectral impurity and internal standard lines of interest used are shown in Table 12.9.

(2) *Hollow-cathode Technique.* Korovin and Lipis [67] reported a highly sensitive and quite accurate method of determining many impurities in pure zirconium and its compounds based on the use of a hollow-cathode discharge as the light source. The hollow cathode is less involved than the evaporation technique employed in the physical separation of impurities because of the elimination of the enrichment step. Thirty to fifty milligrams of sample is placed in a graphite cathode in the sample chamber, the system is evacuated and then filled with helium to a pressure of 15 mm of mercury. Voltage is applied to the electrodes from a high-voltage rectifier of about 1.5 kw power rating to give a 30- to 40-sec exposure at 300 to 350 ma. This leads

Table 12.9—LINE PAIRS FOR DETERMINATION OF IMPURITIES IN ZIRCONIUM BY A CONDUCTING-BRIQUETTE PROCEDURE

Wave length, A	Impurities	
	Concentration range, %	Coefficient of variation
Si(I)2516.12 / Zr(I)2538.00	0. 004 –0. 08	4. 9
Mg(II)2795.53 / Zr(II)2782.84	0. 0002–0. 005	4. 5
Mg(II)2795.53 / Zr(II)2783.56	0. 003 –0. 06	
Ni(I)3002.49 / Zr(I)3022.66	0. 002 –0. 09	5. 2
Cu(I)3247.54 / Zr(I)3223.34	0. 0003–0. 008	6. 9
Cu(I)3247.54 / Zr(I)3254.28	0. 006 –0. 1	
Ti(II)3349.41 / Zr(II)3327.67	0. 002 –0. 08	4. 6
Fe(I)3719.94 / Zr(I)3723.20	0. 01 –0. 2	5. 5
Ca(II)3933.67 / Zr(II)3941.92	0. 0005–0. 006	5. 7
Ca(II)3933.67 / Zr(II)3936.07	0. 004 –0. 07	
Al(I)3944.03 / Zr(I)3952.87	0. 004 –0. 1	3. 1
Cr(I)4254.35 / Zr(I)4256.44	0. 002 –0. 07	----------

mainly to the evaporation of the alkali-metal oxides and those of antimony, arsenic, bismuth, cadmium, lead, silver, and zinc. Exposures of 60 to 90 sec are then made at 1000 to 1200 ma for the elements aluminum, chromium, iron, magnesium, nickel, silicon, etc. A comparison of the sensitivities of detection of the elements as obtained by the several procedures is shown in Table 12.10.

(3) *Point-to-plane Spark.* Farrell, Harter, and Jacobs[68] made spectrochemical examinations of zirconium metal directly by a point-to-plane ignited a-c arc excitation procedure. This procedure was possible only because adequate metal standards of zirconium and

Table 12.10—COMPARISON OF SENSITIVITIES OBTAINED IN THE ANALYSIS OF ZIRCONIUM BY VARIOUS SPECTROCHEMICAL TECHNIQUES (VALUES IN PARTS PER MILLION)

Element	Wave length, A	Hollow cathode	Zaidel' evaporation technique	Scribner-Mullin carrier distillation (10% AgCl carrier)
Ag	3280. 7	0. 1	----------	0. 5
Al	3082. 1	1	----------	10
As	2350. 0	1	----------	----------
B	2497. 7	0. 1	0. 1	0. 1
Be	2348. 6	0. 1	0. 1	----------
Bi	3067. 7	0. 3	0. 05	----------
Cd	2288. 0	0. 1	0. 1	0. 1
Co	3405. 1	1	0. 5	3
Cu	3247. 5	0. 3	0. 5	0. 3
Fe	2395. 6	3	20	20
K	7664. 9	1	10	----------
Li	6707. 8	. 03	0. 02	1
Mg	2790. 8	0. 1	----------	0. 5
Mn	2576. 1	0. 3	0. 1	1
Na	5889. 9	3	10	----------
Ni	3050. 8	3	1	1
Pb	2833. 1	1	0. 5	1
Sb	2528. 5	1	1	----------
Si	2881. 6	1	----------	2
Sn	2840. 0	1	0. 5	2
Ti	3349. 0	10	----------	10
V	3184. 0	10	----------	10
Zn	3345. 0	1	10	----------

Zircaloy were available. With the preparation of satisfactory metal standards, procedures can be used that avoid time-consuming sample manipulation and preparation. In this procedure a solid sample is removed from the fabricated material and machined to a 32-μin. finish. This piece is used as the lower electrode, and a hemispherically tipped graphite rod is used as the counter electrode. An ignited a-c arc is passed between the electrodes for 50 sec exposure time. Special variations of the procedure are made for the determination of boron, hafnium, tungsten, copper, titanium, and cobalt. The spectral lines used in the determination of impurities in zirconium and Zircaloy are shown in Table 12.11. The measurement of precision of this work shows a coefficient of variation of approximately ± 5 per cent.

Easterday [69] applied the direct-reading techniques to zirconium analysis using a spark discharge in a point-to-plane procedure. The results obtained were equal to those reported by the carrier-distilla-

Table 12.11.—ANALYTICAL LINES USED FOR ANALYSIS OF ZIRCONIUM MATERIAL BY POINT-TO-PLANE IGNITED A-C ARC

Zirconium			Zircaloy-2		
Element	Wave length, A	Concentration range, ppm	Element	Wave length, A	Concentration range, ppm
Al	3082.2	20–200	Al	3082.2	20–200
B	2497.7	0.5–5	B	2497.7	0.5–5
Cd	2288.0	0.5–5	Cd	2288.0	0.5–5
Co	3453.5	10–100	Co	3453.5	10–100
Cr	2862.6	20–200	Cr	2687.1	0.05–0.2%
Cu	3274.0	10–200	Cu	3274.0	10–200
Fe	2727.5	100–1500	Fe	2501.1	0.06–0.25%
Hf	2820.2	100–1000	Hf	2820.2	100–1000
Mg	2802.7	5–25	Mg	2802.7	5–25
Mn	2605.7	10–125	Mn	2605.7	10–125
Mo	2816.2	20–150	Mo	2816.2	20–150
Ni	3002.5	10–200	Ni	2992.6	0.025–0.1%
Pb	2833.1	25–300	Pb	2833.1	25–300
Si	2516.1	25–250	Si	2516.1	25–250
			Sn	2495.7	1.0–2.0%
Ti	3349.0	10–100	Ti	3361.2	10–100
W	4008.8	50–350	W	4008.8	50–350
V	2908.8	20–150	V	2908.8	30–150

Internal standard lines

Zr 2944.9
Zr 2538.0 } General impurities
Zr 3275.6
Zr 2820.6 Hafnium
Zr 4007.6 Tungsten

tion procedure and, in addition, had greater accuracy owing to the spark discharge.

(b) *Physical Separation of Impurities.* The carrier-distillation procedure for the determination of impurities in refractory oxides has been used extensively in the spectrochemical analysis of zirconium materials by both producers and consumers.[61-64]

There are a number of carriers that can be used with refractory materials; however, with a zirconium oxide matrix, silver chloride appears to give the best sensitivity for the greatest number of elements. The amount of silver chloride generally used as a carrier is 5 wt.% of the matrix material. Smith and Spitzer[62] used 30 wt.% silver chloride in zirconium oxide. Because of the high melting and boil-

ing points of zirconium oxide, higher amperage arcs, resulting in higher temperatures than are normally utilized in the carrier-distillation procedure, can be used. This will bring out the more refractory impurities in a reproducible manner. Further similarity to the analysis of other refractory materials is noted in the use of the Zaidel'[65] evaporation method in the spectroanalysis of zirconium. The vaporization is effected by heating the sample in a crucible electrode to 2000 to 2100°C. Above 2100°C zirconium itself starts to vaporize. The sensitivity of all elements with the exception of bismuth, tin, lead, cadmium, and antimony can be increased by heating the sample in vacuum.

12–1.11 Analysis of Graphite

Graphite is one of the nonmetals that is of great importance as a nuclear material. Its early use as a neutron moderator in the construction of nuclear reactors resulted in strict criteria for the impurity concentrations especially in regard to the neutron-absorbing elements being placed on the material. Of the possible contaminants in graphite, boron is one of the elements most likely to be present; it also is the one that is most deleterious to the use of the graphite.

(a) *Chemical Ashing.* The determination of boron is commonly accomplished by chemical means, which include igniting the sample in the presence of calcium oxide or fusing it with an alkaline oxidizing mixture and determining the boron by colorimetry or titration. Shugar[70] reported a spectrochemical procedure for the determination of boron following the lime-ashing sample preparation.

> *Procedure.* One gram of the graphite sample is mixed with 224 mg of calcium oxide and 40 cm^3 of water. The slurry is mixed, dried and ignited for 1.5 hr at 850 to 900°C. The lime-ash sample is packed into a 5- by 5-mm cup in an 8-mm electrode and burned in a 10-amp d-c arc for 60 sec. This is a semiquantitative procedure, and the sensitivity of boron detection is estimated to be 0.1 ppm. The determination of boron by this procedure may be biased on the low side. Although the addition of lime to the sample should establish an alkaline system for the ignition of the graphite, there is still the possibility that a loss of boric acid during the ignition may occur. Preparation of the necessary comparison standards in the same manner as the sample treatment is not satisfactory because any loss of boron during ignition is not consistent or reproducible.

(b) *Direct Excitation.* The advantage of speed of analysis that is inherent in spectrochemical analysis is lost when involved sample handling is necessary. The burning of graphite directly in a d-c arc does not give good sensitivity for boron detection. It has been noted that boron is not always completely removed during ignition of the graphite sample. At 2500°C boron, boric oxide, borates, and even

boron nitride react with carbon to give boron carbide. This compound is extremely stable and unreactive; any procedure for the determination of trace concentrations of boron in graphite must therefore provide for the volatilization or excitation of this compound. Feldman and Ellenburg [71] have described two spectrographic procedures for the direct determination of boron in carbon or graphite.

(1) *Cup Electrode.*

Procedure. The lower electrode, the anode, is prepared from a 0.250-in. carbon rod cut back 0.500 in. to form a 0.125-in. rod. A cup, 0.078 in. in diameter and 0.2 in. deep, formed with a No. 47 drill, is made in the end of the rod. The upper electrode is a flat electrode also cut to a 0.125-in. diameter. The sample is ground and mixed for 30 to 60 min and then passed through a 360-mesh silk-screen sieve. A mixture of 90 mg of the sample and 10 mg of fine iridium powder is ground and mixed in a agate mortar. The iridium is for use as a spectroscopic internal standard. The electrode cup is filled with approximately 10 mg of the mixture, and the mixture is tamped. The sample is burned for 90 sec with a 9-amp d-c arc in a controlled atmosphere composed of 76 per cent argon and 24 per cent oxygen.

(2) *Sifter Electrode.* The second procedure discussed by Feldman and Ellenburg [71] was the use of a sifter electrode activated by a high-voltage spark discharge. This type electrode offers the possibility of achieving satisfactory concentrational sensitivity through the use of large samples. Electrodes are prepared from graphite rod as shown in Fig 12.1; the upper electrode is the sifter electrode.

Procedure. The sample is ground and sieved in the same manner as described in Sec. 12–1.11(b)(1), and 576 mg of sample material is ground and mixed with 24 mg of cupric oxide. The cupric oxide is for use as a spectrographic internal standard. The sifter electrode is filled with the sample mixture but not tamped, and the electrodes are excited for 90 sec in a high-voltage spark discharge. The spark discharge takes place in a controlled atmosphere of argon gas. The gas flow is at the rate of 1.8 liters/min. The spectral background from the spark exposures in this procedure is very low; this helps to improve the boron spectral sensitivity. The reported limit of sensitivity of the procedure is 0.25 ppm of boron in graphite.

(c) *Carrier Distillation.* Numerous other investigators have reported on the determination of boron in graphite. The use of copper fluoride as a carrier was successful in the determination of boron in steel. Wenzel and Mullin [72] and Ko [73] adapted this procedure to the analysis of carbons and graphites. In the Ko procedure the graphite sample is mixed with the copper fluoride in a ratio of 2 parts sample to 1 part copper fluoride. The procedure was extended to include the determination of other elements with the following sensitivities: 10 ppm aluminum, 50 ppm calcium, 5 ppm iron, 1 ppm silicon, 5 ppm titanium, and 10 ppm vanadium.

Procedure.[73] Ten milligrams of the mixture is placed in a 3-mm crater in a ⅛-in. graphite rod. The sample is arced for 40 sec with a 5-amp d-c arc. The sensitivity of detection for boron is 0.5 ppm. The sensitivity can be increased to 0.02 ppm boron by prior ashing of the sample.

Procedure.[72] In the procedure reported by Wenzel and Mullin 15 mg of copper fluoride is placed on the bottom of a 9/32-in. cup in a ¼-in. pedestal electrode followed by 100 mg of the sieved graphite sample. The graphite is packed and vented by forcing a needle through the charge into the electrode. The arc current is 21 amp direct current with the electrodes shorted; this is equal to approximately 16 amp during the exposure cycle. The exposure time is 45 sec with no prearc. The sensitivity of the procedure for the detection of boron in graphite is 0.1 ppm.

12–1.12 Radioactive Materials

The spectrochemical analysis of radioactive materials is more concerned with the proper sample-handling procedures than with any special spectrographic technique. In the spectrochemical analysis of many materials, the interest is usually in the accuracy, precision, sensitivity, and speed of analysis. In the analysis of radioactive materials, the main consideration is safety for the operator. This includes protection from alpha, beta, and gamma radiation by adequate shielding and protection from contact through the handling of the material.

The solution to the problem of how best to handle these radioactive materials depends to a great extent on the nature of the radiation emitted. Elements that are primarily beta or gamma emitters require lead shielding and remote handling to protect the operator, whereas alpha emitters in solution can be handled safely with rubber gloves. Pure alpha emitters can also be handled outside the prescribed area if care is taken to avoid contamination of the air with the powder material. Feldman and his coworkers [74] designed an electrode assembly that permits the electrode to be charged with the sample in one area, then carried to the spectrographic laboratory, excited with a spark discharge, and disposed of without exposure of the operators to any dangerous levels of radiation or air-borne contamination. The spectrograph chamber consists of two cassette assemblies containing the electrodes, both of which have sample added to them. A chamber block is shown assembled in Fig. 12.5. The individual cassette assembly, Figs. 12.6 and 12.7, contains a copper electrode on which the radioactive solution is deposited by a remote-control pipet and dried to a residue by means of an infrared lamp. When the liquid has evaporated, the cassette is closed by turning the knurled knob that rotates the section with the electrode (curved section) under the flat shield section. The closed cassettes are carried to the spectrographic laboratory and inserted into the chamber block. After being enclosed in the chamber block, the cassettes are opened to expose the

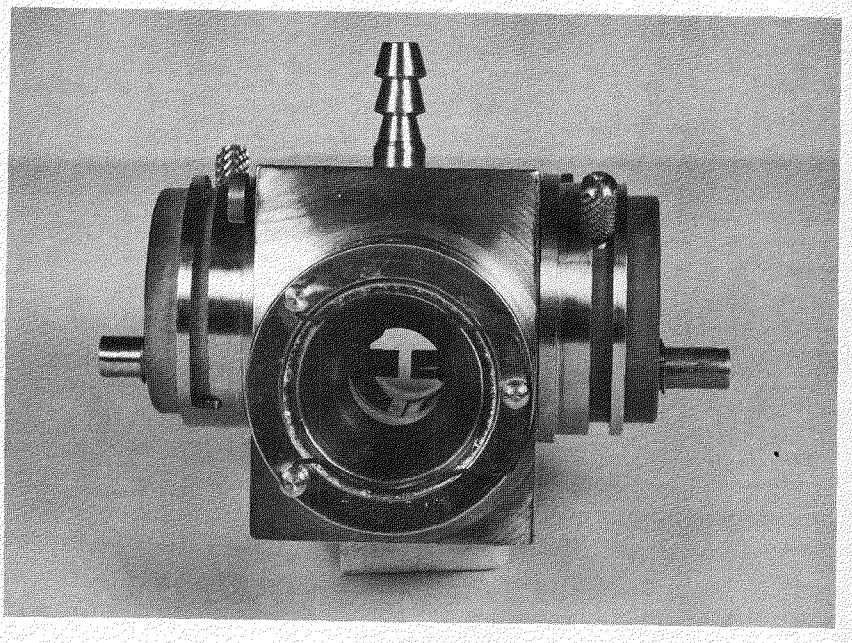


Fig. 12.5—Spark chamber assembled. (From Feldman, Hawkins, Murray, and Ward, *Anal. Chem.*, Ref. 74.)

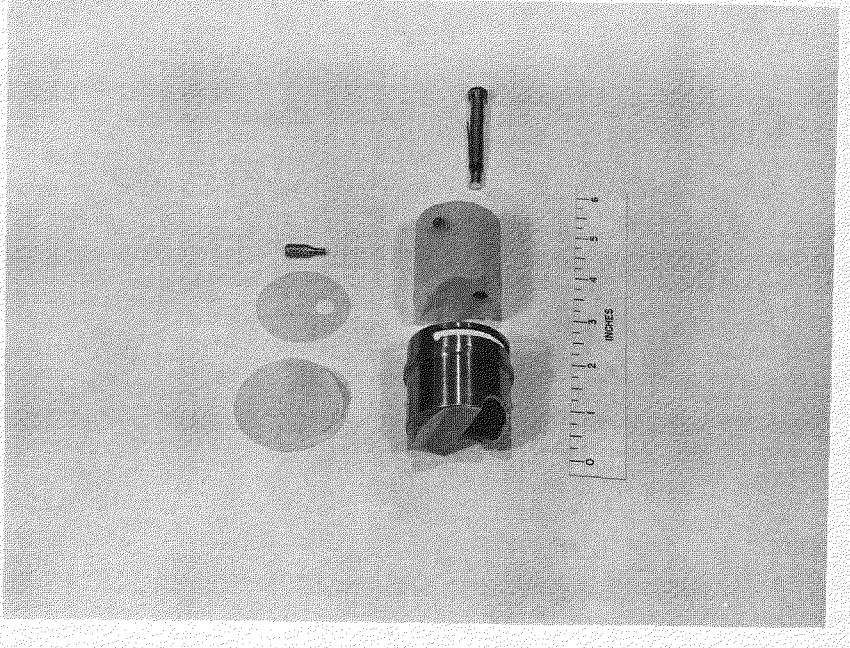


Fig. 12.6—Components of cassette assembled. (From Feldman, Hawkins, Murray, and Ward, *Anal. Chem.*, Ref. 74.)

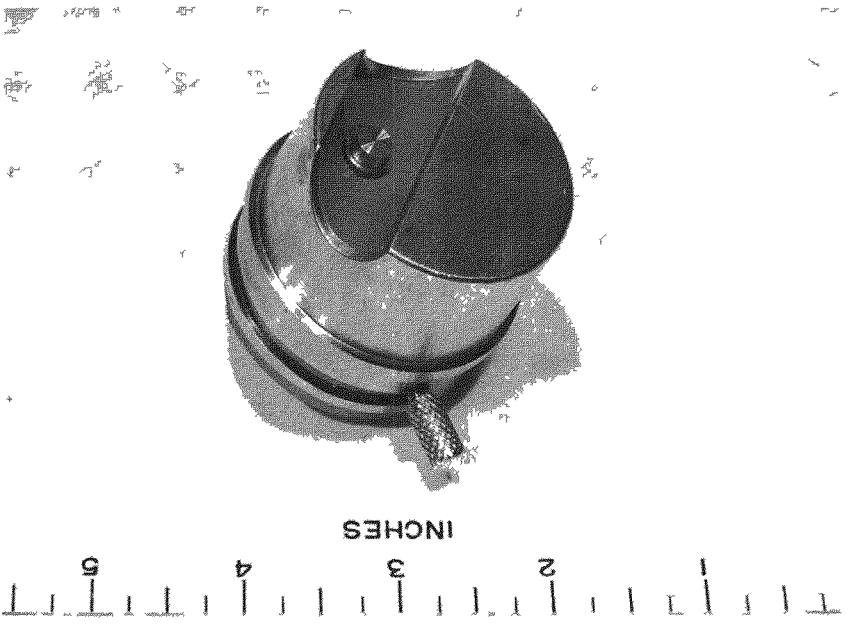


Fig. 12.7—Cassette assembly open. (From Feldman, Hawkins, Murray, and Ward, *Anal. Chem.*, Ref. 74.)

electrodes. The electrodes are spaced by external controls connected to electrical leads and excited with the required source.

After the excitation cycle the cassettes are closed, and the entire chamber is carried to the laboratory for the removal of the electrodes and decontamination. Contamination of the electrode holder can be lessened by coating the surfaces of the unit with a stripable plastic film, such as one called Cocoon (manufactured by R. M. Hollingshead Co., Camden, N.J.). Contamination of the atmosphere during sparking is avoided by pumping the chamber so as to maintain a slight vacuum; the outlet gas is filtered and scrubbed. The scrubbing is required to correspond to the chemical nature of the radioactive species.

A spark discharge is normally used for the spectroanalysis of radioactive materials; however, on occasion it is desirable to use the d-c arc because of the increased sensitivity. Since the arc source is usually at a higher temperature than a spark discharge, the chamber used to contain the arc must be large enough to prevent undue heating of the interior. In contrast to the spark-chamber design, the electrical insulation properties are of secondary importance to the need for dissipating the intense heat that is radiated from the arc. Birks and Thorne[75] have designed a chamber that is suitable for d-c exposures of radioactive materials.

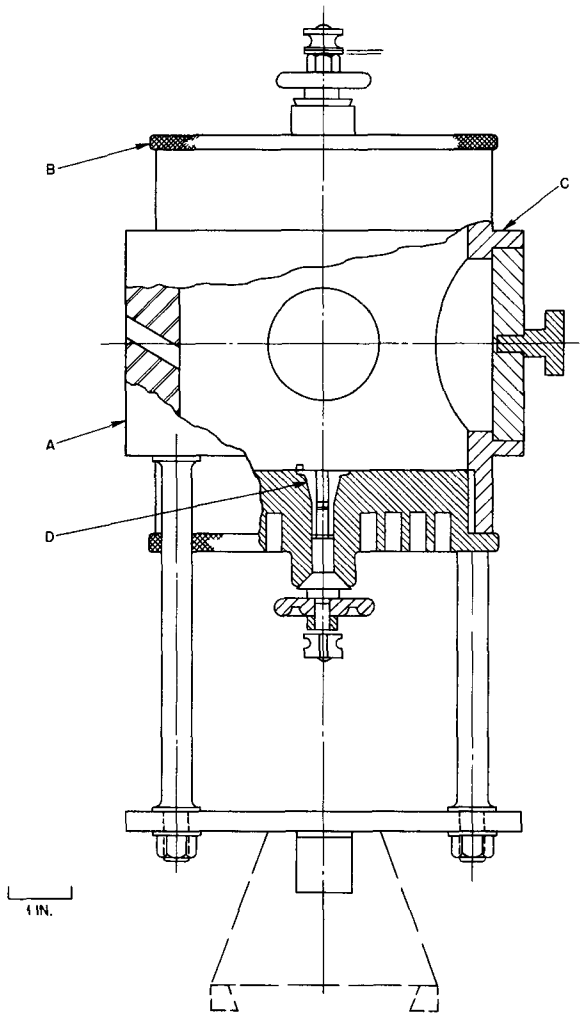


Fig. 12.8—Sectional side view of arc chamber. (From Birks and Thorne, *J. Sci. Instr.*, Ref. 75.)

A general view of the chamber is shown in Fig. 12.8. It consists of a synthetic-resin fabric body with large screwed end caps, which hold the electrodes, and a base plate arranged so that the whole apparatus can be rotated about a vertical axis. A quartz window is provided on the chamber side for the sample light path. The vertical adjustment of the electrodes is obtained by screwing the large end caps in or out, the total movement available at each electrode being ¾ in. The supporting electrodes are held by collets in the center of the screwed caps and consist of ¼-in.-diameter graphite having

a ⅛-in.-diameter graphite pedestal onto which short lengths of high-purity graphite electrode are placed. Access is through a plug door in the side of the resin chamber. Electrical connection (d-c) is made to brass terminals attached to the end of each collet. The d-c arc is struck by means of a spark from a high-frequency initiator circuit. An air inlet is provided through a ⅛-in. channel cut in the top of the door. The exhaust is taken from a tapered hole in the top of the resin chamber by a flexible polyvinyl tube to a filter system.

Decontamination from large accumulations of alpha activity is carried out by swabbing the interior surfaces with moistened tissue. Any film that deposits on the quartz windows is removed with moistened lens tissue. These deposits give rise to an objectionable level of background activity when the material arced emits much beta or gamma radiation. In such cases a greater air flow must be provided so that most of the activity will be carried on to the filters.

The aforementioned units can be used only with samples of low radioactivity or short half lives and then only in spark chambers that have very good exhaust and filter systems. In cases where the sample has a high activity, it is necessary to handle the sample completely in hoods or dry boxes to avoid any possible contamination of the atmosphere. In areas of great radioactivity, the hood train containing the enclosed electrode stand is separated from the spectrograph even to the extent of being placed in a different room. Most laboratories working with radioactive materials use this approach to their spectrochemical analysis of the material. The laboratory room is divided into two sections separated from each other by a wall containing a quartz window at spectrograph height. One section is used for all operations that involve the handling of radioactive samples; this section contains the electrode stand. The other section contains the spectrograph and is kept free of activity. The two sections cannot be connected directly; they must have separate entrances from the so-called "cold" areas. The spectrograph source unit may also be in a cold area, in which case the electrical leads to the electrode stand should be well sealed both into the "hot" room and into the dry box containing the electrode stand. The light from the discharge passes through the quartz windows in the wall and through any necessary optical system into the spectrograph.

The spectrochemical techniques are simple and straightforward. Since solutions are generally involved, the porous-cup or copper-spark technique is most often used.[76, 77] Spark discharges used in spectrochemical analysis are disruptive and when used with radioactive materials definitely must be used within an enclosed chamber to provide adequate shielding and to prevent contamination of the

Table 12.12—SEPARATION OF ISOTOPE LINES OF HYDROGEN

Balmer line	Hydrogen wave length, A	λH–λD*	λH–λT*
α	6563	1.8	2.4
β	4861	1.3	1.8
γ	4340	1.2	1.6
δ	4102	1.1	1.5

*The separation in angstroms between the isotope lines of hydrogen and deuterium and hydrogen and tritium.

air. For routine analysis it must be possible to decontaminate the chamber quickly and safely both as a personnel safeguard and also so that the chamber may be ready for reuse as soon as possible.

12–1.13 Isotopic Determination

The specialized types of spectroscopic analyses such as isotopic determinations have generally been confined to those instruments having resolving powers greater than that provided by ordinary spectrographs. With the development of the atomic energy program, interest in the application of optical spectrographic procedures for the isotopic assay of a number of elements was stimulated. Such methods could provide isotope ratios independent of the mass spectrograph. A number of emission spectroscopic procedures have been developed for hydrogen and lithium at the light end of the atomic-weight scale and for many of the elements at the heavy end of the atomic-weight scale. Relative to the lighter elements, the effects from Doppler broadening and self-absorption have important bearings on the determination of the isotopic ratios.

(a) *Hydrogen Isotopic Determination.* The difference in the masses of the hydrogen isotopes causes a shift in the wave lengths of the Balmer lines of the hydrogen spectrum. The separations of the several hydrogen isotopes are shown in Table 12.12. These separations are readily measured in the higher orders on many types of spectroscopes.

A number of investigators have used emission spectroscopy to either identify the hydrogen or deuterium isotope lines or to determine the isotope ratios in hydrogen-deuterium mixtures.[78–87] The several procedures are basically similar, and the most complete is the method proposed by Broida and his coworkers.[81, 82, 84]

Broida's procedure for the determination of hydrogen-deuterium ratios is based on a gas-flow system whereby the gas mixture is removed from the system after passing through the discharge tube.

The spectrum is obtained with an electrodeless discharge at 150 Mc and is measured with a high-resolution photoelectric recording grating monochromator. The precision measurement of the major component was 0.02 per cent, the day-to-day reproducibility was 0.07 per cent, and the absolute accuracy, which was limited by a lack of standard samples, was 0.35 per cent. The measurements were made on hydrogen–deuterium–air mixtures. Air impurities up to 50 per cent of the isotope mixture do not affect the relative intensities of the isotope lines. The method can be extended to include the determination of hydrogen and deuterium in aqueous samples.[81] If the sample is vaporized and then passed through the system, it is possible to make an analysis on a 1-ml sample with an accuracy of the order of ± 0.1 per cent.

One of the problems associated with hydrogen measurements is the readiness with which hydrogen is adsorbed onto the parts of the sample container. With closed-off systems even after extensive baking and degassing of the container, it is difficult to obtain repeat analyses. Broida [81, 82, 84] reports that, in the analysis of premixed samples of hydrogen–deuterium mixtures in the range of 75 to 95 per cent deuterium, the deuterium decreased approximately 2 per cent per day. In addition to the dilution effect, it was also noted that the apparent concentration changed, but in a smaller amount, with changes in pressure and intensity.

(b) *Lithium Isotopic Determination.* The spectrochemical determination of the isotope abundance of lithium has generally been accomplished by measuring the lithium line at 6707.8 A. This line is part of a close doublet, and the stronger component of the Li^6 doublet coincides with the weaker Li^7 doublet line. This line also is the resonance line for lithium and is affected by self-absorption and Doppler broadening. The amount of self-absorption of the spectral line can be reduced by using smaller samples. A number of workers [88-92] have reported on the determination of the lithium isotopes with a hollow cathode, containing 2 to 4 mg of lithium sulfate, and a high-dispersion spectrograph, using either photographic plates or photomultiplier tubes for spectral recording. An abundance ratio of approximately 13.5 Li^7/Li^6 for normal lithium salts, as compared to a value of 12.4 to 12.9 obtained by mass spectrometry has been reported. Gillieson and Thorne [92] calculated a correction for the Doppler broadening, and, when they applied their correction, they obtained a natural abundance ratio of 12.5 ± 0.3.

(c) *Uranium Isotopic Determination.* The spectrochemical determination of U^{235}, utilizing the isotope-shift effect, differs very little from other spectrochemical determinations. The difficulties usually encountered in spectrochemical analysis, namely, those of reproducible

excitation conditions and equivalent rates of volatilization of several elements are of no significance in spectroisotopic analysis since the spectral lines of interest arise from the same element. The complexity of the uranium spectrum plus the heavy optical background does, however, present certain problems. The shift in the position of the spectral lines due to the difference in isotopic composition was first noted by Long and Smith [93] when they were using standards of normal uranium for the analysis of enriched U^{235} samples. There are several articles that list wave-length tables for the uranium-isotope lines.[94, 95] The greater angstrom shift is found in the spectral lines in the visible and infrared portion of the spectrum. Unfortunately, most of these spectral lines are too weak to be used for isotopic analysis. The uranium line that shows the greatest spectral shift and is likewise strong enough for good intensity measurements is the line at 4244.37 A for U^{238}.

In standard spectrochemical procedures the determination of element concentration is dependent upon the measurement of the density of the spectral lines of the element. As the concentration increases, the line density also increases until the spectral line becomes so dense that accurate densitometric measurement of the spectral line is no longer possible. Variations in isotopic concentration are also noted as variations in the spectral-line intensity, and heavy isotopic concentrations would result in the spectral line being too dense to measure. The U^{235} isotope is the uranium isotope of importance in nuclear material analysis. For low concentrations of U^{235}, the U^{235} isotope spectral line is measured, but, at higher levels of enrichment, this line is much too dense for good measurements. The number of other spectral lines that can be used when the U^{235} isotopic content changes is not so great as in ordinary impurity analyses; therefore another approach must be used for high U^{235} content. Since the total isotopic concentration would always total 100 per cent, the investigators using spectrographic techniques have made use of this fact in their determination of U^{235}. By determining spectrographically the weaker isotope, which in this case is U^{238}, and by assuming a U^{234} value of approximately 1 per cent, or determining this value by alpha counting, investigators can determine the U^{235} isotope concentration by subtracting the U^{238} and the U^{234} sum from 100 per cent. Gordon and his coworkers [96] at Westinghouse Atomic Power Division used such a procedure for the precise assay of highly enriched samples of uranium. The U_3O_8 sample is mixed with an equal weight of graphite buffer then the mixture is packed in a 1.5-mm-deep by 2-mm-diameter crater in a ⅛-in. graphite electrode. The sample electrode is made the anode in a 12-amp d-c arc burned for 50 sec with a 4-mm analytical

arc gap. The density of the U^{238} line at 4244.37 A is measured, and the concentration of U^{238} is determined by regular spectrographic means. The concentration of U^{234} is determined by alpha counting. The sum of the U^{238} concentration and the U^{234} concentration subtracted from 100 will give an acceptable figure for the U^{235} concentration. For production and inventory control, the procedure has proven highly reliable. The precision of the method decreases for enrichments below 85 per cent U^{235}, but, in the range 90 to 95 per cent, the results are within ½ per cent of the amount present and are comparable to those from well established mass-spectrometer work.

With the return of enriched uranium from the various reactors to the processing stream, there has been a build-up in the U^{236} level. Although the concentration of the U^{236} isotope in the enriched material is low, it still interferes with the accurate spectrochemical determination of U^{235}. The wave length of the U^{236} spectral line is at 4244.22 A, which is only 0.1 A away from the U^{235} spectral line. For low levels of uranium enrichment, the dispersion of most commercial instruments is sufficient to detect this separation by densitometric line tracings. There is still some direct interference with the U^{235} spectral-line measurement. Samples of high U^{235} enrichment containing U^{234} and U^{236} on which the U^{238} content is determined directly and the U^{235} content is determined by difference can no longer be treated as a simple single spectrographic determination. Since the U^{236} cannot be determined, the concentration of U^{235} present would be high by approximately the amount of the U^{236} in the sample.

The uranium spectrum on a photographic film under normal d-c arc conditions is composed of rather broad spectral lines and high film background. This adversely affects the determination of the isotopic composition when densitometric measurements of the spectrum are being made. The broad spectral line blends into and interferes with the measurement of the neighboring weak isotopic line, and the continuum commonly associated with d-c arc discharges produces a high background, which gives poor line-to-background ratios in the measurement of the weak spectral lines. The development of the prism-echelle spectrograph permitted workers in the isotopic-analysis field to obtain the high dispersions that are necessary in examining complex spectra. The echelle grating is a coarse-ruled grating (200 grooves per inch) and, when used as an attachment for either the Wadsworth or Littrow type spectrographs, gives a very high linear dispersion. The echelle differs from the echelette and regular gratings in that the latter are usually specially blazed in ruling and the diffracted radiation is concentrated in a particular order or a limited wave-length region. The echelle is ruled so as to reflect all its spectra into a narrow

cone of radiation. Since the echelle will reflect a great many superimposed orders in this narrow cone of radiation, a stigmatic spectrograph of high enough dispersion to separate these multiple orders must also be used. Figure 12.9 shows a portion of echellograms of normal and enriched uranium. R. J. Murphy [97] and R. S. Vogel [98] have used this instrument in production-control problems of enriched uranium. The spectrographic procedures developed by both authors

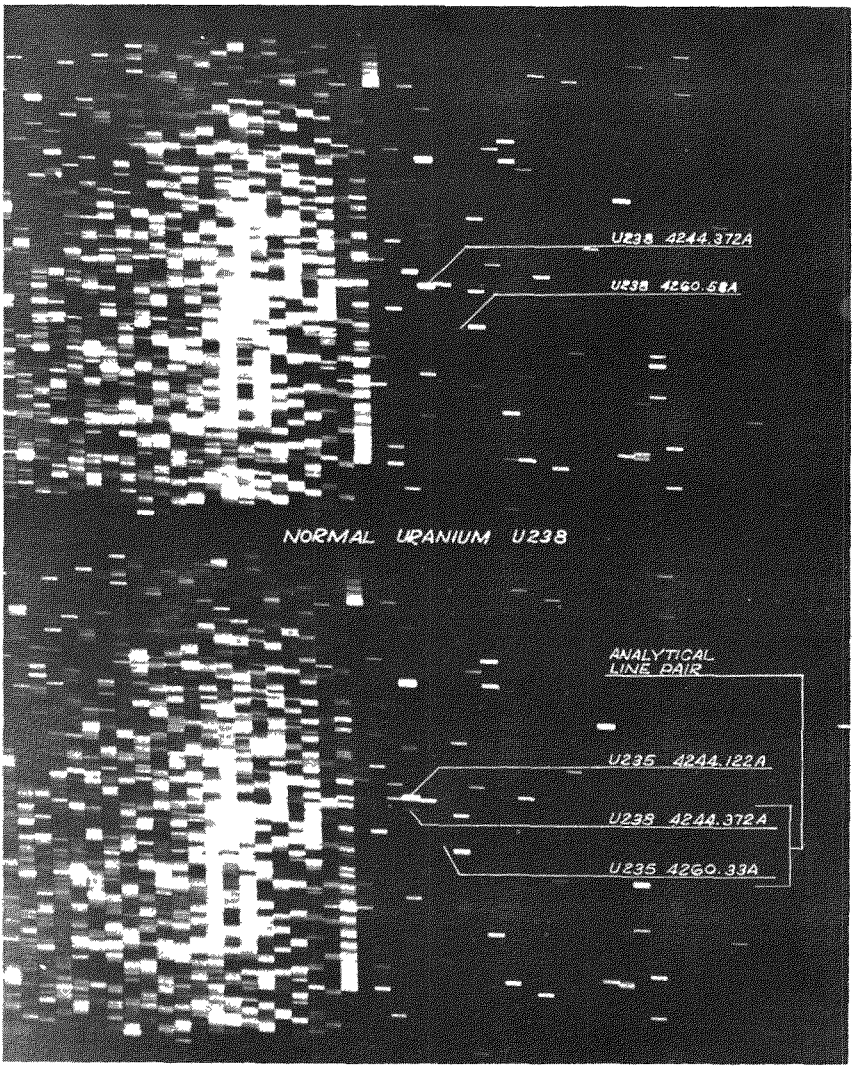


Fig. 12.9—Portions of echellograms of normal and enriched uranium. (Photograph courtesy of R. J. Murphy, Metals and Controls Corporation.)

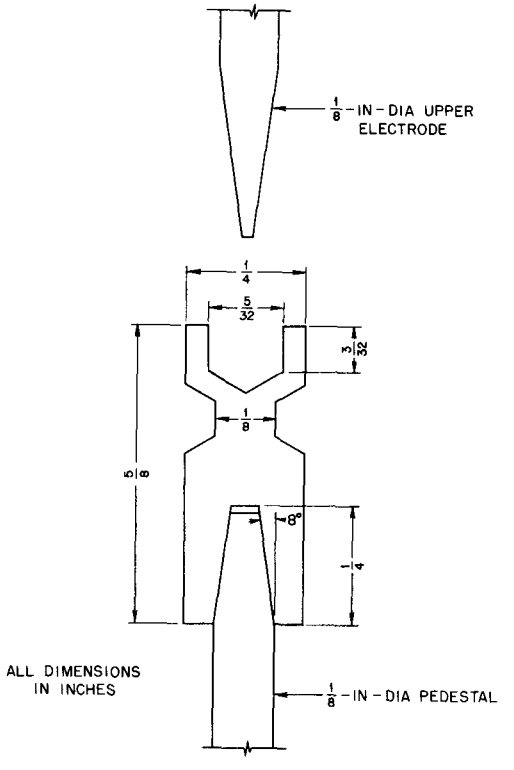


Fig. 12.10—Electrode details.

for these analyses were d-c arc discharges, the main difference between the procedures being the type of support electrode used for the arc discharge. The support electrode used by Murphy was an ⅛-in. graphite rod with a 1/16- by 1/16-in. cup into which a U_3O_8 and graphite (1+1) mixture was packed. Vogel used a special undercut pedestal cupped electrode (Fig. 12.10) into which 35 mg of the sample was placed. Although each procedure was used for only one specific concentration region, each author felt that the procedure could be extended to include the full range of isotopic concentrations. The reported precision of the U^{235} determination is 0.5 per cent absolute at 90 per cent U^{235} by Murphy and approximately 0.05 per cent absolute for U^{235} in normal and slightly enriched uranium by Vogel.

The precision of spectroscopic isotopic values can be improved over that reported by the forementioned photographic techniques in several ways. The use of photomultiplier tubes instead of photographic plates permits a substantial improvement in the precision of the determination. Procedures that would normally give precisions of ap-

proximately 10 per cent of the amount present can be improved to 1 to 2 per cent by use of photomultiplier tubes. Changes in source conditions to give more accurately controlled discharges will also improve the analytical results. The hollow-cathode discharge source gives spectra composed of quite sharp lines with negligible background. These advantages make this type of source very desirable for isotopic analysis. Reported improvements in the isotopic analysis of uranium by spectrochemical procedures generally employed the use of both the hollow-cathode source and photomultiplier-tube receivers. The use of hollow-cathode sources has one serious disadvantage in routine work: the length of time necessary to condition the source and to obtain a steady uniform discharge. In addition, exposure times are generally longer than for conventional types of discharge. Approximately 20 exposures per day are considered good for this type of analysis. Lee [99-101] was able to overcome this objection by setting up a multisource unit of four hollow-cathode discharge tubes and an automatically positioned selector mirror. In this manner, several hollow-cathodes can be conditioning while the exposure is being obtained from another source. The procedure is quite automatic and allows the operator to run about 80 samples per day. The output of the single phototube is put on a strip chart where it can be read conveniently during the conditioning cycle for the next exposure.

Saunderson [102] used a standard 3-meter eagle-mounting spectrograph with a direct-reading attachment and a special 25,000 line per inch grating set in third order which was capable of determining the U^{235}, U^{236}, and U^{238} at the same time. This is not a scanning instrument; therefore it was necessary to develop a special optical device to separate the different isotope lines so that all isotopes might be read simultaneously. The type of optical device used for the separations of the isotope spectral lines is shown in Fig. 12.11. The calculated standard deviation of a single run was determined to be 1.2 per cent of the amount present at about 3 per cent U^{235}.

Procedure. The sample and exposure conditions used in this work are as follows: The U_3O_8 powder is mixed with an equal weight of graphite, and the mixture is then packed into a 2- by 2½-mm crater in a ⅛-in. graphite electrode. The upper electrode is a flat-tipped ⅛-in. graphite rod, and the electrode spacing is 2 mm. The discharge is an automatically ignited 5-amp 2400-volt a-c arc. A prearc period of 80 sec is used. During the prearc period a bead of uranium-containing material, glossy and refractory in appearance, forms on the lower electrode; as the bead forms, the discharge becomes increasingly more stable and quiet. The analytical gap is permitted to widen during the prearc period and exposure. The exposure time was set at 80 sec.

(d) *Other Materials.* In addition to the work performed on the preceding listed isotopes, there have also been investigations made

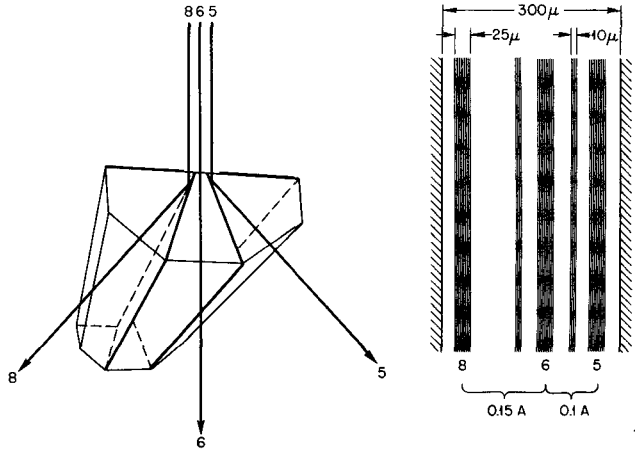


Fig. 12.11—Optical device for separating spectrum lines. (From Saunderson, *Talanta*, Ref. 102.)

on the isotope displacements in the spectra of thorium,[103] plutonium [104-106] and polonium.[107] The spectrochemical procedures used for these determinations were very similar to those used in the uranium isotopic studies. The spectral shifts of these elements are small, and many of the spectral lines are too weak for good intensity measurements. No analytical use appears to have been made of any noted isotopic spectral shifts; rather this information was used as an aid in the study of the atomic configuration of the element.

As a further aid to the worker in the field of spectrochemical analysis of reactor materials Table 12.13 is included; the table separates the references according to the particular element or determination made. Also included are references that have not been directly referred to in the text. There are, undoubtedly, a number of papers which have been omitted from the reference list, but it is hoped that enough have been included to provide the new investigator with necessary information relative to the determination desired.

Table 12.13—LISTING OF REFERENCES ACCORDING TO THE ELEMENT DETERMINED

Element	Ores and compounds	Uranium	Plutonium	Thorium	Beryllium	Graphite	Zirconium
Ag		22, 118, 120, 122.	42, 43, 118, 130, 131	188	55, 146		67
Al		13, 22, 37, 115, 117, 118, 186.	37, 41–43, 118, 130, 131.	48, 137, 188	53, 55, 56, 146.	73, 173	61–64, 66–69, 164–166, 190.
As		22, 37, 118, 120	37, 43, 118, 130, 131.		55, 146		63
Au		22, 24, 25, 36, 37, 119.	37, 43		55		63
B		22–24, 26, 27, 33, 37, 115, 118, 120, 185.	37, 41–43, 118, 128–131.	137, 138	53–55, 138, 146.	70–73, 172, 174–178.	62, 63, 67–69, 165, 166.
Ba		22, 25, 28, 35, 37, 116.	35, 37, 41, 43, 130, 131.	35, 188	35, 55, 146		35, 62, 63
Be	(49, 50, 51, 52, 141, 143).*	22, 24, 25, 37, 111, 118, 120, 140.	37, 41, 43, 118, 130, 131.	48, 137, 138			62, 63, 67
Bi		22, 24, 25, 35, 37, 118, 120.	35, 37, 43, 118, 130, 131.	35, 137	35, 55, 146		35, 63, 67, 165.
Ca		13, 14, 17, 37, 118, 123, 127.	37, 41–43, 118, 130, 131, 187.	48, 139, 188	53, 55, 56, 146.	73, 125	61–63, 66, 165, 166.
Cd		22–24, 27, 32, 35–37, 118–121.	35, 37, 42, 43, 118, 130, 131.	35, 137, 188	35, 53–55, 146.		35, 62, 63, 67–69, 165, 166.

Ce	46	37	37		55		
Co		22, 24, 25, 37, 113, 118, 120.	37, 42, 43, 118, 130, 131.	137, 138, 188	55, 146		62–64, 68, 69, 165–167.
Cr		13, 22–25, 37, 118, 120, 186.	37, 41, 43, 118, 130, 131, 187.	137, 138, 188	55, 56, 146		61–64, 66–69, 165–168, 190.
Cu		16, 22–25, 33, 37, 118, 120, 145.	37, 41, 43, 118, 130, 131.	137, 138, 188	55, 146		61–64, 66, 68, 69, 165–167.
Fe		13, 16, 22, 23, 31, 33, 37, 112, 113, 115, 118, 120, 126, 145.	37, 41, 43, 118, 128, 130, 131, 187.	48, 126, 137, 138, 188.	53–56, 146	73, 173	61–64, 66–69, 165–168.
Ga		25, 36, 37, 119	37, 43		55		
Ge		22, 24, 25, 36, 118, 119.	43, 118		55		63
Hf		37	37, 43		55		58–60, 68, 149–157, 159–163, 166, 167, 190.
Hg		22, 24, 37	37, 131		55		
In		22, 24, 36, 37, 119.	37, 130		55		63
Ir		37	37				
K		22, 24, 25, 28, 35, 37, 116, 118.	35, 37, 42, 118, 130, 131.	35, 138	35, 142, 146	125	35
La		20, 21, 37	37, 43, 131	20			
Li		22–25, 28, 30, 37, 116, 118, 120.	37, 42, 118, 130, 131.	138	54, 55, 142, 146.		62, 63, 166

*Air and biological material.

Table 12.13—LISTING OF REFERENCES ACCORDING TO THE ELEMENT DETERMINED—Continued

Element	Ores and compounds	Uranium	Plutonium	Thorium	Beryllium	Graphite	Zirconium
Mg		22, 24, 37, 113, 115, 118, 120, 186.	37, 41, 43, 118, 130, 131, 187.	48, 137, 188	53, 54, 56, 146.	173	61–64, 66–69, 165–167, 190.
Mn		16, 22–25, 37, 115, 118, 120, 186.	37, 42, 43, 118, 128, 130, 131, 187.	48, 137, 138, 188.	53–56, 146	173	61–64, 67–69, 165–167, 190.
Mo		13, 22, 23, 29, 37, 113, 118.	37, 42, 43, 118, 131.	137, 188	146		62–64, 68, 165, 166.
Na		18, 19, 22, 24, 35, 37, 118.	35, 37, 42, 118, 130, 131.	35, 138	35, 54, 142, 146.	125	35, 62
Ni		13, 16, 22–25, 33, 35, 37, 112, 113, 118, 120, 145.	35, 37, 41, 43, 118, 128, 130, 131, 187.	35, 48, 137, 138, 188.	35, 55, 146		35, 61–64, 66–69, 165, 166, 168.
P		22, 24, 37, 118	37, 118, 130	137	147		166
Pb		22, 24, 25, 36, 37, 113, 118, 119, 120.	37, 41, 43, 118, 130, 131.	137	55, 146		61–64, 67, 68, 165, 166, 190.
Pd		37	37, 43		55		
Pt		37	37				
Pu	40	37					
Rh					55		
Sb		22, 24, 35, 37, 118–120.	35, 37, 43, 118, 130, 131.	35, 188	35, 146		35, 63

Si		13, 15, 16, 22, 37, 118, 186.	37, 41, 42, 118, 130, 131.	48, 137	53–56, 146	73, 173	61–63, 66–69, 165–167.
Sn		13, 22, 24, 25, 37, 118, 120.	37, 43, 118, 130, 131.	188	55, 146		61–63, 67, 69, 165, 166, 168.
Ta		37	37		146		
Th	45–47, 133–136.	37	37				
Ti		13, 37	37, 41–43, 131	188	55, 146	73	61–64, 66–69, 166, 167, 190.
Tl		22, 25, 118	118				63
U	1–12, 108–110.		37				
V	109	13, 22, 23, 25, 33, 37, 113, 118, 120.	37, 43, 118, 130, 131.	137, 188	55, 146	73, 178	62–64, 67–69, 165, 166.
W		37	37, 42, 43		146		68, 166
Zn		22, 24, 35, 37, 118, 120.	35, 37, 41, 43, 118, 130, 131, 187.	35, 138, 188	35, 146		35, 62, 63, 67, 165.
Zr	148, 184	37, 193	37, 41, 43	48			

Alloy analysis: 124, 194, 195, 196, 197, 198, 199
Isotopic analysis: 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 179, 180, 181, 182, 189, 191
Radioactive material analysis: 7, 74, 75, 76, 77, 158, 169, 170, 171, 192
Review papers: 34, 44, 57, 128, 131, 132, 200

Table 12.14—INDEX TO SEPARATIONS FROM SPECIFIC MATRIX MATERIALS

Matrix material	Nonspecific group separations		Separations from rare earths		Separations from platinum-metal group		Separations from refractory metals	
Uranium	Cellulose	12-2.1(a)	Cation exch.	12-2.1(c)(1)	Ethyl acetate extr.	12-2.2(d)	Anion exch.	12-2.1(b)(3)
		12-2.1(a)(1)		12-2.1(c)(3)	Dithizone extr.	12-2.3(c)(2)	Cupferron exch.	12-2.3(b)(1)
	Anion exch.	12-2.1(b)		12-2.1(c)(4)	Sulfide ppt.	12-2.4(b)(1)		
		12-2.1(b)(2)	Fluoride ppt.	12-2.4(a)(1)	Reduction ppt.	12-2.4(c)(1)		
	Ether extr.	12-2.2(a)		12-2.4(a)(3)		12-2.4(c)(2)		
	TBP extr.	12-2.2(b)						
		12-2.2(b)(1)						
	Dithiz. extr.	12-2.3(c)(1)						
	Sulfide ppt.	12-2.4(b)(1)						
	Alk. ppt.	12-2(d)(1), (2), (3)						
Thorium	Cellulose	12-2.1(a)	Cation exch.	12-2.1(c)(2)				
		12-2.1(a)(2)		12-2.1(c)(5)				
	Anion exch.	12-2.1(b)	TTA extr.	12-2.3(a)(3)				
	TBP extr.	12-2.2(b)						
	Penta ether	12-2.2(c)(1)						
	TTA extr.	12-2.3(a)(1)						
	Oxine extr.	12-2.3(d)						
Plutonium	Anion exch.	12-2.1(b)						
		12-2.1(b)(1)						
		12-2.1(b)(2)						
	TTA extr.	12-2.3(a)(4)						
	Cupferron	12-2.3(b)(2)						
Zirconium	TTA extr.	12-2.3(a)(2)	Cation exch.	12-2.1(c)(1)	----------		Cyclohexone extr.	12-2.2(d)
	Dithiz. extr.	12-2.3(c)(3)		12-2.1(c)(3)				
			Fluoride ppt.	12-2.4(a)(1)				
				12-2.4(a)(2), (3)				
Beryllium (magnesium)	----------		Fluoride ppt.	12-2.4(a)(1)				
				12-2.4(a)(2), (3)				
Titanium	----------		Fluoride ppt.	12-2.4(a)(1), (3)				
Sodium	Hydroxide ppt.	12-2.4(d)(4)						

12–2 CHEMICAL SEPARATIONS

By Clara Gale Goldbeck

Most of the separation methods for the concentration of impurities from reactor materials for spectrographic analysis fall into four general categories: (1) chromatography and ion exchange; (2) solvent extractions of ion association systems (ether, tributyl phosphate, etc.); (3) solvent extraction of chelate systems (thenoyltrifluoroacetone, cupferron, etc.); and (4) inorganic precipitation with or without carriers. For discussion the separations will be grouped by these general categories rather than by the elements to be separated or the matrix material since the object of most of the separations is to remove the bulk of the matrix material leaving certain of the impurities concentrated for direct spectrographic analysis or for further separation into groups. As an aid to the reader in locating bulk separations from a given base material, a cross reference is given in tabular form (Table 12.14) by section numbers. The rare-earth group is one that is most frequently sought in a concentrated form; however, the methods used for them may also separate other impurities. For this reason, with the rare earths as well as the other group separations, the method used for the major separation from the matrix will be considered primarily with the understanding that for some elements a combination of treatments may be required for final separation. Procedures that require excessive manipulation are, in general, less desirable than simple ones because of the possibility of contamination or incomplete recoveries at each step.

12–2.1 Chromatography and Ion Exchange

(a) *Cellulose.* The use of cellulose [202-204] for the concentration of impurities is derived from its well known use in the determination of uranium and thorium in ores. In these cases the uranium or thorium is obtained in the nitrate form without excess water. The nitrates are dissolved in an ether–nitric acid solution, and the solution is adsorbed on cellulose. An ether–nitric acid solution is used to wash the uranium and thorium from the cellulose; the impurities are retained. The impurities are then recovered either by elution with a suitable eluant or by igniting the cellulose to obtain the ash.

Another procedure [205] uses a single pass through the column with a comparatively small sample of uranium (5 g). After the uranium has been washed out, the cellulose is ignited, and the ash is used for a direct spectrographic examination of all the major impurities. For a magnesium [206] determination in the 1- to 50-ppm range in 5 g of uranium metal, a similar collection on a cellulose column is used; the magnesium

is finally eluted with a solution of ammonium hydroxide (2 per cent) and ammonium nitrate (1 per cent). This eluant effectively prevents any iron in the sample from contaminating the magnesium.

A cellulose column is employed in some cases to reduce the thorium [207] or uranium [208] content to a low value, but an additional column [209] and/or chemical separation may be necessary. Where a single column is used with large samples (50 g of thorium and 500 g of uranyl nitrate hexahydrate), further separation of the thorium from the rare earths is accomplished with a hexamine precipitation; [210] and the separation of uranium,[211] following ignition of the cellulose, is made using oxalate and hydroxide precipitations with calcium and iron as carriers.

(1) *Separation of Rare Earths from Uranyl Nitrate–Cellulose Column.*

Procedure.[211] The large sample handled by this procedure permits a limit of detection ranging from 0.001 ppm for europium to 0.005 ppm for gadolinium. A glass ion-exchange tube (approximately 4 by 36 cm with a constricted exit tube) is rinsed with ether and allowed to drain for at least 10 min. Twenty milliliters of dimethyldichlorosilane (D.C. 200 silicone) is poured into the tube and the tube is manipulated so that the silicone covers the entire interior surface. The silicone coating is allowed to harden and form a water-repellent surface. A porcelain filter disk is placed in the bottom of the tube, the constricted end is closed off, and the tube is filled with ether–nitric acid solution (950 ml of ether plus 50 ml of nitric acid). Enough cellulose to fill a 100-ml beaker is added to the tube, and the slurry is agitated with a glass plunger in the ether solution.

The dispersed pulp is allowed to settle and is pressed down with the plunger so that it will not run out when the ether is drained. As the ether is draining, the pulp is compressed to form a pad free of air spaces; finally the surface is tamped down to form a level and uniform surface. The rate of flow from the packed column should be such that the ether solution just fails to form a continuous stream.

Five hundred grams of uranium metal is placed in a 2-liter beaker and is covered with water (use massive metal or large chips; powdered uranium may react explosively). Fifty milliliters of nitric acid is added, and the mixture is warmed on a hot plate. Successive 25-ml portions of acid are added as the reaction diminishes until solution is complete. When the metal has completely dissolved, the solution is evaporated carefully until it is about to crystallize; then it is allowed to crystallize with stirring. Finely divided dry crystals are essential.

The prepared cellulose column is rinsed with an ether–nitric acid solution and then filled to the neck with the ether–nitric acid solution. The uranyl nitrate crystals are added to the column a few grams at a time; the level of the ether solution is maintained until all the crystals have been added. The layer of undissolved crystals should never exceed a depth of ½ in. The rate of flow of the solution can be controlled by the depth of the layer.

When all the crystals are in the column, the ether–acid solution is drained completely. The uranium is washed from the column by first filling the tube to the neck with the ether–acid solution and allowing it to drain. The remaining uranium is washed from the column by at least three more washes made by half filling the tube above the cellulose with the ether–nitric acid eluant and allowing it to drain. The acid is washed from the column by repeated washes with water-saturated ether. Gentle suction is applied to free the column from residual ether.

The cellulose is blown from the tube by a rubber blowing bulb into a 3-in. platinum dish and dried cautiously on a hot plate. It is ignited in a muffle furnace at 550°C until the carbonaceous matter has been completely destroyed.

The ash is taken up in 40 ml of hydrofluoric acid and 2 ml of perchloric acid and taken to fumes. The remaining residue is put into solution in hydrochloric acid. A double (or triple) ammonium oxalate precipitation is made to remove any remaining uranium. The oxides from the final oxalate precipitation are dissolved in hydrochloric acid. An iron solution equivalent to 7.5 mg of ferric oxide is added, and an ammonium hydroxide precipitation is made. After filtration and ignition of the precipitate, the silica is removed from the resulting oxide by treatment with hydrofluoric acid. The oxides are again dissolved in hydrochloric acid, and the ammonium hydroxide precipitation is repeated. The hydroxides are ignited at 700 to 800°C in a platinum crucible and are used for spectrographic examination. The limits of detection in parts per million are: europium, 0.001; samarium, 0.003; erbium, 0.003; lutetium, 0.003; gadolinium, 0.005; dysprosium, 0.003; thulium, 0.003; and neodymium, 0.005.

(2) *Separation of Rare Earths From Thorium Nitrate or Uranyl Nitrate: Batchwise Process Using Cellulose.* A batchwise procedure [212] rather than a column is employed at Oak Ridge National Laboratory for both uranium and thorium; this procedure is capable of handling 20-*g* samples in a comparatively short period of time. In this case the cellulose absorbing the solution is filtered from the ether–nitric acid solution on a glass frit, and the rare earths are removed from the cellulose with nitric acid at a pH of 2. The iron, zirconium, scandium, and thorium in the nitric acid solution are removed by extraction into 0.5*M* thenoyltrifluoroacetone (TTA) in xylene at a pH of 1, and the rare earths are extracted into TTA at a pH of 4.5.

Procedure. About 50 g of shredded, ashless filter paper is soaked in 2 liters of water for 2 hr. The paper is macerated in a Waring blender for 30 sec and filtered on a Büchner funnel. The mat is washed five times with water and then transferred to a 4-liter beaker. The mass is washed twice with 3 liters of distilled water, once with 1 liter of absolute alcohol, and once with 1 liter of diethyl ether; between each wash the mass is filtered on the Büchner funnel. While the cellulose is still damp, it is spread in a thin layer to dry at room temperature.

Approximately 3 hr before the analysis is to be performed, 2 g of pulp for each sample is put in a beaker and covered with a 11.1 per cent (v/v) nitric acid–ether mixture consisting of 100 ml of ether and 12.5

ml of nitric acid. The solution is decanted immediately before the pulp is used.

The thorium nitrate dodecahydrate is dissolved in a minimum of nitric acid (about 45 ml for a 20-g sample). The solution is added slowly with rapid stirring to sufficient absolute diethyl ether or di-*n*-propyl ether to form a 11.1 per cent (v/v) nitric acid–ether mixture. The ether should not contain preservatives.

Two grams of conditioned cellulose is added to the sample–nitric acid–ether solution, and the solution is agitated for 10 min at high speed with an air-driven stirrer. The pulp is then filtered on a coarse fritted glass disk with suction. A convenient apparatus for washing and filtering has a fritted disk and a stopcock joined to a large cylindrical tube equipped with a stirrer. The pulp is washed five times with 100-ml portions of 11.1 per cent nitric acid–ether solution, and the mixture is stirred for 3 min each time. The washings are discarded.

A clean suction flask is connected to the washing–filtering apparatus, and the rare earths are stripped from the cellulose by stirring for 5 min with 100 ml of nitric acid solution (pH 2.0) and then drawing the solution into the flask. The acidic solution in the flask is then diluted with nitric acid (pH 2.0) until the solution is pH 1.0. Diluting with water or nitric acid at a pH greater than 2 produces a colloidal form of thorium hydroxide which redissolves very slowly at pH 1.0 and which cannot be extracted by the subsequent purification procedure.

The residual thorium is extracted from the solution by agitating with an equal volume of 0.5*M* TTA in xylene or kerosene. The organic phase is discarded. This extraction removes the thorium, iron, zirconium, and scandium and can be completed in 5 min at 60°C. The aqueous layer is backwashed with xylene or kerosene to remove any dissolved TTA. The organic layer is discarded. The pH of the aqueous phase is increased to 4.5 and agitated as above with a fresh portion of TTA. The rare earths are extracted into the organic phase, which is then agitated for 5 min with about 15 ml of 1*N* hydrochloric acid at 60°C. The aqueous layer is backwashed with xylene or kerosene to remove the TTA; backwashing leaves only the rare earths in solution. This procedure should take about 2.5 hr to complete.

With uranium the sample must be in the form of uranyl nitrate hexahydrate. The cellulose is conditioned as above, but the solvent used is 24.7 per cent (v/v) nitric acid–ether mixture consisting of 100 ml of ether plus 5 ml of nitric acid instead of 11.1 per cent.

(b) *Anion-exchange Resin.* The use of anion exchangers depends upon the formation of anions of uranium, thorium, plutonium, and other material and upon the retention of these anions by a column of anion-exchange resin. Cationic impurities are not retained by the resin. This method is limited to small samples when the matrix material is retained on the column.

The fact that thorium is complexed by strong 8*N* nitric acid and thus is held on Dowex-1 resin [213] is the basis of one procedure to separate yttrium, scandium, and the rare earths.[214] A strong nitric acid medium will also cause plutonium to be retained. This fact is the basis for the separation of impurities in general [215] and of zirconium [216]

from Pu(IV) solutions. In addition to thorium, Ce(IV) and Ag(II) also may form nitrate complexes and be retained on the resin. Chromium and cerium can be reduced to their lower valence states with hydroxylamine before placing the solution on the column to avoid their retention.

(1) *Separation of Plutonium in Nitric Acid Medium: Anion Exchange.*

Procedure.[215] With 50-mg samples of plutonium, concentrations as low as 2 ppm of manganese, nickel, and chromium, and 10 ppm of iron, aluminum, calcium, magnesium, and zinc have been determined.

For the ion-exchange column, 3 ml of wet resin (Dowex-1), 4 per cent cross-linked, 50 to 100 mesh, is packed in a glass column 0.6 by 10 cm. The rate of throughput is 3 ml/min/cm^2. Fifty milligrams of plutonium is weighed (in a gloved box), and the sample is transferred to a 25-ml Erlenmeyer flask. Hydrochloric acid is added dropwise until about 0.5 ml has been added. If dissolution appears incomplete, the flask is placed under a heat lamp. When the sample has been dissolved, 5 ml of 8.25*M* nitric acid and 100 μl of cobalt solution (0.01 per cent in 4*M* nitric acid) are added. The solution is transferred to the ion-exchange column after the resin has been pretreated with 3 ml of 8.25*M* nitric acid. The effluent is collected in another 25-ml flask. The column is washed with 8.25*M* nitric acid by adding 6 ml to the original sample flask, rinsing, and transferring to the column. The total effluent is evaporated to dryness, and then 500 μl of hydrochloric acid is added. One hundred microliters of the solution is transferred to a 3-mm crater electrode treated with Fluorolube solution, and the solution is evaporated under a heat lamp. The electrode is transferred to the excitation glove box and exposed on the spectrograph.

(2) *Separation of Impurities in Hydrochloric Acid Medium.* Hydrochloric acid will also serve to complex uranium and plutonium and has been used as the medium for the separation of impurities.[217] After the uranium or plutonium solution in 12*N* hydrochloric acid has been put on the column of Dowex-1, successive elutions are made with hydrochloric acid solutions of 11*N*, 10*N*, 9*N*, etc., down to 6*N* hydrochloric acid with plutonium or 5*N* hydrochloric acid with uranium. At 6*N* hydrochloric acid, the plutonium starts to move down the column. A second effluent solution is collected by washing with 8*N* nitric acid. This wash recovers iron, cobalt, molybdenum, gallium, zinc, cadmium, and tin. With uranium samples the 5*N* hydrochloric acid starts to move the uranium band appreciably. At this point the effluent is evaporated to recover the impurities. The uranium is washed out with 1*N* hydrochloric acid, and then a second effluent is collected by washing the column with 0.1*N* and 0.05*N* hydrochloric acid and water. This second effluent is examined for zinc and cadmium.

(3) *Separation by Complexation of Impurity Elements.* Anion-exchange resins can also be used to hold impurities that occur as

anions. The matrix element passes through the column. This method [218] is used to determine tungsten, tantalum, and niobium in uranium by passing a 20-g sample of uranium in a solution of 10 per cent (v/v) nitric acid containing 5 mg of tin as a carrier through a 3-g Dowex-1 column. After the uranium has been washed from the column with 10 per cent nitric acid, the resin is ignited at 700°C to obtain the elements held on the resin. Probably the resin in this case is acting as a filter bed more than as an ion-exchange column.

(c) *Cation-exchange Resin.* The use of cation-exchange resins, such as Dowex-50 or Amberlite IR–120, depends on the use of specific eluants to selectively remove successive elements or groups of elements. Separation of the elements depends on the relative degree of retention of the elements by the resin and on the stability of the complex formed by the element with the eluting agent.

(1) *Separation of Rare Earths in Hydrofluoric Acid Medium.* Several procedures employing dilute hydrofluoric acid as the eluting solution are given for the separation of rare earths from the matrix material. It is claimed that this is not simply a means of filtering out precipitated insoluble rare-earth fluorides since in many cases the rare-earth concentration is too low to permit precipitation in the acid conditions present. This general procedure has been used for separations of uranium [218, 219] with lanthanum as a carrier. After removal of the uranium by washing with dilute hydrofluoric acid solution, the resin is removed from the column and ignited.

Procedure.[218] A slurry of 3 g of Dowex-50, 8 per cent cross linkage, 50 to 100 mesh, is prepared in 25 ml of 10 per cent hydrofluoric acid (dilute 100 ml of 48 per cent HF to 1 liter). The slurry is added to a polyethylene column (6-in. long by ½ in. inside diameter plugged with a one-hole rubber stopper covered with Saran wool and fitted with ¼-in.-OD polyethylene tubing) with a water rinse to ensure complete transfer of the resin to the column. About 20 g of uranium in the form of uranyl nitrate hexahydrate is taken up in 25 ml of 10 per cent hydrofluoric acid and evaporated to dryness. The residue is dissolved in 100 to 150 ml of 10 per cent hydrofluoric acid. One milligram of lanthanum in 1 ml of solution is added as a carrier, and the solution is mixed. The sample solution is allowed to flow freely through the resin column. When the solution level has reached the top of the resin, the sample beaker and the walls of the column are thoroughly rinsed twice with about 25 ml of distilled water.

An additional 75 ml of 10 per cent hydrofluoric acid is passed through the column to completely remove any uranium remaining. When the solution has drained from the column, the plug is removed from the bottom of the tube, and the resin is rinsed with about 10 to 15 ml of water into a funnel holding a No. 40 Whatman filter paper. The filter paper and resin are placed in a 30-ml platinum crucible and ignited at 875°C. The ash is then ready for a spectrographic analysis.

The above method was also used to determine less than 2 ppm of gadolinium, terbium, dysprosium, holmium, and samarium in 100-g samples of zirconium,[220] with yttrium as a carrier. After the zirconium has been dissolved with hydrofluoric acid and the solution has been passed through the column, the rare earths are eluted with 6*N* hydrochloric acid and further separated from cationic impurities by standard chemical methods. It is stated that the method should be applicable for the separation of these five rare earths from any element that dissolves in hydrofluoric acid to form a stable anionic complex.

(2) *Separation of Rare Earths in Hydrochloric Acid Medium.* Hettel and Fassel [221] have presented a method that separates the rare earths from thorium and at the same time separates the rare earths from the other common impurities in thorium with 4*M* hydrochloric acid as the eluting agent. The method has the disadvantage of using large amounts of reagents and taking considerable time.

(3) *Separation of Rare Earths in Sulfate Medium.* Hettel and Fassel [221] reported on a method for the separation of rare earths from uranium and zirconium which involved the formation of neutral or anionic sulfate complexes with thorium, uranium, and zirconium. The rare earths remain in the cationic form. This process with thorium failed to give complete separation from rare earths. With uranium and zirconium the sample is placed on, and washed through, the column with 0.75*M* ammonium sulfate at a pH of 3. The rare earths are eluted with 2*M* ammonium sulfate with about 2 liters of elutriant. A similar procedure for rare earths in uranium has been reported [222] in which 6*M* hydrochloric acid is used to elute the rare earths after removal of the uranium with sulfuric acid.

(4) *Separation of Rare Earths in Oxalic Acid Medium.* Another procedure [223] used for the separation of traces of rare earths from uranium with Amberlite IR–120 involves the elution of the uranium with 1*N* oxalic acid. The rare earths are then eluted with 5*N* hydrochloric acid. In a similar procedure [224] uranium, iron, and copper are eluted by 0.5*N* oxalic acid; cadmium, nickel, cobalt, and manganese are eluted by 1*N* hydrochloric acid medium; and the rare earths are then eluted with ammonium citrate at a pH of 4.

(5) *Separation of Rare Earths in Citric Acid Medium.* In earlier work [225] on cation-exchange resins, lanthanum was separated from thorium by elution with 10 per cent citric acid at a pH of 3. Sulfuric acid (6*N*) was used to elute the thorium.

12–2.2 Solvent Extraction

(a) *Ether.* The use of solvent extraction for the concentration of impurities in reactor materials dates back to the use of diethyl ether to purify uranyl nitrate; the impurities are left in the aqueous layer. The older references deal with the separation of alkaline earths and

rare earths by extraction of the uranium with ether and employ varying combinations of precipitation procedures to separate the desired elements from the other impurities and residual uranium. In these procedures the solid uranyl nitrate hexahydrate is dissolved in ether directly, and the ether solution is shaken with small portions of water to collect the impurities.[226-231] A continuous ether extractor has also been used. The rare earths are separated from the residual uranium and other impurities with combinations of precipitations employing hydrofluoric acid,[226-230] ammonium hydroxide,[226, 227] sodium peroxide,[227, 232] hydrogen peroxide,[228] or oxalate,[226, 227, 231] with appropriate carriers such as yttrium,[228, 233] iron,[227, 229] copper,[232] or calcium.[229] A more recent use of ether extraction has been to concentrate lanthanum, iron, and magnesium from uranium for their subsequent determination by flame photometry.[21]

(b) *Tributyl Phosphate.* Another organic solvent commonly used for the purification of uranium is tributyl phosphate (TBP). Tributyl phosphate is utilized with both uranium and thorium to concentrate impurities in the aqueous layer for subsequent spectrographic analysis. In typical procedures [7, 234] the uranium is obtained in 5*N* nitric acid solution and shaken two to three times with 20 per cent TBP in kerosene or hexane. Oxalate added to the solution prevents the extraction of zirconium.[7] The aqueous solution can be used directly for spectrographic analysis,[234] or further separations can be made of the impurities in the water layer by precipitation of the sulfide or ammonium hydroxide group or extraction of the rare earths with thenoyltrifluoroacetone (TTA). A similar procedure is used in which the aqueous solution is analyzed by flame-photometric methods to determine sodium and other elements.[234] This extraction of uranium from the solution reduces the health hazard that would exist if the uranium were aspirated into the atmosphere in the flame-photometric analysis.

Tributyl phosphate is also used for the extraction of thorium from nitric acid solutions. In a procedure for the concentration of rare earths and other impurities, extractions are made of thorium in 6*N* nitric acid.[235] The presence of fluoride ion adversely affects the removal of thorium. The thorium content of the aqueous layer is further reduced by extraction with 0.5*M* TTA in benzene. The rare-earth recovery is 85 per cent as shown spectrographically.[235] In a procedure [236] for the determination of aluminum, beryllium, nickel, copper, chromium, and manganese, the thorium is dissolved in nitric acid with a trace of ammonium fluosilicate and is extracted from 5*N* nitric acid. The aqueous phase is analyzed by the porous-cup method.

One procedure [237] determines the rare-earth content of a solution of uranyl nitrate hexahydrate in 22.5 per cent TBP such as a raffinate

by extracting 3 to 4 liters of this solution with two 40-ml portions of hydrochloric acid (1+1). This aqueous extract is backwashed with TBP. One milligram of lanthanum is added as an internal standard and is carried through the precipitation steps to separate the rare-earth fraction from the remaining uranium and other impurities.

Extraction of uranium with 100 per cent TBP from hydrochloric acid is used as a separation for the determination of rare earths.[238] The rare earths in the water layer are concentrated with 1 mg of lanthanum as a carrier. This procedure is described in detail.

Procedure for Separation of Rare Earths From Uranium.[238] The equivalent of 100 g of uranium trioxide in 70 ml of hydrochloric acid is transferred to a 1-liter separatory funnel with the aid of 50 ml of hydrochloric acid. Two hundred milliliters TBP is added, the funnel is shaken for 1 min, and the phases are allowed to separate. The organic phase is discarded. Four additional extractions are made with 200, 100, and 50 ml of TBP. Finally, the aqueous phase is washed with 50 ml of a hydrocarbon diluent of the kerosene type. The aqueous layer is drawn off into a 250-ml beaker, and 1 mg of lanthanum in 1 ml of solution and 1 ml of 30 per cent hydrogen peroxide are added. The solution is neutralized with a freshly prepared 50 per cent sodium hydroxide solution, and then 5 ml is added in excess. Cellulose pulp in the form of one pad of filter accelerator is added, and the mass is filtered through a 9-cm Whatman No. 42 filter paper with suction. The precipitate is dissolved with 50 ml of hot dilute hydrochloric acid (1+2). One milliliter of 30 per cent hydrogen peroxide and 50 ml of ammonium hydroxide are added to precipitate the hydroxides. After the precipitate has been digested for 30 min on a steam bath, it is filtered as before with macerated pulp.

If thorium is present, a hexamine separation is made at this point. The final precipitate from the hexamine separation or from the above step is ignited in a tared platinum crucible. After it has been weighed, the final oxide residue is examined spectrographically.

(c) *Penta Ether.* The rare earths are successfully determined in thorium by extraction from 8*N* nitric acid solution by dibutoxytetraethylene glycol (penta ether).[239] The procedure is rapid and can handle large amounts of thorium. The residual thorium and other impurities are removed by 8-quinolinol (oxine) in chloroform, and the rare earths are precipitated as 8-quinolinolates (oxinates) with lanthanum as a carrier. About 95 per cent recovery is claimed.

Procedure for Separation of Rare Earths from Thorium.[239] To 300 ml of preequilibrated penta ether-diethyl ether mixture (add 140 ml of diethyl ether and 250 ml of 8*M* nitric acid to 280 ml of penta ether in a 2-liter separatory funnel; shake the funnel; allow the phases to separate; and discard the aqueous phase) in a 500-ml separatory funnel are added 50 g of thorium nitrate tetrahydrate and 7.0 ml of nitric acid. (This quantity of acid will yield, with the water of hydration, an aqueous phase about 8*M* in nitric acid.) The funnel is shaken until the salt has completely dissolved. The aqueous phase is drained into a 250-ml separatory funnel. The organic phase is washed with 15 ml of 8*M* nitric

acid, and the aqueous phases are combined. The organic phase is discarded. The aqueous phase (combined) is extracted with 200 ml of fresh penta either–diethyl either mixture. The aqueous phase is drained into a 150-ml beaker, and the organic phase is washed with 10 ml of nitric acid. The aqueous layers are again combined, and the organic layer is discarded.

The aqueous solution is diluted to 100 ml, 10 ml of glacial acetic acid is added, and the pH is adjusted to about 1.5 with ammonium hydroxide. The solution is cooled in an ice bath, 3 g of oxine is added, and the pH is adjusted to 4.2. The solution is cooled again, if necessary, to avoid oxidation of the oxine. The contents of the beaker are transferred to a 250-ml separatory funnel and extracted with five 10-ml portions of oxine in chloroform (10 g per 50 milliliters). The aqueous layer is washed with two 25-ml portions of chloroform.

The solution is transferred to a 250-ml beaker, and 1 mg of lanthanum carrier and 50 μg of titanium as a solution of the sulfate, to act as a spectrographic internal standard, are added. About 10 per cent by volume of ammonium hydroxide is added, and the solution is heated until the precipitate flocculates. The hot solution is filtered through Whatman No. 42 paper, and the precipitate is ignited in platinum to the oxides for spectrographic analysis.

Further separation can be made when required. When the calcium and magnesium contents of the residue are so high as to interfere with the spectrographic determination, the residue, after ignition at about 600°C, is dissolved in 5 ml of hot 6*N* hydrochloric or nitric acid. The solution is diluted to about 25 ml; and, after the addition of 2 g of ammonium chloride, the rare earths are reprecipitated with ammonium hydroxide.

Beryllium and aluminum, when high in certain samples, are reduced by a precipitation with an excess of 3*M* sodium hydroxide immediately following the penta ether extraction. The separation is incomplete owing to coprecipitation; however, the dilution effect of these metals, which would lead to decreased spectrographic sensitivity, is materially lessened. The sodium hydroxide precipitate is filtered immediately and washed with 0.1*M* sodium hydroxide before it is dissolved in 25 ml of warm 4*M* nitric acid for the oxine extraction.

When it is desired to remove both large amounts of cerium and the last traces of thorium in the final residue, the addition of titanium is omitted before the precipitation of the rare-earth oxinates. After the ignition step the residue of the rare earth and the lanthanum oxides is dissolved in 50 ml of 4*M* nitric acid. About 100 mg of solid sodium bromate is added, and the solution is warmed until the salt dissolves. Ten milligrams of mercurous ion, as a solution of the nitrate, and 5.0 ml of a saturated solution of potassium iodate in 4*M* nitric acid are added,[240] and the solution is stirred until the iodates precipitate and become flocculent. The precipitate is filtered through a sintered-glass Büchner funnel and washed with about 10 ml of the potassium iodate–4*M* nitric acid solution. The titanium is next added to the filtrate, and the hydroxides are precipitated with concentrated ammonium hydroxide.

(d) *Miscellaneous Solvents.* Cyclohexanone has also been used as an extractant to separate traces (0.01 per cent) of tantalum as the fluoride complex from zirconium.[241]

As described in Rodden [242] the platinum-group metals, palladium, platinum, and rhodium, have been separated from uranium by extraction with ethyl acetate after treatment of an acid solution with stannous chloride. The sum of the platinum and rhodium combined is estimated colorimetrically, but, if the amount of platinum and rhodium together is more than 4 ppm, the determinations are made spectrographically on the extract.

12–2.3 Extraction With Organic Reagents

Extraction separations with organic solvents are also employed in conjunction with organic reagents that will form chelate systems with specific ions under controlled conditions. These organic reagents include thenoyltrifluoroacetone, cupferron, dithizone, and 8-quinolinol.

(a) *Thenoyltrifluoroacetone.* (1) *Extraction of Thorium.* Thenoyltrifluoroacetone (TTA) finds most use in the extraction of thorium from dilute acids although it will also extract many other elements under certain conditions, such as zirconium from dilute hydrochloric acid (1+1) and rare earths from a solution of pH 4.5. In the analysis of thorium, the sample size is limited since the thorium is extracted. In a simple, yet typical, application [236] by Knolls Atomic Power Laboratory, a thorium nitrate solution, 0.25*N* in nitrate, is extracted five times with equal volumes of 0.5*M* TTA in xylene. Thorium removal is followed colorimetrically. The raffinate is concentrated and analyzed spectrographically.

Thenoyltrifluoroacetone extractions have also been used for separating thorium from rare earths and other impurities after the bulk of the thorium has been removed by other means, such as tributyl phosphate (TBP) extraction [235] or a cellulose column.

Oak Ridge National Laboratory has used a similar procedure [243] to concentrate all the impurities except zirconium, iron, and scandium by extracting up to 5 g of thorium. For instance, a 0.5-g sample of thorium as nitrate is dissolved in 500 ml of a solution at pH 1.0. This is extracted with 500 ml of a 0.5*M* solution of TTA in benzene in a 1-liter separatory funnel with the solumtions heated to 70°C to accelerate the extraction. The extraction is repeated; the rare earths are freed of thorium by coprecipitating on ferric hydroxide, redissolving in a small volume, and re-extracting thorium and iron as above.

Thorium is also extracted from chloride solutions where the concentration is 0.1*N* hydrochloric acid.[244] (In a separation from rare earths, it was found that all but 200 μg of thorium could be extracted from 25 ml of a solution containing 100 mg of thorium by one extraction with 50 ml of 0.02*M* TTA.) This quantity of thorium was not enough to interfere with the spectrographic determination of rare earths in the aqueous layer.

(2) *Extraction of Zirconium.* Zirconium can be removed from thorium [243] if a chloride solution of the thorium in dilute hydrochloric acid (1+1) is extracted with a 0.5*M* solution of TTA in xylene at 70°C. The zirconium in the organic layer is recovered by shaking the solution with 1 per cent (v/v) hydrofluoric acid. The zirconium is determined spectrochemically in the concentrated solution.

(3) *Extraction of Rare Earths.* Rare earths can also be extracted into TTA solutions [245] when it is desired to separate them completely after their initial concentration. This can be done by adjusting the aqueous solution to a pH of 4.5 and extracting with TTA solution. The rare earths are recovered from the organic layer by re-extracting into hydrochloric acid solution. This procedure is described in Sec. 12–2.1(a)(2). Use is made of TTA extractions to concentrate both lanthanum [246] and aluminum [247] prior to their determination with the flame photometer. In each case the radiant intensity from a hexone solution is enhanced about 100-fold over that given by an aqueous solution. Each element is extracted from an acetate-buffered solution with a 0.1*M* TTA solution in hexone, and the hexone solution is aspirated directly into the flame photometer. If the elements are to be determined from a sample containing thorium, uranium, copper, and iron as the major constituents, the sample is initially extracted [246] at pH 1.5 with TTA before the lanthanum is extracted at pH 5. Both extractions are made from a 1*M* acetate solution.

(4) *Extraction of Plutonium.* At the Hanford Engineering Works [248] use is made of TTA extractions for the spectrographic analysis of plutonium. Thenoyltrifluoroacetone in benzene or hexone will extract Pu(IV) from dilute nitric acid solutions. Plutonium (III) is not extracted; so two types of extractions will separate most of the metallic impurities.

For satisfactory separation of plutonium from the impurities, the Pu(III) and Pu(IV) solutions extracted must contain less than 1 per cent of the other plutonium valence states. Plutonium (III) can be prepared by reducing the higher oxidation states of plutonium with hydroxylamine in 1*N* hydrochloric acid. After a hexone extraction the plutonium is oxidized to the (IV) state with nitric acid. Hexone proved to be a more satisfactory solvent for the TTA and its chelates than hydrocarbons or petroleum ether. Iron and gallium chloride are extracted by hexone alone from the aqueous phase with no TTA present.

Procedure.[248] So that as many elements as possible can be determined in plutonium, most of the extractable elements are removed from the Pu(III) solution by extraction with pure hexone. A solution containing 50 mg of plutonium per milliliter of 6*N* hydrochloric acid is prepared, and 100 μl of this solution is placed in a 1-ml pyrex volumetric tube.

One drop of 0.5*M* hydroxylamine is added, and the solution is heated for 5 min or until it becomes bright blue, whichever is longer. Then 500 μl of hexone is added, and the tube is shaken for 2 min. The organic phase is removed and analyzed by the copper-spark method. Then, to remove hafnium and zirconium, extract the Pu(III) solution for 2 min with 500 μl of 0.5*M* TTA in hexone. The organic phase is removed, evaporated to dryness, and heated strongly to remove TTA. The residue is analyzed by the copper-spark method. The aqueous phase is made 6*N* in nitric acid and is extracted for 2 min with 500 μl of 0.5*M* TTA in hexone. The organic phase is removed, and the extraction step is repeated to remove any remaining plutonium. The aqueous phase is removed and analyzed by the copper-spark method.

Table 12.15 shows the distribution of impurity elements resulting from these separations.

(b) *Cupferron.* (1) *Separations From Uranium.* Cupferron is commonly used for the separation of many elements from uranium, but, for the spectrographic analysis of impurities in uranium,[238, 249] its primary use is preliminary to the determination of gallium, hafnium, molybdenum, niobium, palladium, tantalum, titanium, vanadium, tungsten, zirconium, and tin.

The cupferron is added to a solution of U(VI), and the cupferrates are extracted with chloroform. The chloroform is evaporated, the

Table 12.15—DISTRIBUTION OF IMPURITY ELEMENTS IN THE EXTRACTION OF PLUTONIUM SOLUTION WITH HEXONE AND TTA[248]

Elements Remaining in Aqueous Phase				
Ag	Cr(III)	Li	Pr	Sr
Al	Cs	Lu	Pt(IV)	Ta
As(V)	Dy	Mg	Rb	Th
B	Er	Mn(II)	Rh(III)	Tm
Be	Eu	Na	Ru(III), (IV)	
Bi	Gd	Nd	Sb(V)	U(IV), (VI)
Ca	Ho	Ni	Sc	V(III), (IV), (V)
Cd	K	Os(III), (IV)	Se(IV)	Y
Ce(III)	La	P	Si	Yb
Co		Pb(II)	Sm	Zn

Elements Extracted Into Organic Phase			
As(III)	Ga	Mo(III), (V), (VI)	Sn(II), (IV)
Au(III)	Ge	Pt(II)	Te(IV)
Nb(V)	Hf	Re(VII)	Tl(III)
Fe(II), (III)	In	Sb(III)	W(VI)
			Zr

cupferrates are destroyed, and the residue is prepared for spectrographic analysis. Bismuth is added as an internal standard, or the residue can be concentrated on ferric oxide for spectrography by the iron-flux technique. The rotating-disk technique has also been used on solution concentrates with palladium as an internal standard.[218]

Procedure. A sample containing 5 g of uranium is obtained in 50 ml of dilute sulfuric acid (1+9). While the solution is hot, a slight excess of 0.1*N* potassium permanganate solution is added (2 drops after the pink color has developed). The solution is cooled to 5°C with ice and is transferred to a separatory funnel. The cupferrates are precipitated by adding 3 ml of an 8 per cent solution of cupferron. The mixture is shaken well, and the cupferrates are extracted with 10 ml of chloroform. The chloroform layer is drained into another extraction flask, and the extraction of the water layer is repeated several times until all the cupferrates have been removed. The combined chloroform layers are backwashed with a solution of 10 ml of 10 per cent sulfuric acid plus 2 ml of 8 per cent cupferron solution.

The chloroform layer is drained into a folded 18.5-cm No. 42 Whatman filter paper which has been fitted into a No. 4 porcelain crucible and dampened slightly with water to hold it in place. Usually some precipitate remains at the chloroform–water interface in the separatory funnel after extraction of the original solution. The precipitate should be drained off with a little of the solution through a small filter paper and washed free of uranium with hot 1 per cent sulfuric acid and then with water. The filter paper is set aside.

The large crucible containing the chloroform solution is placed under a hood at room temperature to permit evaporation of the chloroform from the paper. The paper is kept damp by adding a small amount of water to the bottom of the crucible. When all the chloroform has evaporated, 1 ml of a solution containing 1 mg of bismuth per milliliter is added to the filter paper. The filter papers are combined and placed in a No. 1 porcelain crucible.

The crucible is set in a cold furnace and heated gradually to 350°C. After 1 hr the temperature can be increased to 500°C to burn off any remaining paper. The residue is used for the spectrographic analysis.

(2) *Separations From Plutonium.* For the analysis of plutonium, cupferron is used to extract the Pu(III) and Pu(IV) leaving many impurity elements in the aqueous layer.[250] The extractions are best done from hydrochloric acid solution since it permits a wider pH range for the extraction. Hydrochloric acid alone does not oxidize the cupferron as does nitric acid, nor does it attack the copper electrodes as much. This procedure is also applicable to milligram-sized samples of other materials such as U(IV) (for alkali determination),[251] iron, vanadium, tantalum, titanium, niobium, zirconium, tin, bismuth, or antimony, which also form cupferrides.

The procedure developed at Los Alamos Scientific Laboratory [250, 252] gave satisfactory results. It was found necessary to destroy the organic matter in the residue with perchloric acid and to visually com-

pare the impurity-element spectra from the samples with the spectra of standards carried through the identical procedure. The original Los Alamos procedure was reported by Van Tuyl [132] to give low results as compared to the carrier-distillation procedure, but a later report [253] claims greatly improved precision when cobalt is added as an internal standard to the aqueous solution before evaporation.

Procedure.[252] A sample of plutonium metal, 200±10 mg, is dissolved in a 4-ml quartz volumetric flask by adding three 200-μl portions of hydrochloric acid (redistilled in a quartz still) at not less than 3-min intervals. An additional 1 ml of acid is added, and the flask is heated if any undissolved particles remain. The solution is diluted to volume. In general, the formation of insoluble plutonium oxide can be prevented by placing the first addition of 200 μl of acid in the flask before adding the sample. Three aliquots of 200 μl, each containing 5±0.25 mg of plutonium, are transferred to 1-ml stoppered quartz extraction vials (test-tube shape, standard taper 9/15), 100 μl of hydrochloric acid is added to each, and the vials are filled to the mark with water.

Standards (in triplicate) are carried along with the procedure by adding one of the lower and one of the higher concentration level standards to 1-ml extraction vials along with 130 μl of hydrochloric acid to each and diluting to volume. (The standards should be prepared by dissolving the metals or compounds in a minimum of hydrochloric acid and diluting to volume with water.) A greater volume of acid is added to the standard extractions to make their normality the same as those of the samples.

Two grams of purified cupferron is dissolved in 18 ml of water in a graduated cylinder. Four milliliters of ether is added, and the cupferron is extracted as the free hydroxylamine into the ether phase by adding 2.5 ml of hydrochloric acid. To each extraction vial is added a 100-ml aliquot of the ether phase, and the two phases are agitated vigorously for 2 min. To each of only three vials at a time, 100 μl of chloroform is added. Excessive air oxidation of the extractions will occur if chloroform is added to all the vials at one time. The vials are gently agitated, and the aqueous phases are transferred to platinum crucibles. (The cobalt internal standard may be added at this point.)[253]

The solution is evaporated slowly to dryness (about 1 hr) in a drying chamber. One hundred microliters of nitric acid (redistilled from quartz) is added, and the solution is evaporated slowly to dryness (about 30 min). One hundred microliters of perchloric acid (redistilled under vacuum in a quartz still) is added, and the solution is again evaporated slowly to dryness. The last traces of perchloric acid are removed by heating to about 116°C for 10 min.

With a different pipet for each sample, 100 μl of water is added to each crucible, and the residue is loosened to aid its solution by thoroughly scraping the inside of the crucible with the tip of the pipet. The water addition is transferred in nearly equal portions to a pair of copper electrodes placed in a heated copper drying block. Fifty microliters of 1*N* hydrochloric acid is added to the crucible, and again the crucible is thoroughly scraped with the tip of the pipet. This acid solution is transferred to the previously coated pair of electrodes, which are now ready for spectrographic analysis.

(c) *Dithizone.* (1) *Separations of Cadmium and Indium From Uranium.* Extractions of the dithizone complexes of impurity metals from uranium solutions have been used in a manner similar to the cupferron extractions. Although the extracted elements have been examined directly for the determination of silver, gold, paladium,[254] and cadmium, more recent work has recommended separations where the specific dithizonates are concentrated chromatographically on alumina, which is subsequently examined spectrographically using the carrier-distillation technique. The British have used this method for the spectrographic determination of cadmium [255] and indium.[256] For indium it was found necessary to also add cupferron to the solution before extracting with the carbon tetrachloride solution of dithizone to ensure that all the indium is extracted from the citrate solution.[256] The cupferron was not necessary for extraction of the cadmium.

(2) *Separations of Silver, Gold, and Palladium From Uranium.* Successful extractions, as reported in Rodden,[254] have also been made of silver, gold, and palladium from uranium solutions with dithizone in carbon tetrachloride. The extracts are evaporated to a small volume and transferred to a copper electrode, where they are treated with hydrochloric acid, evaporated, and flamed with a burner preparatory to spectrographic examination.

(3) *Separations With Dithiocarbamate.* Extractions are made in a chloroform medium with dithizone and ammonium pyrollidine dithiocarbamate [257] mixed together to separate a number of elements from zirconium prior to spectrographic analysis. The extraction is carried out on a solution containing 1 g of zirconium at four successive pH levels: 3, 5, 7, and 9. Beryllium is added as a reference to the residue from the chloroform layer, which is then analyzed spectrographically. The limit of sensitivity of the extracted impurities is said to be 0.001 per cent.

(d) *8-Quinolinol.* 8-Quinolinol (oxine) in chloroform will extract thorium and thus effect a separation from rare earths. This separation has been used for obtaining the rare-earth oxides concentrate suitable for spectrographic analysis. For the separation of rare earths from thorium nitrate,[239] the bulk of the thorium is removed by pentaether and then oxine extractions, and the rare earths are collected by precipitation of the 8-quinolinolates (oxinates) with lanthanum as a carrier. The details of this procedure are given in Sec. 12–2.2(c)(1).

12–2.4 Precipitation Separations

(a) *Fluoride.* (1) *Separation of Rare Earths With Thorium as a Carrier.* Some separations are accomplished by precipitations unaccompanied by any complexing agents or extractions for the bulk separation.

Direct precipitation of the rare earths as fluorides or oxalates has been commonly used as a separation. Where thorium has been used as a carrier, it has been subsequently removed from the rare earths by 8-quinolinol (oxine) extraction.[258] These direct precipitations using a thorium carrier are the basis for a method for separating rare earths from solutions of beryllium, magnesium, zirconium, titanium, uranium, and stainless steel. With solutions of zirconium, titanium, uranium, and stainless steel, the preliminary bulk separation is made by precipitation of the rare earth fluorides with a thorium carrier; but, for essentially complete recovery, it was found necessary to add ammonium fluoride in addition to hydrofluoric acid. This presumably precipitates the thorium as a double salt, $NH_4ThF_5 \cdot H_2O$. From beryllium and magnesium solutions, the oxalate precipitation with thorium as a carrier is satisfactory.

Procedure for Separation From Beryllium and Magnesium.[258] A 10- to 40-g sample is suspended in water and dissolved with enough hydrochloric acid to give a solution 0.25*M* in excess acid when made up to 300 to 800 ml. Beryllium solutions are digested on a hot plate for a few minutes and then filtered through Whatman No. 42 paper to remove traces of undissolved oxide. The paper is ignited in a platinum crucible. The residue is fumed with a few drops of sulfuric acid, dissolved in water, and added to the main solution.

One hundred milligrams of purified thorium nitrate tetrahydrate is added and dissolved. With continued stirring 3 g of oxalic acid, dissolved in 100 ml of hot water, is added. The solution is heated on a hot plate to near boiling and then cooled for about 1 hr.

The oxalates are filtered with vacuum on a medium-porosity fritted glass filter crucible. The crucible sides and precipitate are washed with 1 per cent oxalic acid. The crucible is placed in a 150-ml beaker, 15 ml of nitric acid and 1 ml of 70 per cent perchloric acid are added, and the beaker is heated on a hot plate until the precipitate dissolves. The crucible is washed and removed. The solution is then evaporated to near dryness, and the residue is taken up in 2 ml of nitric acid and about 5 ml of water. If the solution is not clear, the evaporation is repeated to near dryness after the addition of a few more drops of 70 per cent perchloric acid. When the solution is clear, it is diluted to about 100 ml.

The oxalates are reprecipitated by adding 1 g of oxalic acid in 30 ml of hot water. After filtration and destruction of the oxalates as before, the residue is taken up in 2 ml of nitric acid and diluted to about 50 ml.

To the solution is added 10 ml of glacial acetic acid, and the pH is adjusted with a meter to about 2.0 with ammonium hydroxide. The solution is cooled to room temperature, 3 g of 8-quinolinol (oxine) is added, and the pH is adjusted to 4.20. The mixture is transferred to a 250-ml separatory funnel and extracted with five 10-ml portions of oxine in chloroform, 10 g per 50 ml, and washed with two 25-ml portions of chloroform.

The aqueous solution is transferred to a 250-ml beaker, and 1 ml of lanthanum is added as a solution of the nitrate. A volume of ammonium hydroxide equivalent to 10 per cent of the solution volume is added, and the solution is heated until the precipitate flocculates. The hot

solution is filtered through Whatman No. 42 paper and ignited in platinum to the oxides for the spectrographic determination.

Procedure for Separations From Zirconium and Titanium.[258] A 5- to 10-g sample is suspended in water in a 150-ml Bakelite beaker and dissolved by adding 48 per cent hydrofluoric acid in small increments. About 5 ml of acid is added in excess. A solution of 200 mg of thorium nitrate hexahydrate in 10 ml of water is added rapidly with stirring to the sample solution. Three grams of ammonium fluoride is added and stirred until in solution. When the thorium precipitate becomes white and granular, the suspension is transferred with washing to a Lusteroid centrifuge tube and centrifuged at 2000 rpm for about 5 min. The supernatant liquid is discarded.

The precipitate is washed back into the original Bakelite beaker with about 10 ml of water. One gram of solid boric acid and 5 ml of nitric acid are added, and the mixture is stirred until the solids completely dissolve; if necessary, water is added to dissolve the excess boric acid. The solution is transferred to a 600-ml beaker and diluted to about 300 ml; then 1 g of oxalic acid dissolved in about 50 ml of hot water is added. The solution is heated to near boiling, cooled, and filtered. The oxalates are destroyed and the rest of the procedure is continued as for beryllium.

Procedure for Separations From Uranium.[258] A 5-g sample is dissolved in dilute nitric acid (1+1) and evaporated to dryness on a steam bath. The salt is dissolved in 40 ml of water, and the solution is transferred to a 150-ml Bakelite beaker. Five milliliters of 48 per cent hydrofluoric acid is added, and the procedure is continued as for zirconium.

(2) *Separation of Rare Earths With Yttrium and Ytterbium Carriers.* Another fluoride precipitation procedure [259] has been given for the determination of traces of rare earths in zirconium. It is based on solution of the sample with hydrofluoric acid, addition of yttrium and ytterbium, precipitation of the insoluble fluorides, and purification of the precipitate before spectrographic examination of the oxides.

A similar procedure is used to separate rare earths from beryllium [55] with added lanthanum as a carrier.

(3) *Separation of Rare Earths With Calcium and Magnesium Carriers.* Another fluoride procedure for the separation of rare earths from beryllium, uranium, zirconium, and titanium uses calcium [260] and magnesium fluorides to collect yttrium (used as a carrier) and the coprecipitated rare earth fluorides. With both calcium and magnesium fluorides precipitating, the recovery of the yttrium and rare earths is said to be virtually complete. For the analysis of beryllium, the addition of the yttrium carrier is unnecessary. The calcium, magnesium, and other non-rare-earth elements are subsequently removed from the rare-earth portion by a cation-exchange column (for uranium or beryllium samples) or by a cation-exchange plus anion-exchange resin (for titanium or zirconium samples). The yttrium and rare earths are finally precipitated as oxalates from the eluate and converted to the oxide.

(b) *Sulfide. Separation of Molybdenum, Platinum, and Palladium.* Separations are made for the determination of elements that form insoluble sulfides with cuprous sulfide as a carrier. This separation is employed for molybdenum [29, 236] in the range of 0.1 to 20 ppm, for platinum [261] down to 1 ppm, and for palladium [261] to 0.3 ppm. Germanium [262] in amounts down to 1 μg from 1 g of uranium has been precipitated as the sulfide with kieselguhr as a carrier, but the initial separation is made by distillation from 5*N* hydrochloric acid.

Procedure for Molybdenum in Thorium.[236] Two grams of thorium metal is dissolved in a 250-ml beaker with 40 ml of dilute hydrochloric acid (1+1). To assist in the solution of the sample, a few drops of a dilute (about 10% v/v) solution of hydrofluosilicic acid is added from time to time. During the process of heating the solution, 10 ml of nitric acid is added. The solution is then evaporated to low volume. Ten milliliters of nitric acid is again added, and the solution is evaporated nearly to dryness. The sample is redissolved in distilled water.

Two milliliters of sulfuric acid is added to the sample, which is then heated to decompose the nitrate and convert the sample to the sulfate. Thorium sulfate is soluble in cold 0.2*N* to 0.3*N* sulfuric acid. Two grams of thorium metal as a sulfate will dissolve in 200 ml of 0.2*N* to 0.3*N* sulfuric acid.

The pH is adjusted to 6 to 7 with ammonium hydroxide using pH paper. Some precipitation of thorium occurs, but this goes back into solution when the proper acidity is attained later. The volume of the solution is adjusted to approximately 250 ml by adding 12.5 ml of 6*N* sulfuric acid. The solution is now 0.3*N* with respect to sulfuric acid.

One milliliter of 1 per cent copper solution is added, and the sulfides of copper and molybdenum are precipitated in the cold solution by passing a gentle stream of hydrogen sulfide into it for 20 min. The sulfides are allowed to settle. The copper and molybdenum sulfides are filtered through a No. 42 Whatman filter paper. The filter is washed 10 times with 0.3*N* sulfuric acid. The filter is drained thoroughly, and the paper with the sulfides on it is transferred to a porcelain crucible. This is dried on a hot plate, transferred to a muffle furnace at 450°C, and ignited. Overnight ashing is convenient for this step. The oxides of copper and molybdenum are transferred to a $\frac{3}{32}$-in.-deep spectrographic electrode.

Four standards and a blank are prepared and put through the same process as the sample. The standards are prepared by adding molybdenum from a stock solution to molybdenum-free thorium.

(c) *As the Element.* (1) *Separation of Platinum-group Metals With Gold Carrier.* The platinum-group elements, ruthenium, rhodium, palladium, iridium, and platinum are separated from uranium solutions by gathering with gold.[232] Standard samples containing added amounts of the platinum metals are carried through the entire procedure to compensate for the incomplete precipitation of iridium by the zinc.

Procedure.[232] To prepare a gold solution, a 2.500-g sample of gold metal is dissolved in a solution made up of 3 ml of nitric acid, 18 ml of

hydrochloric acid, and 9 ml of water. This is evaporated to a paste on the steam bath. Ten milliliters of hydrochloric acid is added, and the solution is evaporated again. This is repeated three times. If the gold precipitates, a few crystals of chlorate are added to take it into solution again. Finally, an additional 10 ml of hydrochloric acid is added to the paste, and the solution is diluted to 250 ml in a volumetric flask. This solution contains 10 mg of gold per milliliter.

To a 3.75-g sample (as U_3O_8) are added 30 ml of dilute hydrochloric acid (1+1) and 2 ml of nitric acid. The beaker is covered and placed on a steam bath or hot plate until solution is complete; then the solution is evaporated to dryness. After cooling and washing the beaker with water, 5 to 7 ml of sulfuric acid and 15 mg of gold in solution are added. The solution is diluted to 125 ml, and enough 20-mesh metallic zinc (1 to 2 g) is added to completely reduce the gold to metal (solution turns green). The solution is allowed to stand several hours or overnight. The precipitate is filtered through a 9-cm No. 42 Whatman paper and washed well with hot 2 per cent hydrochloric acid. The residue is ignited at 500°C, and the product (gold plus platinum metals, except osmium) is spectrographically analyzed. The separation of iridium is not satisfactory because of the incomplete reduction of the element by zinc. For this reason it is necessary to run the standards in the same manner as the substance being analyzed.

(2) *Separation of Platinum-group Metals With Tellurium Carrier.* Tellurium has also been used as a gathering agent for determining platinum and gold in various materials.[242] Uranium is removed by a hydroxide precipitation in the presence of sodium bromate, and the platinum and gold are coprecipitated with tellurium, with stannous chloride as the reducing agent.

(d) *Hydroxide.* (1) *Separations From Carbonate or Alkaline Peroxide Solutions of Uranium.* Separations are commonly made from alkaline solutions of uranium containing carbonate or peroxide. This precipitate can be examined spectrographically for cobalt, indium, scandium, titanium, zirconium, and hafnium. The limit of determination for cobalt in this precipitation is 5 μg.[263]

(2) *Separations from Bicarbonate and Ammonium Hydroxide Solutions of Uranium With Iron Carrier.* For the determination of iridium, ferric iron has been used to carry the iridium from uranium solutions upon the addition of sodium bicarbonate and ammonia.[242]

(3) *Separation of Calcium From Uranium in Alkaline Solution.* Calcium [127] is separated from a uranium matrix prior to a flame photometric determination with the disodium salt of ethylenediaminetetraacetic acid (EDTA) in alkaline solution. Above a pH of about 8, calcium appears to be completely complexed, but the uranium, although it forms a complex with EDTA, precipitates as the diuranate when the equivalent of hydroxide added equals the sum of the EDTA and uranyl ion equivalents. In practice, the sample dissolved in hydrochloric or nitric acid is placed in a 15-ml centrifuge tube, and the

pH is adjusted to pH 9 to 10 with ammonium hydroxide. Three milliliters of EDTA (0.0250 g per milliliter) is added, and the solution is digested at 60°C for 30 min in a water bath. The tube is centrifuged; the solution is poured off, diluted to 25 ml, and measured on the flame photometer.

(4) *Separations of Hydroxide Group From Alkali Metals.* For the separation of impurities in the alkali metals, a combination of precipitations is used.[264] The sample is dissolved in water, and the initial impurity separation is made by filtration of the insoluble material and the hydroxides of cobalt, molybdenum, titanium, uranium, vanadium, and zirconium from the original solution. Since beryllium, chromium, iron, nickel, niobium, and managanese are appreciably soluble in the hydroxide solution, further separation is necessary. Iron, chromium, manganese, and nickel are precipitated by ammonium sulfide, and beryllium and niobium are recovered by precipitation with 8-quinolinol (oxine). The precipitates are combined and dissolved for analysis by the porous-cup method. Arc techniques on the ignited residue are employed if tantalum and tungsten are to be determined in the sample.[264]

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CHAPTER 13

MASS SPECTROMETRY

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Mass-spectrometric methods of analysis of essential reactor materials are principally concerned with the heavy elements uranium and plutonium and with the light elements hydrogen, lithium, and boron. These are the elements whose isotopic compositions are important in some phase of reactor operation. Although numerous other elements, such as aluminum and zirconium, are extensively used in reactors, analysis of their isotopic compositions has not been needed because, owing to their low capture cross sections, the changes in isotopic compositions are very small.

By far the most extensive mass-spectrometer effort, not only in connection with reactor materials but also in atomic energy research, has been on uranium. The general applications for uranium isotopic analyses are:

1. Isotopic analysis in separation plants.
2. Uranium-235 determination for a quantitative measure of fissionable-fuel content, e.g., in the make-up of fuel rods for correct loading and after fuel has been used in reactor, to determine fuel burn-up.[1, 2]
3. Total uranium determination by isotopic dilution technique using U^{233} as spike.[3, 4]
4. Uranium-236/uranium-235 analysis for breeding-gain studies.[5]

In the first three categories, routine analyses are performed at numerous Atomic Energy Commission (AEC) facilities.

Mass-spectrometric analysis of the hydrogen isotopes is performed routinely in several cases and is discussed in Chap. 9.

The analysis of gas mixtures with a mass spectrometer is carried out routinely in the case of the Argonne CP–5 reactor, where the helium gas surrounding the core is checked for nitrogen content to ascertain air inleakage. The use of the mass spectrometer in analyzing the composition of the gas stream in a uranium gaseous diffusion plant has been described.[6] This instrumentation has been highly developed for continuous monitoring of the process.

Some special analytical problems encountered in reactor operation and studies in which mass-spectrometric determinations have been involved are: (1) thorium impurity in uranium by isotopic dilution,

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(2) U^{235} contamination of fabricated fuel rods, (3) analysis of gases for hermetic sealing of fuel pins, and (4) analysis of gases in the Experimental Boiling Water Reactor (EBWR) water system.

Another general field in which the mass spectrometer is used is in the analysis of impurity elements in solids. This method was used for determining impurities in uranium in the Manhattan Engineering Project [7] during World War II. This job is now done entirely by emission-spectrographic methods. Hannay and Ahearn [8] have used the technique extensively in the field of semiconductor development. It is likely that the technique will find application in the future in analytical problems involving reactors.

Cameron has given [9] the historical development of the isotopic analysis of uranium from Nier's first measurement of the natural abundance of U^{235} up to, and including, the methods used in the Manhattan Engineering Project. This review was concerned with the UF_6-gas electron-bombardment methods and the analyses performed in connection with the Y–12 electromagnetic plant. This UF_6-gas electron-bombardment method is still used extensively in uranium diffusion plants and, to a small extent, in reactor technology. The improvements and innovations of this method are described.

Since World War II, a whole new area of mass-spectrometer isotopic analysis of uranium has mushroomed, namely, the technique of surface ionization of solid uranium samples. Reactor technology and research have been the prime reason for the development of this method. The extensive application of the method for uranium stimulated the use of the method for other elements; thus today there are about 70 elements that have been isotopically analyzed by surface ionization compared to only an isolated few research cases before World War II.

13–1 MASS SPECTROMETRY OF URANIUM HEXAFLUORIDE

By A. E. Cameron

In 1942 Prof. A. O. C. Nier and coworkers at the University of Minnesota developed and constructed a number of mass spectrometers specifically for the measurement of the isotopic composition of uranium. In the course of the next few years, these instruments were replicated with few changes in design. The techniques of measurement remained essentially the same.

The first extensive experimental application of these instruments was in the development of the gaseous-diffusion method of isotope separation and in the gas centrifuge studies. Since both these methods are characterized by relatively low stage separation and since

sample size was no limitation, it was natural that uranium hexafluoride be used in the mass spectrometer, particularly since that was the process gas and no pretreatment was required other than some distillative purification to separate it from fluorocarbons and hydrofluoric acid. High-speed pumping systems, vacuum locks, and the general technique of measuring isotopic composition by thermal production of ions had not been developed, and no time was available to pursue such investigations.

The electromagnetic-separation method produced a solid product and did not involve small separation factors. However it was quite natural to use a gaseous compound in the mass spectrometers. Use of a gas required the development of laboratory methods for the preparation and handling of relatively small amounts of uranium hexafluoride. The small differences in composition which were characteristic of the competitive processes employing gaseous UF_6 were not a limitation in the control of the electromagnetic process. A large number of measurements had to be made, however, to control isotopic composition at the intermediate recycle levels, and to make it possible to composite product batches to meet specifications of isotopic composition. As soon as the Y–12 electromagnetic plant began to produce early in 1944, it was necessary to analyze at two widely different levels of isotopic composition.

An immediate result of the analyses of these materials was the discovery of *memory** in the mass spectrometers; thus it became necessary to assign instruments to operate only within rather narrow ranges of concentration. Careful segregation of materials in sample preparation was necessary to avoid cross contamination. In addition, spent samples and residues from preparations had to be kept separate for recovery. The amount of material handled, particularly at the product level, was appreciable.

Fission counting was used as a back-up method together with alpha counting for verification of the U^{234} content and for a determination of gross uranium in materials of low uranium content, such as were found in salvage operations. The counting methods also permitted at least a rough measurement of the enrichment level of unknown material so that it could be correctly assigned to a mass spectrometer for a more precise determination.

Uranium-234, when a mass measurement was required, was analyzed on a mass spectrometer that happened to be giving sufficiently good resolution. There was no way to predict which instrument would be able to provide good resolution on any given day. The problem of re-

*Memory is defined as that fraction of the ion-beam intensity for a given sample which can be atributed to previous samples. The effect on the measurement of isotopic ratios depends on the relative isotopic concentrations and on the size of the samples.

solving U^{236} from an adjacent, large U^{235} peak did not exist at that time since no recycle uranium of reactor origin was being processed.

The discussion of measurements with uranium hexafluoride in Sections 13–1.1 to 13–1.3 of this chapter is heavily slanted to the type of measurement necessary to monitor fuel-element fabrication or recovery of uranium from spent reactor slugs. The problems encountered in the operation and monitoring of a gaseous diffusion plant from which one can withdraw a gaseous sample in a form ready to measure in a gas mass spectrometer are not discussed. Unless a fuel-recovery method is used in which the uranium is removed by fluorination, no ready-made sample of uranium hexafluoride is available for mass spectrometry.

13–1.1 Comparison of Isotopic Analysis by Electron Bombardment of Uranium Hexafluoride Gas and Surface Ionization of Solid Samples

The reader is referred to Sec. 13.2 of this chapter for a detailed discussion of the techniques of measurement by thermal emission of ions from solid samples.

A comparison of the surface-ionization method with the uranium hexafluoride gas electron-bombardment method is given in Table 13.1. The uranium hexafluoride gas method is used when a high relative precision between two samples is required. Where one of the samples is a known standard, such as normal uranium, an unknown sample can be measured to within ± 0.01 per cent of the known, hence, the usefulness of this method where extremely small differences in isotopic distribution occur, as in a gaseous diffusion plant. This method is also of value in the analysis of fuel rods from a normal-uranium reactor and in cases where the amount of U^{235} burned up is small.

One of the chief advantages of the surface-ionization method is the small sample size, which may range from 10^{-8} to 10^{-4} g, depending

Table 13.1—COMPARISON OF ISOTOPIC ANALYSIS OF URANIUM BY SURFACE IONIZATION OF SOLID SAMPLES AND ELECTRON BOMBARDMENT OF UF_6 GAS

	Surface ionization	*Electron bombardment*
Sample size	10^{-8} to 10^{-4} g	10^{-1} g
Sample form	Nitrate, oxide, metal	UF_6
Precision	± 0.25 to $\pm 1.0\%$	± 0.01 to $\pm 0.1\%$
Memory	Less than 0.01%	1 to 10%
Sample introduction	Samples inserted one at a time with loss of vacuum by opening instrument or, using vacuum lock, with no loss of vacuum	Standard gas introduction with no disturbance of vacuum
Purity	Can be analyzed with up to 20 × other metals present	High-purity UF_6

somewhat upon the type of ion-beam detection used, compared to that required for the uranium hexafluoride method, which may range from a minimum of 20 mg to, preferably, more than 50 mg. Decontamination of this latter amount of material from a dissolver solution is likely to be expensive and time consuming and to greatly increase the chance of cross contamination in the high-radioactive level cell work required. With the very small samples required for surface ionization, radioactive decontamination need not be so complete since, in general, minor impurities do not interfere seriously with the isotopic measurement.

Another important advantage of the surface-ionization technique is the essential lack of memory compared to the serious memory problem encountered with the uranium hexafluoride technique. One machine can analyze samples covering the entire range of isotopic abundance in any order; this is virtually impossible with the uranium hexafluoride gas method. Another advantage is that sample preparation is generally easier since the uranium to be analyzed in many cases is available as metal, oxide, or a salt, and it is a simple matter to produce uranyl nitrate solution in all these cases compared to producing uranium hexafluoride from these forms.

Measurements on thermal ions have been made either on the UO_2^+ ion or on the U^+ ion. The technique used determines which ion is more abundant. For the gas measurements it has been customary to use the UF_5^+ ion since this is the most abundant of the series of ions formed by successive removals of fluorine from the uranium hexafluoride molecule. Resolution is thus slightly favored by the surface-ionization method since the ion masses are lower than the 330 and 333 used in the gas measurement.

With the surface-ionization method, a new filament assembly must be installed for each sample. This, in turn, requires breaking the vacuum and pumping down for each measurement. With a suitable vacuum-lock arrangement, however, it might be possible to approach the same speed of measurement with surface-ionization sources as with gas measurement. The convenience of small sample size is paid for by a decrease in precision of measurement, which probably must be accepted in the case of highly radioactive material. This is certainly true for the measurement of transuranic materials or for other highly active alpha emitters like U^{233} where the hazard of handling milligram quantities of a volatile compound is too great to be considered for normal purposes.

(a) *Precision of Measurement.* The surface-ionization method is less precise than the gas-measurement method because with the former the conditions of ionization are not the same between successive samples. The introduction of a new surface-ionization filament causes

changes in geometry in a very critical region of the source. These changes in geometry can change the mass discrimination in source transmission. Also it is difficult to reproduce the conditions on the surface that affect the complex process of surface ionization. Experience has shown that improvements in precision of measurement are, in general, attained by improvements in the mechanical alignment and reproducibility of positioning of the filament. The difference in precision between the two methods may be as much as two orders of magnitude. Surface-ionization measurements are generally good only to about 1 per cent of the ratio in precision, with a minimum, under the best conditions, of 0.1 to 0.25 per cent.

Gas measurements in which comparisons are made between a standard material and an unknown separated by only a small difference in isotopic composition can give precisions on the order of 0.01 per cent of the value at the 95 per cent confidence level. In practice the limitations are imposed by the speed with which comparisons can be made and by the memory effect where the difference between sample and standard is appreciable. The limitations upon absolute accuracy are set by the limits within which standards can be prepared from separated isotopes of high purity.

A detailed discussion of the preparation of standards and of their application in uranium hexafluoride mass spectrometry is given in an Atomic Energy Commission book entitled *Selected Measurement Methods for Plutonium and Uranium in the Nuclear-fuel Cycle.*[10]

(b) *Speed of Measurement.* It is possible to make 16 determinations in 8 hr with a surface-ionization instrument equipped with a vacuum lock. This generally requires a two-man team, e.g., it is advantageous to have a technician load the filaments while the operator is running the instrument. The filament assemblies may require prebaking, particularly if very small samples are being run. The advantage of the gas method is apparent when one considers that one analyst can make 40 or more determinations of the U^{235}/U^{238} ratio in an 8-hr shift, including attaching samples and calculating results. If, however, the time required to prepare the uranium hexafluoride samples is considered and if a complete isotopic determination is being made, rather than simply the U^{235}/U^{238} ratio, the two methods are probably fairly comparable in the time required for a single determination. An additional 0.5 man-hour is needed for the uranium hexafluoride preparation from oxide; however, this time will vary, depending somewhat upon the number of samples being prepared per day. No account is taken of the extra time required to decontaminate the larger sample needed for the gaseous method, when a radioactive solution is being measured.

(c) *Memory.* Mass-spectrometer memory is the phenomenon that causes the reading obtained upon a given sample to be more or less biased toward the reading for the previous sample or group of samples. The measurement of sample "B" following the measurement of sample "A" is so influenced by memory that the "A"–"B" observed is less than the difference between the two isotopic compositions. In the uranium hexafluoride mass spectrometer, memory occurs both in the sample-handling system and in the ion source itself.

Uranium hexafluoride is a vigorous fluorinating agent. It will deposit on a clean metal surface a layer of uranium tetrafluoride or other fluorine-containing uranium compound until the surface has become "conditioned." When this conditioned surface is exposed to uranium hexafluoride of another isotopic composition, an isotopic exchange takes place between vapor and solid phases. The exchange appears qualitatively to take place in two steps: An initial exchange, which appears to occur fairly rapidly, followed by a much slower exchange with what is postulated to be underlying solid.

The effect of memory in the sample system, if it is constructed from proper materials and if the surface that is in contact with the hexafluoride is minimized, can be made a minor part of the overall effect. The amount of uranium to which the surface is exposed is comparatively large because of the relatively high pressure behind the gas "leak" through which sample is admitted to the ionization region. The effect of the exchange on the bulk isotopic composition is thus comparatively small. This is not true of memory which occurs beyond the gas leak in the entrance to the ionization region and in the source itself where the amount of gas is small compared to the exposed surface and where the uranium hexafluoride has been deposited as a result of ionization.

In spite of much thought and experimentation, there has not been much success in eliminating memory. The best which can be hoped for is that its effect upon the measurement can be kept small and fairly reproducible so that it can be accounted for. To this end, the volume of sample handling systems is kept small, and nickel, monel, and copper are used as materials of construction. Although the fluorine plastics, Teflon and Fluorothene, are inert to uranium hexafluoride, they do show a tendency to dissolve this gas; therefore nickel tubing is preferred. Fluorothene or Teflon, however, are frequently used for gaskets and valve seats.

The surface-ionization method can be made relatively free of the effects of memory if fresh filament mounts are used for each sample and if the plates in the region surrounding the filament are cleaned periodically, e.g., every 50 to 100 samples or more frequently if suc-

cessive samples of widely different abundances are run. Very small amounts of contamination can occur because of (1) re-evaporation as a result of arcing in the source, (2) loose dust-size particles falling onto the sample, and (3) re-evaporation of uranium from deposits on plates adjacent to the surface-ionization filament. Memory should always be suspected and checked by measurements with standard materials.

13–1.2 Gas Mass Spectrometers for Uranium Hexafluoride

The instruments used for hexafluoride measurements have largely been of the small-radius type, in contrast to the 12-in.-radius instruments that are customarily employed in surface-ionization measurements. The reason for this is largely historical. The original instruments for laboratories engaged in this type of measurement had a 6-in. radius and 60° deflection. The equipment was built by the General Electric Company during the war.[9] These instruments, in use both at the Oak Ridge Gaseous Diffusion Plant (ORGDP) and at the Y–12 Plant, have gone through numerous modifications of tube type, electronic components, and sample systems. The Union Carbide Nuclear Company at Paducah, Ky., was supplied with 5-in.-radius 180°-deflection spectrometers by the Consolidated Electrodynamics Corp. These instruments were a modification of the type of equipment they had developed for general use in the chemical industry. The Goodyear Atomic Corporation, Portsmouth, Ohio, was supplied with 6-in.-radius 60°-deflection instruments by the General Electric Company. The small radius of these instruments leaves something to be desired in resolution at masses 330 and 333, the masses of the UF_5 ions containing the principal uranium isotopes. Except perhaps for the determination of minor isotopes, the resolution is adequate for routine control purposes.

The laboratory at the ORGDP has built and operated routinely a pair of 12-in.-radius 60°-deflection mass spectrometers for uranium hexafluoride work. These instruments use permanent magnets and are therefore limited in the mass range that can be covered. The vacuum requirements become more stringent in this type of tube because of the greatly increased ion path, and the gain in effective resolution over the smaller radius instrument is not great.

(a) *Tubes and Envelopes.* In both the 6-in., 60° and 5-in., 180° instruments, the analyzer tube serves both as a vacuum container and as the mechanical support for positioning the source and receivers. In the original instruments of the 60°-sector type, the tube carcasses were made of 1-in.-diameter copper tubing. The vacuum envelopes on the source and receiver ends were of glass and were attached to the copper analyzer section by means of Kovar-to-glass

graded seals. The mechanical properties of the copper tubing, which had to be bent and flattened to pass within the magnet pole gap, left something to be desired. Some improvement was made by using 1.25-in.-diameter copper tubing, but more rigidity was secured by going to stainless-steel or Inconel tubes.

Stainless-steel tubes introduced a further complication in that, unless the alloys were carefully chosen, the surface exposed to the ion beam was likely to build up charges on nonconducting patches which would cause "fuzzing" of the ion beam and loss of resolution. This effect does not occur in the Consolidated Electrodynamics instruments because of the alloy used and, possibly, because there is no pinched-gap and surfaces are farther from the ion beam. It is eliminated in the other instruments by cleaning that involves electrostripping or, more permanently, by gold-plating the interior surfaces of the tube.

With metal envelopes there is less danger of breakage from thermal shock or from careless handling. They are not, however, as readily pumped down to the desired pressure. All-metal tubes of a type developed in the Oak Ridge National Laboratory for solids-analysis instruments are now being used in the Y–12 uranium laboratory for hexafluoride measurements. In these tubes the difficulties of bending and flattening stainless-steel tubing have been overcome by machine fabrication of the midsection of the tube. The end result of this technique is an analyzer that is uniform in cross section and has greater rigidity than the older tubes.

The general method of construction is shown in Fig. 13.1. A ring of nonmagnetic stainless steel of the appropriate radius, 6 or 12 in., is prepared with the cross section shown in Fig. 13.1. It is desirable to leave the sidewalls of this U-shaped ring somewhat heavier to minimize distortion during the machining operation. Frequent normalizing is required during machining in any case. A ring of stainless-steel sheet is cut and laid inside the prepared ring; it rests on the slight lip shown. The sheet is then fusion welded into place with a shielded arc without the addition of any metal. A ring of uniform rectangular cross section is thus prepared. From this are cut sections of the desired angle. These are welded to adaptor rings, which, in turn, join to sections of 2-in.-diameter stainless-steel tube which provide the supports for source and receiver mountings. The source and receiver cans may also be made of stainless steel with Teflon gaskets or metal gaskets, if baking to higher temperatures is required. The electrical leads may be hard-soldered or soft-soldered in place. The latter method of attachment limits the temperature to which the envelopes can be heated for outgassing.

690–457 O—64——64

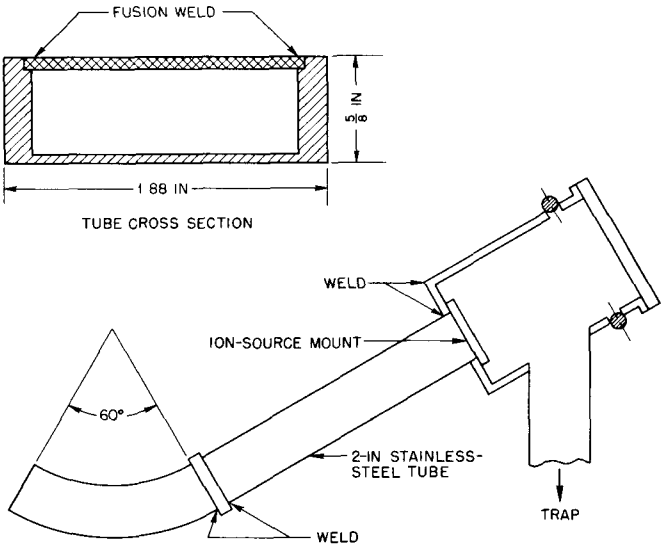


Fig. 13.1—Stainless-steel spectrometer tube.

Some means must be provided for ready access to the ion-source envelope so that sources can be removed for cleaning. In metal envelopes the closure flanges may be sealed with metal gaskets (aluminum or gold) or with O-ring gaskets of various materials. Teflon and Viton-A have generally been preferred to various neoprene compositions because of lower outgassing. The ORGDP glass envelopes were fabricated with a flange that was ground flat and to which a metal closure plate was attached with black wax (Apiezon-W). The Y–12 laboratory used a large standard-taper male joint (71/60); the female cap was either black waxed or greased with Apiezon-N. This cap has been replaced with a standard fruit-jar lid of the self-sealing type (Kerr-Mason, $2^{11}/_{16}$ in. diameter), which is simply laid on the end of the male standard-taper joint. The white-rubber sealing compound used flows under pressure to make a vacuum seal and apparently does not outgas sufficiently to give trouble. These jar lids are used only once.

(b) *Vacuum Systems.* Pressures on the order of 10^{-7} mm mercury or lower are desirable in instruments using uranium hexafluoride. Mercury pumps have been used in preference to oil pumps to avoid any difficulty that might arise from the spectra of the organic pump fluids should any inadvertently get back into the tube through the cold trap. The cleanliness requirements are more stringent in an instrument in which ionization is by electron bombardment than they are for surface-ionization instruments.

Liquid-nitrogen refrigeration is required on the traps for the required level of pressure. The connections from the source region to the trap and the trap itself are made to have conductance as high as is possible consistent with physical-size limitations. Glass mercury pumps are generally used; so the trap and connecting lines are also fabricated from this material. Large ball joints, assembled with a film of Apiezon-W, provide a convenient means of securing a strain-free alignment and assembly.

Various laboratories have experimented with the getter type of ion pump now available, such as the Vac Ion pump supplied by Varian Associates. These pumps do not use refrigerated traps and are apparently satisfactory on clean vacuum systems where the pumping load is not high and where clean gases, other than inert gases, are to be pumped. Water vapor is reported to be undesirable and to cause this type of pumping device to operate poorly. It would probably be desirable to isolate the pump when the spectrometer is let up to atmospheric pressure. One would then rough down with a mechanical pump before opening the Vac Ion to the system. The ORGDP laboratory reports that for uranium hexafluoride work a single 5 liter/sec pump is hardly adequate for the pumping load on a 6-in.-radius spectrometer. A second pump is required or one with larger capacity.

(c) *Sample-handling Systems.* The systems that introduce gaseous uranium hexafluoride to the mass spectrometer must be constructed of materials that are as resistant to chemical attack as possible. Nickel, Monel, and copper are generally used. The volume and therefore the surfaces in contact with the sample should be minimized to reduce the size of sample required and to minimize the effect of memory.

Bellows-sealed valves in small sizes are available from several suppliers. The seals between the bellows and the valve body are made with thin Teflon gaskets, and the seal in the closed position is a Teflon-to-metal combination. The Hoke valve uses an Inconel diaphragm and is a needle valve with a metal-to-metal seal in the closed position. The conductance of these valves in the open position is not as high as that of other valves. They are more useful for throttling. They do offer the advantage of minimum interior volume. A series 1384 Hoke valve is available with a $\frac{3}{16}$-in. port and removable diaphragm.

Samples are attached to the sample manifold by copper flare fittings, by metal standard-taper joints (Hoke), or even by plastic tubing, depending to a large extent upon the source of the uranium hexafluoride and the type of container from which it is supplied to the spectrometer. If the sample container is glass, then a metal-to-glass seal may be required.

(d) *Controllable Gas Leaks.* Some means of controlling the amount of sample gas admitted to the spectrometer is required. In order for a mass spectrometer to give rigorously valid analytical results either in the analysis of a mixture or in the measurement of absolute isotope ratios, the leak should be molecular in character, since only such a leak will give a pressure in the ion source which is proportional to the partial pressure of a certain component in the sample bottle and independent of the partial pressure of other components. Such a leak, however, will cause the lighter components in a mixture to be pumped out more rapidly than the heavier ones so that the measured isotope ratio changes during the course of a ratio measurement, which makes the measurement very awkward to perform.

The essential difference between viscous and molecular leaks as far as the analytical results are concerned is that in the viscous leak all components in the sample bottle are depleted at an equal rate, whereas in the molecular leak each component of the sample flows out of the sample bottle at a rate which depends only on the properties of the component itself. In uranium hexafluoride measurements it has been customary to use viscous or nonfractionating leaks. This is in contrast to other gas measurements, where molecular leaks are used.

It is possible in principle to devise a leak in which the flow from the sample bottle into the ion source is viscous throughout, but in practice it is both difficult and unnecessary. It is necessary only to ensure that if fractionation does occur the line between the point where fractionation occurs and the sample bottle will be so dimensioned with respect to the pressure, flow rate, etc., that the fractionated sample, at the point where molecular flow occurs, cannot communicate with the sample bottle by back diffusion. If this criterion is satisfied, then it truly makes no difference whether the character of the flow at the point where the flow impedance is a maximum is viscous, molecular, or mixed. The various components flow out of the sample bottle at uniform rates and changes in the chemical composition or isotope ratio of the sample with time do not occur.

In the case of uranium hexafluoride, very little gas leaves the ion source if the efficiency of the source is high. It is much more likely to be deposited as a solid, either as a result of ionization or as a consequence of reaction with, or sorption on, metallic surfaces. Thus, although its effect is not too serious in the case of relative measurements, fractionation in the leak is to be avoided.

The leaks must be built of material that is as resistant as possible to chemical attack to prevent changing flow properties or plugging. A hairpin of flattened nickel tubing [12] which is wound into a loose

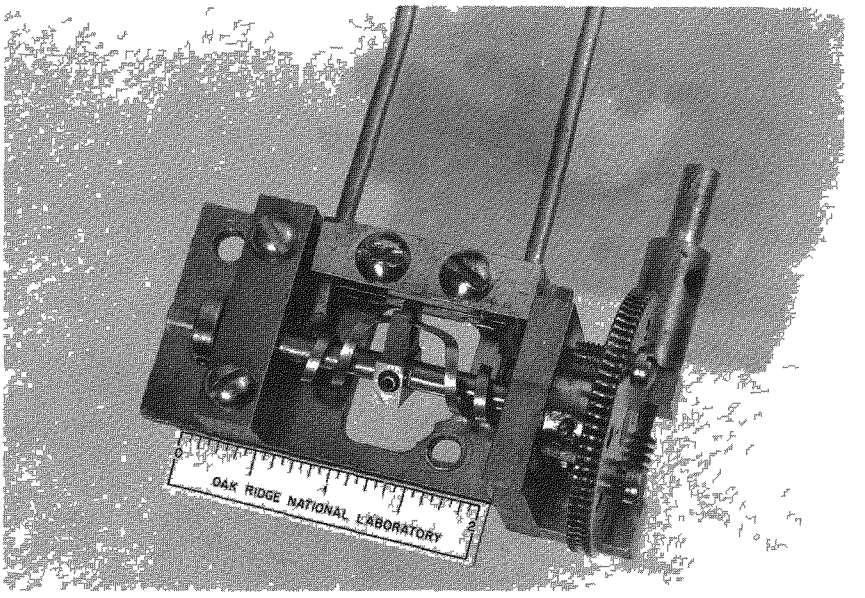


Fig 13 2—Controllable gas leak

helix and which can be mechanically changed in radius by wrapping it around a spindle is shown in Fig. 13.2. A second type is made from one of the Hoke needle valves by adapting a very slow mechanical drive to position the needle.[13] A wedge of low angle which drives the valve stem and a double-thread drive with slightly differing pitch for the two threads are both used.

Flow through this latter type of leak is largely molecular. The gaseous diffusion plants are now using variations of the HP sample-system valves (type HP valves have replaceable bellows sealed with a flat Teflon gasket) in which a Teflon-tipped flat plunger is driven by an air motor against a flat metal seat. The normal valve opening is reduced in diameter by a metal plug with a small metering port. The air drive makes automatic leak operation easily possible. Gas flow occurs between two flat surfaces in close contact.

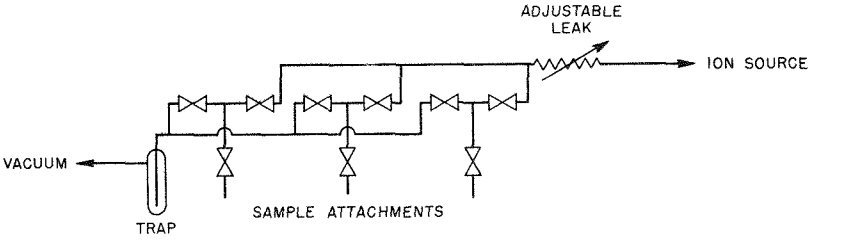


Fig. 13.3—Schematic diagram of a sample-introduction system

Figure 13.3 is a schematic diagram of a typical sample system with provision for the attachment of three samples. In arrangements where operation is carried on by comparison to a standard or to two standards, more connections may be desirable. The valves can be either manually operated or pneumatically operated by remote control to permit more rapid changing between standard and sample.

(e) *Ion Sources.* The ion sources for work with uranium hexafluoride must be built so that they can be disassembled for cleaning. Various arrangements are used. Probably the simplest of these uses studs, with sleeve insulators and spacer insulators. Such construction is generally useful to 5 to 8 kv. Above this potential, arcing and breakdown may occur; thus more specialized structures would be required. Except in large-radius instruments, such potentials are not common.

Ion-source materials must be nonmagnetic. When the source is not immersed in the magnetic field, as is the case in the 60°-sector instrument, an auxiliary source magnet must be used to maintain collimation of the ionizing electron beam. The auxiliary magnet is usually a pair of poles of permanent-magnet material with a soft-iron yoke adapted for proper positioning. Electromagnets have been used, but they offer no particular advantage. A field of 100 to 150 gauss in the source region serves to collimate and focus the electron beam.

The source elements are usually made of nonmagnetic stainless steel, Nichrome V, or copper. The latter material is not as convenient as the others because it cannot be spotwelded. One general arrangement of the ionization region and the ion lenses is shown in Fig. 13.4. The filament is usually a ribbon of tungsten. In one popular structure used in the ORGDP laboratory the electron trap is also a metallic ribbon which is heated. The heating of the trap serves to keep it free from deposits that might lead to erratic positioning of the electron beam and also appears to reduce memory somewhat.

Filament temperature is controlled through an automatic circuit that controls the emission by measuring the total current to trap, case, and filament shield. The electron-trap current is maximized by adjustment of the source magnet. It may typically run about 1/10 of the total emission current, or on the order of 0.5 ma. The ORGDP source uses a sharply bent point on a tungsten wire for electron emission, and 200-μa trap current is secured with less than 5 μa to other elements in the source. The electron energy used is approximately 75 volts. There is no particular advantage in making this voltage adjustable.

Bentley, Hamer, and Evans[14] have described an ion source that offers advantages over the conventional Nier source with the ion box

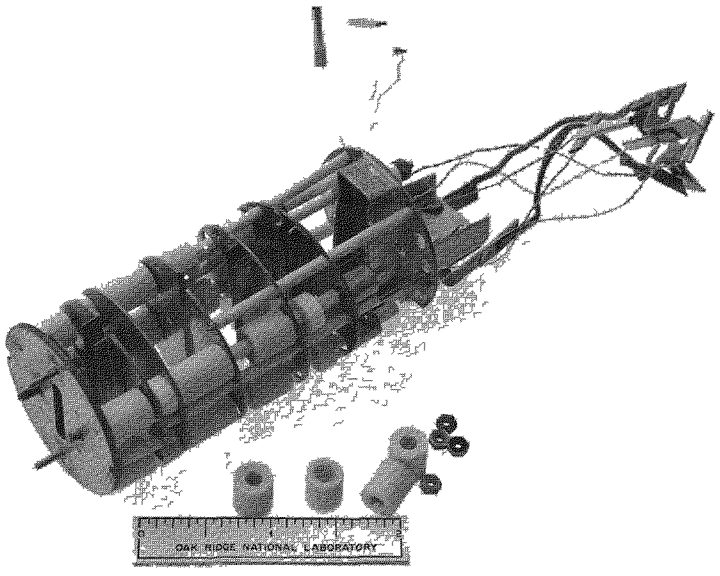


Fig. 13.4—Uranium hexafluoride ion-source structure.

where corrosive gases, such as hydrogen fluoride, chlorine trifluoride, etc., are to be analyzed. The sample is introduced as a molecular beam, and the sides of the structure are open. With this arrangement the pumping speed is very high for the removal of sample gas. Metal surfaces in contact with the sample gases are minimized, and a four-fold increase in life over that displayed by the standard Nier box is claimed. It is reported that there are about 4 collisons of gas with heated surfaces, compared to about 100 for the conventional structure.

(f) *Electronics.* The electronic requirements of the uranium hexafluoride spectrometer are essentially those of a normal gas mass spectrometer. They will differ from those of a solids instrument in that an emission regulator is substituted for the filament-heating controls.

Stability of both accelerating voltage and magnet supply is critical. Regulation to 1 part in 20,000 is desirable. When a scanning method is used, long-term stability is not nearly so critical as short-term stability. Some slow drifts can be tolerated. When ratio recording is used, a peak positioner driven from the low-current amplifier will adjust the accelerating voltage to compensate for drifts in magnet or high-voltage supplies.

The general electronic requirements are indicated in the block diagram of Fig. 13.5. Some simplification is attained if a permanent magnet is used. A permanent magnet, however, limits the instru-

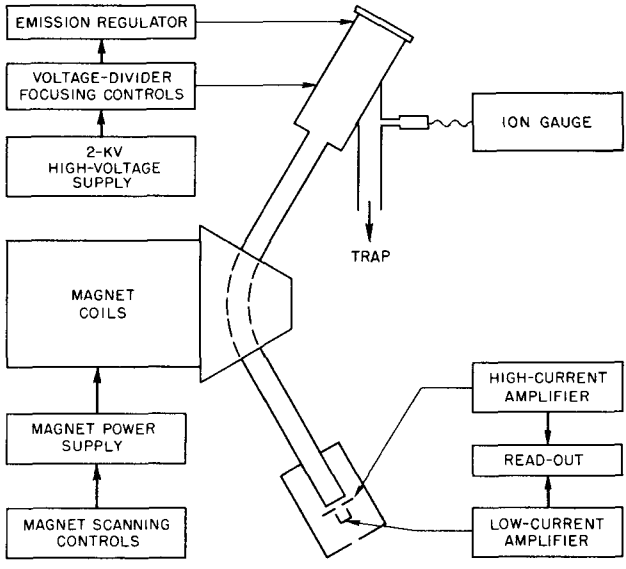


Fig. 13.5—Uranium hexafluoride mass-spectrometer block diagram.

ment to a narrow and essentially predetermined mass region. Shunting of the magnet will alleviate this restriction. Scanning of the ion beams must be done by changing the accelerating voltage. Such a change necessitates a voltage correction because the intensity of the ion beam is a function of the source voltages. If the data are taken without scanning, i.e., by simultaneous collection of the ion beams and measurement of a ratio, this effect is eliminated.

(g) *Read-out Methods.* Three principal read-out methods have been used in hexafluoride measurements: (1) vibrating-reed and strip-chart recorder, (2) galvanometer and precision potentiometer, and (3) ratio recorder or printer.

The ion content (measured in amp) of the major isotopic peak may be as high as 1×10^{-9} amp so that an adequate signal can be secured from minor isotopes. If only a 235/238 ratio is required, such a high level of signal may not be needed.

(1) *Vibrating Reed and Strip-chart Recorder.* In the first method measurements are made with a vibrating reed electrometer and its associated equipment and a strip-chart recorder. The spectrum is caused to scan across the receiver slit, which may be conveniently set for a 25 to 35 per cent "drop through." That is, the major isotopic peak when centered upon the receiver slit will be reduced in total intensity by 25 to 35 per cent. This method assumes that there is a means of reading the current from the slit plate. Automatic magnetic-field alteration can be attained electronically by a condenser–

resistor arrangement in the control-tube circuit or by a motor-driven potentiometer. It is desirable that it be possible to make the scan repetitively and in both directions.

The scale of the amplifier can be adjusted to keep the peaks on the chart and to ensure maximum-sensitivity measurements. This measurement system is adapted to the determination of all the isotopes in the sample. Lack of perfect resolution requires that a correction be made. This can be done by graphically extending the "toe" of the large peak under the smaller one and subtracting what appears to be the contribution made to the smaller peak by the scatter from the big one. With the small-radius instruments, the resolution between the 329 and 330 peaks ($U^{234}F_5^{19}$ and $U^{235}F_5^{19}$) may be only 15 per cent, as measured by the height of the valley between the two peaks above recording-system zero (no signal) and referred to the $U^{234}F^{19}$ peak.

An appropriate number of repetitive scans should be taken with a well-stabilized ion-beam intensity. The net peak heights are measured from the chart and multiplied by the appropriate scale factors; then the composition is calculated.

(2) *Galvanometer and Precision Potentiometer.* In the second method a galvanometer, lamp, and scale arrangement is connected in the output of a d-c amplifier of suitable characteristics. A precision potentiometer is connected between the ground end of the input resistor to the amplifier and ground. Thus precisely measurable voltages can be introduced at this point until the galvanometer indicates that the input signal has been "nulled." When this happens the voltage across the potentiometer equals precisely the voltage developed in the high resistance by the ion current. Nonlinearities in the amplifier and indicating system are eliminated by this arrangement. It is convenient to use decade potentiometers and to use more than one set operated in parallel from the same potential source. Ratios are thus conveniently measured by causing the switch, which selects the magnet current to bring a given peak on to the receiver slit, to select the potentiometer which is introduced into the circuit. One can then go rapidly between a pair of ion peaks, taking a galvanometer zero while the magnet field changes, and have the proper buck-out voltage introduced. In general, it is not necessary to take the time for a precise buck-out of the signal; instead the net galvanometer deflection can be converted to potentiometer readings by means of an interpolation factor that gives galvanometer deflection in terms of potentiometer readings. This factor is determined experimentally at the end of a data series.

(3) *Direct Ratio Determination.* This method is not readily adaptable to the determination of all the isotopes. Its principal application is to the measurement of the U^{235}/U^{238} ratio. A block diagram of

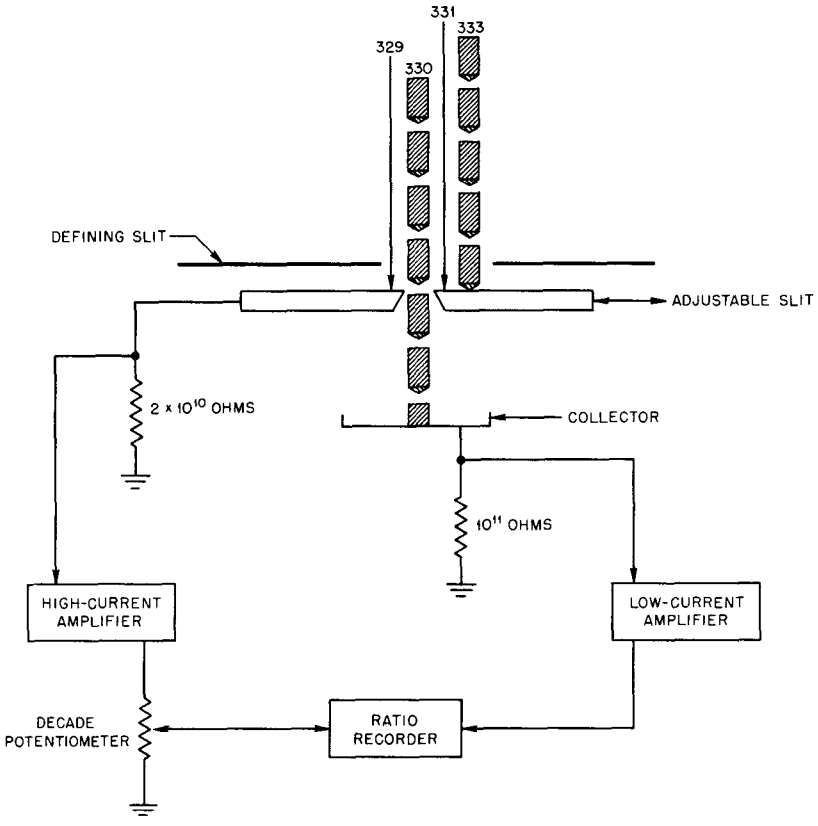


Fig. 13.6—Ratio recording system.

the system is given in Fig. 13.6. The receiver, with adjustable slit, is so dimensioned that the ion peak being observed passes through the slit to the low-current collector and amplifier. The other isotopic peaks all fall on the slit plate, and the total current from them is indicated by the high-current amplifier. A portion of the output of the high-current amplifier is taken from a precision voltage divider and used to buck the entire output of the low-current amplifier. The balance of this system can be indicated by a galvanometer or other sensitive indicating device or final significant figures in the ratio can be taken from the chart of a ratio recorder.[15] In more recent modification of this equipment at the ORGDP, a digital voltmeter has been used to display the ratio directly to the required number of significant figures [16] and to print it on a tape. The method is best operated by repetitive introductions of a standard and an unknown. Each introduction results in the measurement of one ratio.

To determine the minor isotopes by this method, as would be required in reactor-fuel analysis, it would be necessary to make three ratio measurements upon each introduction of material, obtaining the ratio of $U^{234}/U^{235}+U^{236}+U^{238}$; $U^{236}/U^{235}+U^{234}+U^{238}$; and $U^{238}/U^{235}+U^{234}+U^{236}$ in the case of highly enriched material. Where the concentration of the minor isotopes is known and constant, as is the case in gaseous diffusion plant product, only the one ratio measurement is required for the evaluation of the sample. Measurement of the minor isotopes will generally require that the resolution be improved somewhat by narrowing the receiver slit.

Ratios are not absolute even though the drop-through is greater than 95 per cent. Comparison to a standard under identical conditions of focus, slit width, etc., is mandatory.

13–1.3 Sample Preparation

Two methods have been used routinely for the preparation of small amounts of uranium hexafluoride for mass-spectrometer use. The one that has perhaps been used on the largest number of samples involves cobalt trifluoride (CoF_3) as fluorinating agent. It avoids the necessity of having a fluorine generator or of handling fluorine in elemental form in low-pressure cylinders. In most laboratories, apart from those associated with the large-scale production of uranium hexafluoride, elemental fluorine is not readily available. Cobalt trifluoride is, however, readily available from commercial suppliers in 5-lb cans. It should be free of uranium. (Baker and Adamson quality, General Chemical Division, Allied Chemical Company, Code 1589.)

The glass systems in which uranium hexafluoride samples originally were routinely prepared have been described.[11] The apparatus has been greatly simplified in recent years, and the necessity for glass blowing has been almost entirely eliminated. The procedure described briefly here is that used in the Y–12 laboratory. It is preferable that the uranium be precipitated by ammonium hydroxide in the presence of filter-paper pulp because the U_3O_8 formed by subsequent ignition tends to be less dense and is friable. Approximately 200 mg of this oxide is placed in a 12-mm test tube that has been flamed to drive off moisture and allowed to cool. The oxide is crushed with a 6- to 8-mm stirring rod and mixed intimately with 2 g of CoF_3.

The mixture is then transferred to the 12-mm portion of the sample-preparation tube shown in Fig. 13.7. It is contained loosely between two wads of Fiberfrax ceramic fiber. The 12-mm tube is placed in a small tube furnace and attached to a vacuum manifold with a short section of Tygon tubing. The system is evacuated to an indicated pressure of 100 μ or less. A diffusion pump may be used, if desired,

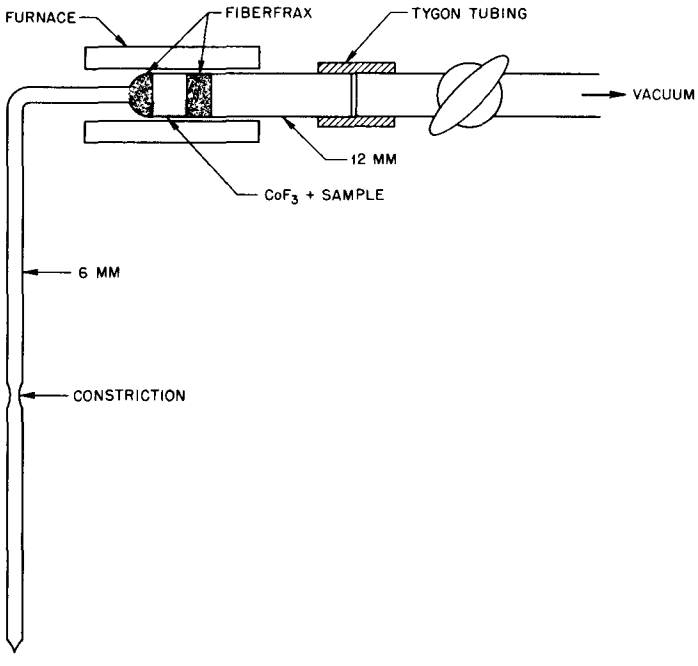


Fig. 13.7—Sample-preparation system used at Y-12.

but a mechanical pump with a liquid-nitrogen trap is adequate. The glass collection system is repeatedly flamed to drive off absorbed moisture while the furnace around the portion of the reaction vessel containing the uranium oxide and cobalt trifluoride is gradually raised in temperature to outgas the powder. The temperature is held at 100°C for 10 min, at 200°C for 10 min, and at 300°C for 20 min. The valve to the vacuum system is closed, liquid nitrogen is placed about the collection tube, and the furnace temperature is raised to 400°C. After a few minutes at this temperature, the valve is opened briefly and noncondensable gases are pumped out. The temperature is finally raised to 500°C and maintained for about 20 min. Uranium hexafluoride crystal formation will be observed above the surface of the liquid nitrogen.

When the reaction appears to be complete, the vacuum valve is opened again briefly and then closed; then the liquid nitrogen is replaced with a dry-ice slush. The valve is again opened, and the system is pumped until the pressure is below 100 μ. The sample-containing tube is then sealed off at the constriction.

The tube is attached to the mass-spectrometer sample manifold with a piece of Tygon tubing. The space between the tip of the tube and the sample manifold is evacuated, the sample is cooled in dry-ice

slush, and the tip is broken by pressing with the fingers through the Tygon tubing. It may be desirable, if the sample appears to be gassy, to warm the sample and then refreeze it with dry-ice slush and repump or to flash off some of the sample at ice-water temperature before admitting it to the spectrometer. During spectrometer operation the sample is usually immersed in a Dewar flask of cool water to prevent changes in room temperature from affecting the ion-beam intensity by changing the vapor pressure of the uranium hexafluoride sample.

The furnace arrangement used in the Y–12 laboratory consists of a series of sections of stainless-steel tubing of appropriate diameter and length which are series connected with heavy copper bus bar. The low-voltage current from a welding transformer capable of delivering 500 amp at 5 volts heats the entire assembly. An automatic temperature control makes programming of the operation possible.

The direct-fluorination procedure is described by Greene and Petit,[17] and the reader is referred to their work for details that are of extreme importance. Briefly, however, the procedure is to place 1.3 g of U_3O_8, to which has been added 1 mg of KCl as a reaction promoter, in a tubular copper reactor attached through a flare fitting to a diaphragm-sealed Monel angle valve. The copper reactor tube is silver-soldered or welded shut at the bottom. Pressures in excess of 70 atm are attained in the reactor.

The sample and reactor are evacuated, and a measured quantity of fluorine is condensed into the tube by cooling with liquid nitrogen. The amount of fluorine is twice that required by stoichiometry and will give a pressure at room temperature of 750 to 1000 lb. The reactor valve is closed, and the liquid nitrogen is removed. The reactor should be in an explosion shield in a hood. The reaction will occur spontaneously as the temperature approaches ambient and will be indicated by a rise in temperature measured by a thermocouple strapped to the reactor.

After the reaction the reactor is allowed to cool in air; then it is chilled with liquid nitrogen and oxygen, and excess fluorine and a trace of ClF_3 are pumped off. Heating to 100°C with the valve closed, cooling in an ice-brine mixture, and pumping again purifies the sample sufficiently for introduction to the spectrometer.

Explosions as a result of unduly rapid reaction with the uranium oxide are infrequent. Metal shavings react too rapidly and must be converted to oxide before fluorination. All uranium oxides react successfully, but uranium tetrafluoride does not. It may be made to react, however, by using potassium iodide as a promoter instead of potassium chloride.

Samples are subject to cross contamination if the valves and other reactor parts have been used to prepare a sample of a different level of enrichment. Ideally, no parts which have come in contact with uranium hexafluoride should be reused, but this is not economically feasible in all cases.

Samples prepared and stored in metal are stable indefinitely. This is not true for those prepared in glass unless care is taken to remove all traces of hydrogen fluoride. If the sample is sufficiently pure, it is stable indefinitely in contact with glass.

13–1.4 Use of Isotopic Standards

Standards of known isotopic composition are required in uranium hexafluoride mass spectrometry to put the measurements on an absolute basis by eliminating instrument bias. Measurements are made by comparison with a standard at nearly the same isotopic composition, and high precision can be attained. Furthermore, the only way in which the effects of memory can be determined and corrected for is through the use of standards. A detailed discussion of the preparation of gravimetric standards and their application through the preparation and standardization of working standards is beyond the scope of this chapter. Details of this and of the methods of using standards in uranium hexafluoride measurements will be found in *Selected Measurement Methods for Plutonium and Uranium in the Nuclear-fuel Cycle.*[10] Further details of operating procedures as used in different laboratories are also presented in Ref. 10.

In the "Interpolative Method," two standards are used which bracket the concentration of the unknown sample.[18] The three tubes of uranium hexafluoride are attached to the instrument sample manifold. They are introduced into the spectrometer through the same controllable gas leak or through one for each valve set if the leaks are made nonfractionating by addition of a capillary or if the fractionating characteristics are known to be matched. The measurement sequence is A, X, B, B, X, A, where A and B represent the two standards and X is the unknown sample. The introductions are for 2 min in each case followed by a 1-min period in which no material is flowing into the ion source. The timed intervals are to be maintained within 5 sec.

During the introduction periods the "tuning" of the instrument is checked to make sure that the ion beam that passes through the slit to the low-current amplifier is maximized and that the total ion intensity is set at the desired level, which is about 10^{-9} amp, as measured by the high-current amplifier operating from the ion beams striking the slit plate. Data from the second half of the introduction period are recorded from the ratio-measuring device. The sequence is re-

peated as many times as necessary to give the desired precision for the measurement.

When the U^{235} content of the sample is below 50 percent, the data obtained from the determination are average values of r_A, r_X, and r_B. These values, which are proportional to the mole ratio of the U^{235} in the sample and standards to the total of the other uranium isotopes, are used together with the established values for the two standards to calculate the weight per cent. The value of R_D is calculated as follows:

$$R_D = \frac{r_X - r_A}{r_B - r_A}$$

and then the weight per cent U^{235} in the sample is obtained by

$$X = \frac{R_D(B-A) + A(1-B)}{R_D(B-A) + (1-B)}$$

where X = weight per cent U^{235} in the sample
A = weight per cent U^{235} in the low standard
B = weight per cent U^{235} in the high standard

When the sample contains more than 50 per cent U^{235}, the values of r_A, r_X, and r_B are proportional to the mole ratio of U^{238} to the other uranium isotopes in the standards and unknown. The calculation is made in a similar way, but the U^{235} weight per cent is finally determined by

$$X = 100 - Q - P$$

where Q is the weight per cent U^{238} and P is the weight per cent of all the other uranium isotopes. This value will require independent determinations.

In the interpolative method the effect of memory is automatically corrected, and no separate determination is required. In the single-standard method as used at the ORGDP, the memory for a given mass spectrometer is evaluated as often as is found to be necessary by the measurement of a pair of standards. Experience has shown that standards with a ratio of ratios of 1.10 are suitable for most applications. The unknown sample is then compared to a standard, which may conveniently be one of those used for the memory determination. From these measurements it is possible then to calculate the weight per cent U^{235} in the unknown sample.

Sample and standard are introduced into the instrument alternately; the series is always ended with the same material that was introduced initially. A five-introduction series is the one most commonly used. The ion current for each introduction is adjusted by the controllable gas leak to be within 2 per cent of the target value indicated by the output of the high-current amplifier. The average of the ratio meas-

urement over a 1- to 2-min period is taken as the value for that introduction. It is better to make more introductions of sample than to compile more data on each. It is recommended that the analysis be made on more than one spectrometer whenever this is possible. The memory determination is made in the same fashion, using a pair of standards.

The portion of the high-current signal which is necessary to cancel the entire signal from the low-current amplifier is called the "scaler." The average of the scaler values obtained for the $n+1$ sample introductions is divided by the average scaler values obtained for the n sample introductions to give R_o, or the observed ratio of sample mole ratio to standard mole ratio:

$$R_o = \frac{\text{Av. sample scalers}}{\text{Av. standard scalers}}$$

The memory factor, M, is calculated from one or more determinations on a pair of standards whose ratios of mole ratio R is known

$$M = \frac{R-1}{R_o-1}$$

The observed ratio, R_o, for the unknown and standard, is corrected for memory effect to give R_{corr}:

$$R_{\text{corr}} = MR_o - (M-1)$$

The weight per cent U^{235} in the sample is then calculated

$$\text{Weight per cent } U^{235} = \frac{100\,R_{\text{corr}}S}{100+R_{\text{corr}}S}$$

where S is the weight ratio of U^{235} to the sum of the other isotopes in the standard material.

13–2 ISOTOPIC ANALYSIS OF SOLID SAMPLES BY SURFACE IONIZATION

By C. M. Stevens

Many solids can be ionized directly from the solid form when heated on the surface of a metal having a high work function, such as tantalum, tungsten, and rhenium. Such ionization is called "surface" ionization or thermionic emission of positive ions. This technique is used as a source of ions in the isotopic analysis of many elements. The essential steps in surface-ionization analysis are as follows: The sample is deposited from a soluble form, such as the nitrate, onto a small ribbon filament and evaporated to dryness. This filament is placed in the proper position in the ion source. Ions emitted from the filament surface when the filament is heated are accelerated through a potential by an electron optical system, which also focuses an image on the entrance slit to the analyzer section. With the accelerating

voltage and magnetic field set properly, the filament is heated to the temperature at which ions of the masses of interest are observed. After proper focusing and intensity adjustments have been made, the mass spectrum is scanned, and an ion detector or collector located behind the exit slit of the analyzer measures the intensity of each isotope as it goes by the slit. Except for small corrections the intensity of each isotopic species is proportional to the abundance of that species in the original solid. Calibration of the instrument and technique with known uranium isotopic standards is necessary to determine the mass-discrimination correction.

Thompson, Leland, and Nier [19] first showed that the technique of heating a uranium salt, in this case uranyl nitrate, produced uranium oxide ions that was used as a source of ions in a mass spectrometer. Their sample size was large (>1 mg), and the intensities were too unstable to be of value in the applications of isotopic analysis at that time, namely, isotope-separation processes. Next, the work of Inghram and Hayden [20] and Hess showed that only 50 μg of uranium deposited as the nitrate on a flat-ribbon filament and fired in air to the oxide produced an adequate intensity of UO_2^+ ions with sufficient stability to determine isotopic ratios to ± 0.5 per cent precision. Their work led to the routine isotopic analysis of uranium by this method, the identification of many new nuclides, the determination of fundamental properties of nuclides, such as half lives and cross sections, and other research studies. Their method involved the design of a new machine with a larger radius of curvature (12 in. radius) than had been used in the uranium hexafluoride gas method. With a larger radius of curvature and a higher accelerating voltage, increased resolution and sensitivity were both achieved. This basic instrument has become the standard in the field today for high-mass work.

The technique of surface ionization has become the standard method of analysis for numerous elements, namely, the alkali, alkaline-earth, trivalent, some quadrivalent (transition), the transition elements, all but a few of the rare earths, and the actinide elements up to californium. Variations of the method have been developed which have extraordinarily high sensitivity, namely, the multiple filament of Inghram and Chupka [21] and the V-filament of White, Collins, and Rourke [22] and Dietz.[23]

A fundamental difference between surface-ionization sources and gas electron-bombardment sources is that stable or constant ion intensities cannot be obtained from the former by merely controlling the conditions in the source producing the ionization, such as filament current or temperature. In certain instruments the isotopic analysis must be carried out with small allowable and usually present intensity

690-457 O—64——65

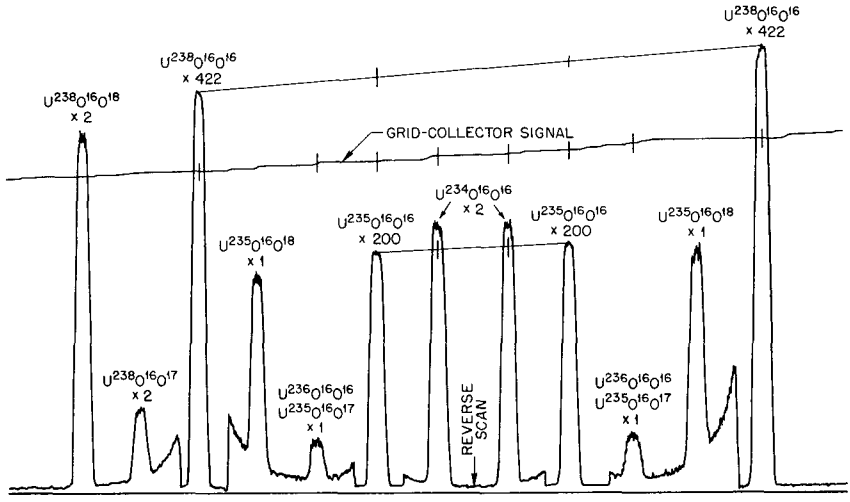


Fig. 13.8—Mass spectrum of UO_2^+. Accelerating voltage, 8000 volts; analyzer pressure, 2×10^{-7}; source pressure, 3.5×10^{-6}.

changes. Multiple scanning of the mass spectrum for the isotopic range of interest is necessary so that the effect of drifts in the ion intensity can be averaged out by interpolation assuming linear changes over short times. Figure 13.8, a plot of several multiple mass-spectrum scans, illustrates the change in ion intensity with time. Special techniques have been developed to compensate for intensity–time drifts: (1) dual ion collector,[24] (2) grid collector,[25] and (3) filament temperature control from an ion-beam intensity.[26]

The difficulty of maintaining stable and reproducible conditions in the location of the emitting ionization filament and ionizing conditions on the filament surface, not only from sample to sample but also during the analysis of any one sample, introduces variable discrimination factors that prevent the use of the highly precise method of comparing an unknown and standard as is done in the isotopic analysis of gases. This problem is dealt with by analyzing a U^{235}/U^{238} 1 to 1 standard several times to determine the average mass-discrimination bias and the standard deviation of a single typical analysis. In addition, the intensity linearity of the measuring circuit is determined with another standard having two isotopes of minimum mass difference whose ratio is large and accurately known. The corrective terms thus determined can be applied to any mixture of uranium isotopes over a wide concentration range.

A comparison of surface ionization with gas electron-bombardment methods is given in Table 13.1.

13–2.1 Theory of Surface Ionization

The surface ionization of molecules hitting a hot surface is explained by the Saha–Langmuir theory,[27, 28] which shows that in certain ideal cases the temperature dependence of the ratio of ionized to neutral molecules is given by

$$\frac{n^+}{n^0} \cong A \exp -\left[\frac{(I-\phi)e}{kT}\right] \tag{13.1}$$

where

e = the electronic charge
k = Boltzman gas constant
T = absolute temperature
I = ionization potential of the molecule, and
Φ = the work function of the surface.

The proportional constant A involves the statistical weight factors (ω) and reflection coefficients (r) of the ionized and neutral species and is independent of temperature if the reflection coefficients are also independent of temperature.

$$A = \frac{\omega^+}{\omega^0} \frac{(1-r^+)}{(1-r^0)}$$

This theory accounts adequately for the ionization of alkali elements where the degree of ionization is high.[29] Werning [30] has shown this relation to hold for a number of elements, including uranium, at temperatures above 2500°K. However, at temperatures below 2500°K the theory does not account for the observed ionization characteristics of uranium. Surface chemical reactions of uranium with impurities are important. The ionization of UO^+ and UO_2^+ is greatly enhanced and that of U^+ is reduced at lower temperatures by the presence of oxygen.

Studier [31] has studied the effect of oxygen and carbon on hydrocarbon impurities at various temperatures. At 1000° K, much below the temperature at which U^+, UO^+, and UO_2^+ are observed, the presence of oxygen may cause the loss of UO_2 as UO_3. The ionization to U^+ from UO_2 sample deposits is greatly influenced by carbon either by carbonizing the base filament material, tungsten or rhenium, or by heating to 1000°C with a low partial pressure of benzene. Even hydrocarbon impurities in the sample or filament material can result in appreciable reduction. The formation of U^+ from the solid phase above 2000°K indicates either the diffusion of uranium into the filament metal or the formation of a refractory compound, such as uranium carbide.

Prior chemical treatment of the sample is said to have an effect on the efficiency of ionization with some surface-ionization methods. For example, in some laboratories the best results are obtained by dissolving the uranium samples in aqua regia. The solution, after evaporation to dryness, is taken up in dilute ($0.05M$) nitric acid for deposition on the filament. Just how the chemistry procedures influence sensitivity is not understood.

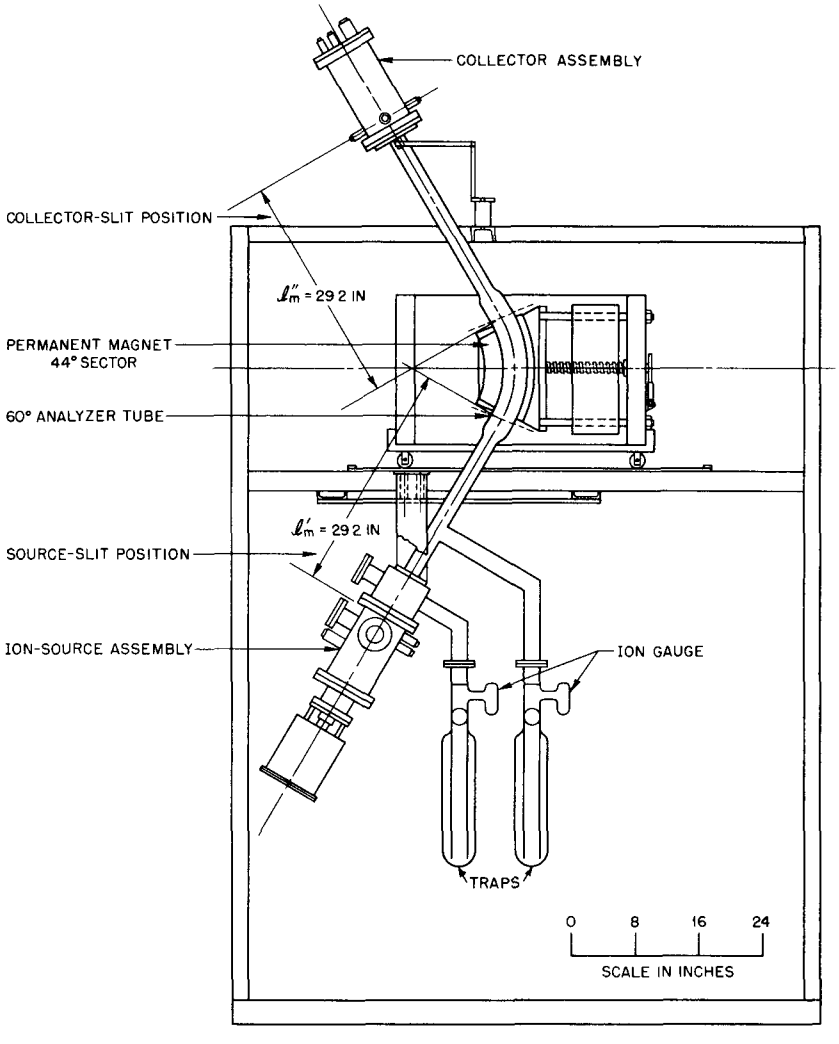


Fig. 13.9—Over-all view of 12¾-in.-radius 44°-sector permanent-magnet mass spectrometer.

13–2.2 Instrument Description

A basic 12-in.-radius instrument for use in the surface ionization of uranium will be described first. The application of this basic instrument to the analysis of elements other than uranium, such as transuranic elements, boron, and fission products, will be discussed in another section.

The first 12-in.-radius 60°-sector instrument was designed by M. G. Inghram, D. C. Hess, and R. J. Hayden. The literature does not contain a description of this first instrument although it was the prototype for most of the later models. Many variations of this 12-in. instrument are in existence. Single analyzer types are described by Stevens and Inghram[32] and by Echo and Morgan.[33] A two-stage model is described by White et al.[34] Commercial models of equivalent instruments for surface-ionization isotopic analysis of uranium are: model MS–5, Associated Electrical Industries; model 21–702B, Consolidated Electrodynamics Corp.; model 12–60, Nuclide Analysis Associates; and model CH 4/58 Model II, Atlas-Werke A.G., Bremen.

Numerous improvements have been incorporated in later versions of the 12-in.-radius instrument, and they have resulted in an instrument with more sensitivity, higher resolution, less scattering, and easier operation. The latest model of the instruments in use at the Argonne National Laboratory (ANL) will be described in detail. A vacuum-lock model has been described.[35]

Figure 13.9 is a scale drawing of an instrument with a 60° deflection analyzer and a 44° magnet sector giving partial axial focusing by virtue of the non-normal entrance and exit boundaries $\epsilon' = \epsilon'' = +8°$. Figure 13.10 shows the focusing arrangement in the

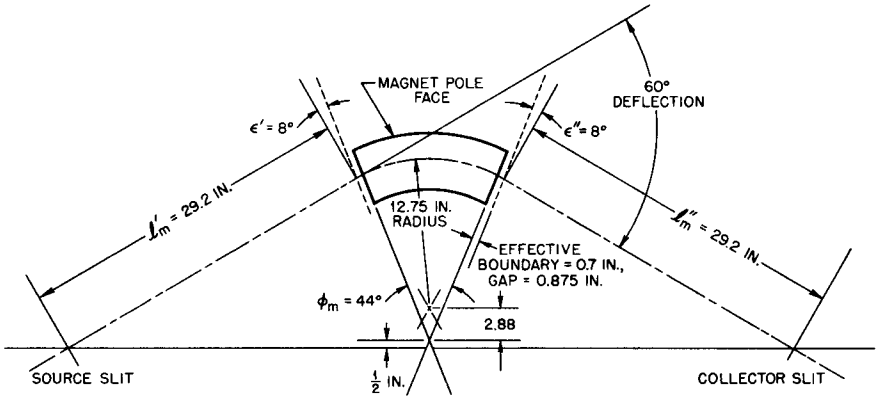


Fig. 13.10—Focusing arrangement for the 12¾-in.-radius 44°-sector permanent-magnet mass spectrometer.

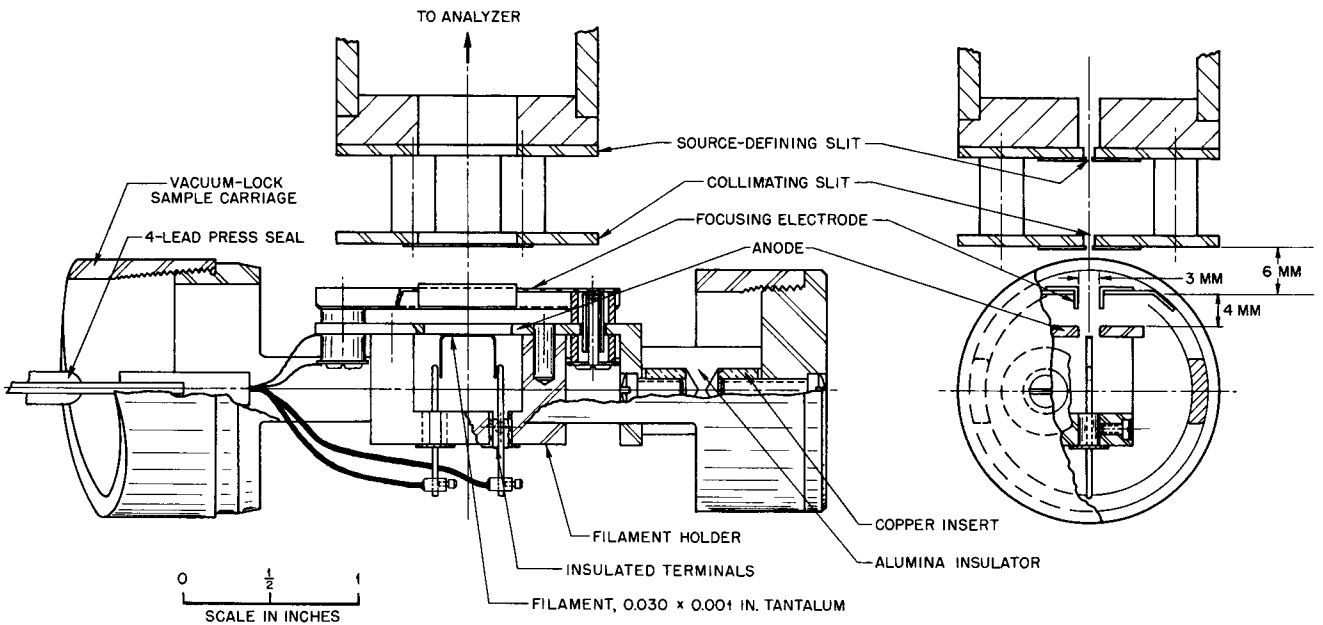


Fig. 13.11—Single-filament surface-ionization source with vacuum lock.

Herzog notation. This instrument was modified from a 60° sector magnet type by cementing 8° wedges to the magnet pole faces and attaching 8¾-in.-long extensions to both source and collector chambers (see Fig. 13.26). The radius of curvature of 12¾ in., as shown in Figs. 13.9 and 13.10, was worked out from the experimentally determined position of the magnet for best resolution. If the effective boundary of the uniform field is taken as 0.7 in. instead of the same as the gap width, 0.875 in., then this agrees with the Herzog focusing relationship,

$$(l'_m-g')(l''_m-g'')=f^2$$

when l'_m and l''_m are the distances from source and collector slits to the effective boundary and

$$g'=\frac{r\cos\epsilon'\cos(\phi-\epsilon'')}{\sin(\phi-\epsilon'-\epsilon'')}$$

$$g''=\frac{r\cos\epsilon''\cos(\phi-\epsilon')}{\sin(\phi-\epsilon'-\epsilon'')}$$

$$f=\frac{r\cos\epsilon'\cos\epsilon''}{\sin(\phi-\epsilon'-\epsilon'')}$$

$l'_m=l''_m=29.2$ in. for an actual radius of curvature $r=12.75$ in.

The most important performance characteristics of an instrument are resolution, sensitivity, transmission, and scattering. These characteristics are discussed in the following sections.

(a) *Resolution.* The full peak-width resolution for a standard 60°-sector instrument is:

$$\text{Res}_{60°}=\frac{m}{\Delta m}=\frac{r}{W_{eff}} \tag{13.2}$$

where m=the mass
r=the radius of curvature
W_{eff}=the effective slit width

For a 44°-sector magnet and a 60°-deflection path, $\epsilon'=\epsilon''=+8°$, the resolution is somewhat greater:

$$\text{Res}_{44°}=\frac{1.14r}{W_{eff}} \tag{13.3}$$

Including all the terms contributing in practice to the effective slit width, this is

$$\text{Res}_{44°}=\frac{1.14r}{W_c+[W_s+1.14r(dV/V)+1.14r\alpha^2]} \tag{13.4}$$

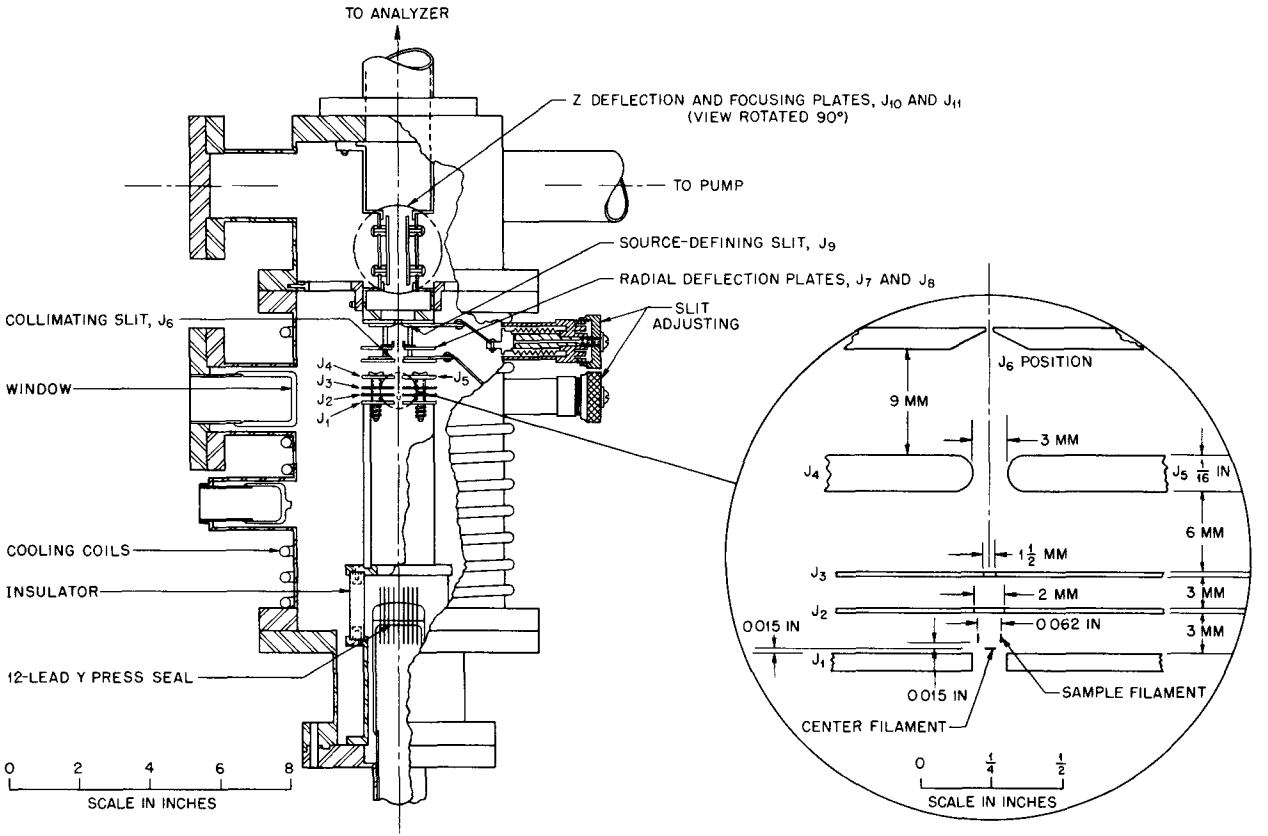


Fig. 13.12—Multiple-filament surface-ionization source.

where W_c = the collector slit width
W_s = the source slit width
dV = the energy spread in the ion beam
V = the energy of the beam
α = the half angle of divergence

For a surface-ionization source, the energy spread, dV, amounts to 1 to 2 volts from filament voltage and about 0.5 volt from thermal-ion energy for a maximum of 2.5 volts in a total accelerating voltage of 15,000 volts. The second-order divergence term for $\alpha = \pm 1/80$ radians is 0.0021 in. Thus

$$\text{Res}_{44°} = \frac{1.14r}{W_c + W_s + 0.0044} \tag{13.5}$$

The transmission of the ion source is the fraction of ions produced which is transmitted through the ion-gun system and the entrance slit, W_s; it decreases when the resolution is increased by narrowing W_s. Table 13.2 shows the usual operating slit widths and calculated

Table 13.2—RESOLUTION AND SOURCE TRANSMISSION OF A 12-IN.-RADIUS 60°-DEFLECTION 44°-SECTOR MAGNET MASS SPECTROMETER

Resolution	W_s, *in.*	W_c, *in.*	*Source transmission, %*
500	0. 0093	0. 014	70
1000	0. 0025	0. 0069	18

source transmission for resolution values of 500 and 1000 with a 12-in.-radius 60°-deflection 44°-sector magnet instrument.

The transmissions given are calculated from the theoretical limiting source transmissions based on a minimum image width of 0.0135 in. for a 0.030-in.-wide filament at 3000°K with a final angle of divergence of $\pm 1/80$ radians and accelerated through 15,000 volts.

By way of comparison, for a 6-in.-radius 60°-sector instrument with the same magnetic field of 8300 gauss ($V = 3750$ volts for mass 238), angular divergence, and voltage spread,

$$\text{Res}_{60°} = \frac{r}{W_c + W_s + 0.008 + 0.0019} \tag{13.6}$$

Table 13.3 shows the theoretical maximum source transmissions for such an instrument for a 0.030-in. ionization filament at 3000°K with

Table 13.3—RESOLUTION AND SOURCE TRANSMISSION OF A 6-IN.-RADIUS 60°-SECTOR MAGNET MASS SPECTROMETER

Resolution	W_s, *in.*	W_c, *in.*	*Source transmission, %*
200	0. 0054	0. 0154	20
250	0. 002	0. 012	7. 4
500	0. 001	0. 001	0. 35

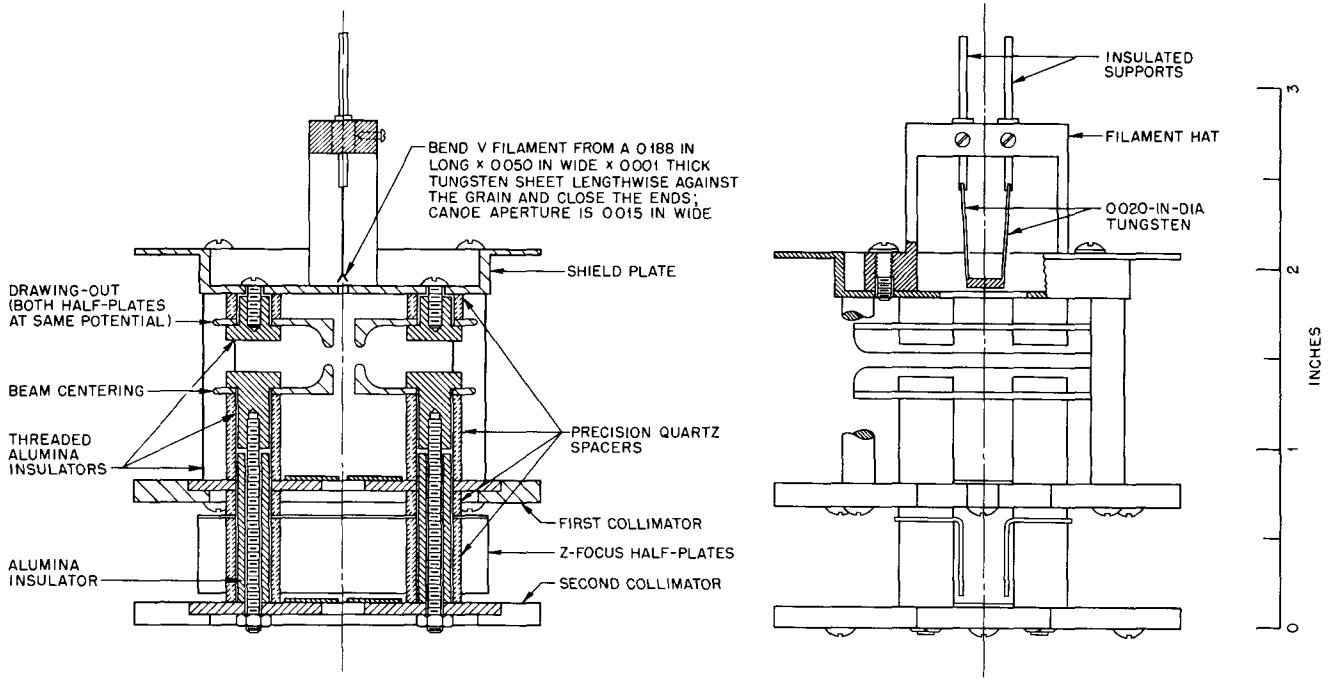


Fig. 13.13—High-voltage Z-focus ion gun with V-filament.

a final angle of divergence of $\pm 1/80$ radians and accelerated through 3750 volts. The table illustrates clearly the advantages of the higher radius of curvature and higher accelerating voltage. With a 6-in.-radius instrument, the maximum resolution is limited to about 500, mainly by the voltage-spread term. For high transmission or sensitivity, the resolution of the 12-in. instrument is five times greater than the 6-in. instrument, and, at a resolution of about 500, which is needed for heavy-element isotopic analysis, the 12-in.-radius instrument is about 200 times more sensitive than an instrument with a 6-in. radius.

(b) *Sensitivity.* The basic specific sensitivity of a mass spectrometer for a given element is dependent on four factors: (1) efficiency of ionization, (2) transmission of ion source and analyzer, (3) ion-detector sensitivity, and (4) background ion current due to impurities and scattering. The first and third factors are more or less independent of the size or focusing properties. Efficiency of ionization will depend on the specific surface-ionization technique. For uranium there are three techniques in common use: (1) single filament,[20] (2) multiple filament,[21] and (3) V-filament.[22, 23] The three types of ion sources are shown in Figs. 13.11 to 13.13. The ion optical systems shown with each technique are those given in the indicated publications.

Table 13.4 gives the efficiency and sensitivity for the single-filament and multiple-filament surface ionization of uranium. The measurements were made on the transmitted ion beams by integrating the current to a grid collector to complete depletion of known weights of sample deposited on the filament. The measurement of the total ionization of uranium directly from the filament is not possible because of the presence of other ions, such as alkali ions, and the filament material itself. The total or absolute ionization efficiency given is based on transmission values that are, for the most part, calculated [see Sec. 13–2.2(c)]. The axial transmission factors are based on the beam-shaped measurements shown in Fig. 13.14. The radial transmission of the source in these cases was calculated from the theoretical upper limit for the optics using Langmuir's relation (Eq. 13.7).

The absolute efficiencies, for the multiple filament technique, 1 to 3×10^{-3}, determined as described above, are compared in Table 13.4 with the ionization efficiency for uranium-metal vapor hitting the filament at the same temperature calculated by the Saha–Langmuir relation (Eq. 13.1). The number of molecules hitting the center filament is estimated to be 10 per cent of the total molecules evaporating from the sample filament.

The tantalum single-filament technique using UO_2 ions has an ionization efficiency of about 1.6 per cent of the maximum rhenium

Table 13.4—IONIZATION EFFICIENCY, TRANSMISSION, AND SENSITIVITY OF SURFACE-IONIZATION SOURCES FOR URANIUM

Source type	Instrument characteristics	Transmitted efficiency, ions/atom	Transmission calculated for resolution = 500, %	Absolute efficiency, ions/atom		Usable sensitivity, g of U
				Measured ÷ transmission	Saha–Langmuir	
Single-filament tantalum (UO_2^+)	60° magnet, 8 kv, direction detection	1.7×10^{-6}	10	1.7×10^{-5}	----------	1.6×10^{-9} (10^{-15} amp for 10^3 sec)
Multiple-filament rhenium (U^+)	60° magnet, 8 kv, electron multiplier	2.8×10^{-4}	10	2.8×10^{-3}	2.4×10^{-3}	1.2×10^{-13} (10^{-17} amp for 10^3 sec)
Multiple-filament rhenium (U^+)	44° magnet, 15 kv, z focusing, electron multiplier	9.3×10^{-4}	60	1.2×10^{-3}	2.4×10^{-3}	4×10^{-14} (10^{-17} amp for 10^3 sec)

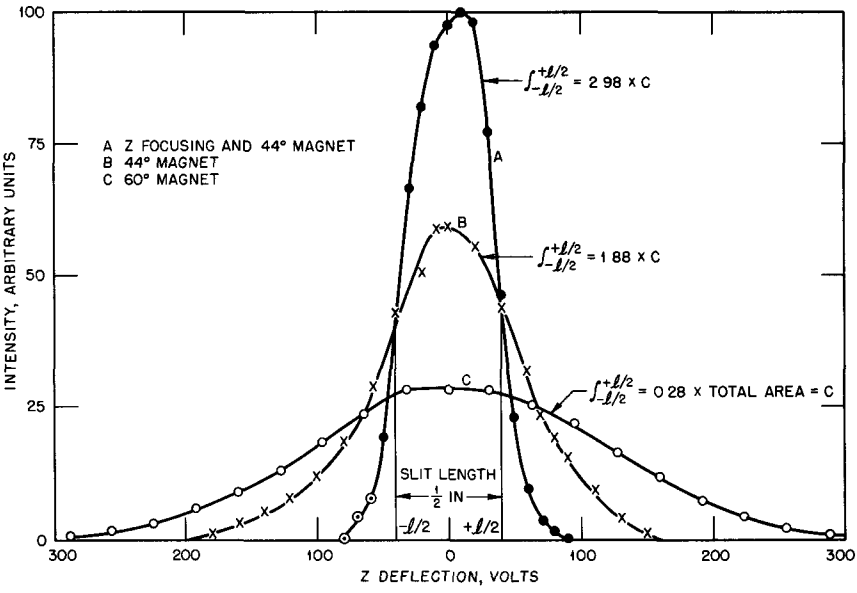


Fig. 13.14—Axial distribution of ion-beam intensity at the collector of a 12-in.-radius mass spectrometer.

multiple-filament efficiency. Since it is rarely used as a high-sensitivity method, the usable sensitivity given in Table 13.4 is for direct ion-current measurement without electron-multiplier amplification.

The V-filament using a tungsten filament, a two-stage analyzer, a 5000-volt accelerating voltage, and a pulse-counting system has a just-detectable sensitivity for uranium of about 5×10^{-15} g of sample, which corresponds to about 100 ions counted,[16] but not identified. The sensitivity with a 15,000-volt accelerating voltage is much higher.[36] By comparison, the multiple rhenium filament using a single-stage analyzer, 15,000 volts accelerating voltage, and current integration of electron-multiplier output while scanning, requires about 6×10^{4} ions to identify uranium. The principal reason for this difference is that fewer impurities are produced by the V-filament. This is probably due to the much lower temperature of ionization as compared to the multiple filament. In addition, many analytical situations in which the ultimate sensitivity is needed involve the detection of an isotope of very small abundance adjacent to one of very large abundance. The use of the two-stage analyzer further reduces the background due to scattered ions from adjacent peaks of high intensity. Thus, with a low background signal from all extraneous ions, not only can lower counting rates be detected but also the instrument can be tuned to the mass in question and the counts can be integrated. With the multiple filament the high temperature of the ionizing filament requires greater

wattage dissipation, which increases the vapor pressures of background gases, such as hydrocarbons. The scattering of a single-stage analyzer is also greater. Both these factors make it necessary to scan the spectrum to identify a peak as distinctly being an isotope of uranium. During the scanning each uranium peak is monitored only about 3 to 10 per cent of the time which, at the level of 10^{-17} amp during 10^3 sec, corresponds to 1800 to 6000 ions actually measured.

(c) *Transmission.* The transmission of an ion source and analyzer is a function of the area and the temperature of initial ionization, ion energy, slit apertures, acceptance angles, and focusing properties and can more or less be approximately determined for a given ion source, mass-spectrometer size and design, and a given resolution.

According to Langmuir,[37] the limiting intensity or brightness of an image of a source of ions produced by an electron optical system is

$$I_{\max}=\frac{E_f+E_i}{E_i} I_0 \sin^2 \alpha \tag{13.7}$$

where E_i and E_f = the initial and final energies
I_0 = the initial current density
α = the half angle of maximum divergence

Ninety-five per cent of the ions from a source at 2500°K with a cosine distribution will have an energy spread less than 0.4 electron volt. Since the image size is inversely proportional to the current density, the minimum image size that can be produced by an electron optical system with a focal length such that the angular divergence is less than $\pm 1/80$ and a final voltage of 15,000 volts, is 0.55 the object size. For a 0.030-in.-wide center filament in a multiple-filament source, this is 0.0125 in. The only factor limiting the attainment of the theoretical focusing is aberration of the lens system. The measurements of Dietz have shown lens aberrations to be negligible for the multiple-filament source.[38]

For a resolution of 500 with a 60°-sector magnet (slit width, 0.008 in.), the source transmission is 66 per cent, assuming 100 per cent axial transmission.

The V-filament is very favorable for high transmission because of the lower temperature, 1500–2000°C, and the smaller area of emission (approximately 0.062 by 0.015 in.).[38] At 15,000 volts and a resolution of 500, the transmission is estimated at greater than 95 per cent.

The principal losses in the region between the source and collector slits are due to axial divergence. In addition to the normal axial divergence of the ion beam as it leaves the source with no lens action in this direction, with a standard 60°-sector magnet and 60° deflection, there is a diverging effect on the off-axis rays at both entrance and exit

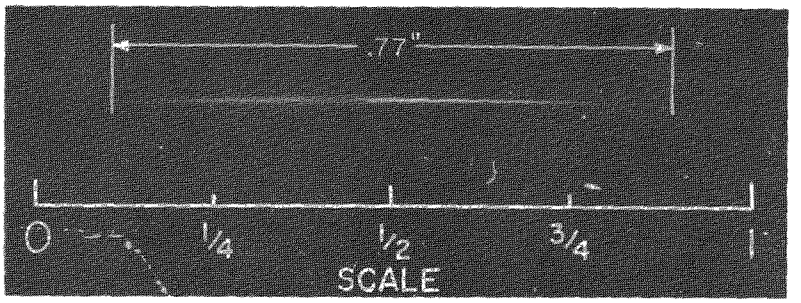


Fig. 13.15—Autoradiograph of ion-beam image for 12-in.-radius 44°-sector mass spectrometer.

boundaries of the magnet.[39, 40] This effect is a result of the beam's being slightly deflected in the region near the boundary; thus there is a small component of the curved fringing magnetic field at right angles to the z-axis and ion direction for ions off the central plane. The effect is of a lens with a negative focal length ($f=r/\tan\epsilon'$), where ϵ' is effectively about $-4°$ and r is the radius of curvature. This produces a virtual demagnified image closer to the magnet; thus at the collector the beam is spread farther in the z direction because of the greater angular magnification or simply by diverging action. If the nonnormal entrance and exist angles are in the opposite direction, this lens effect can be made to produce convergence. For example, a 44° magnet with a 60° analyzer tube produces a positive focal length with ϵ' effectively about $+4°$ as the ion beam enters the fringing field; thus the lens produces a magnified virtual image farther from the magnet with a corresponding angular demagnification and compresses the beam width at the collector.

Figure 13.14 shows the axial cross section of the beam at the collector for both a 60° and a 44° magnetic sector. The transmission of the analyzer is improved about 65 per cent by the 44° magnet. Figure 13.14 also shows the shorter beam length and, consequently, greater transmission produced by the z-axis electrostatic focusing plates (Fig. 13.12). Figure 13.15 is an autoradiograph of the image of the beam at the collector slit in the 44°-sector magnet instrument. This was obtained by collecting a beam of U^{232} on a plate alongside the slit and autoradiographing this deposit.

Balestrini and White [41] have described shims for obtaining second-order angular focusing. With these shims, it should be possible to accept a beam having a radial divergence of $\pm 1/40$ while at the same time using an ion-source optical system with greater demagnification so that 95 per cent of the beam can be transmitted in the radial direction. As can be seen in Fig. 13.14, if the collector-slit length is increased to $3/4$ in., then the axial transmission can be made about 95 per

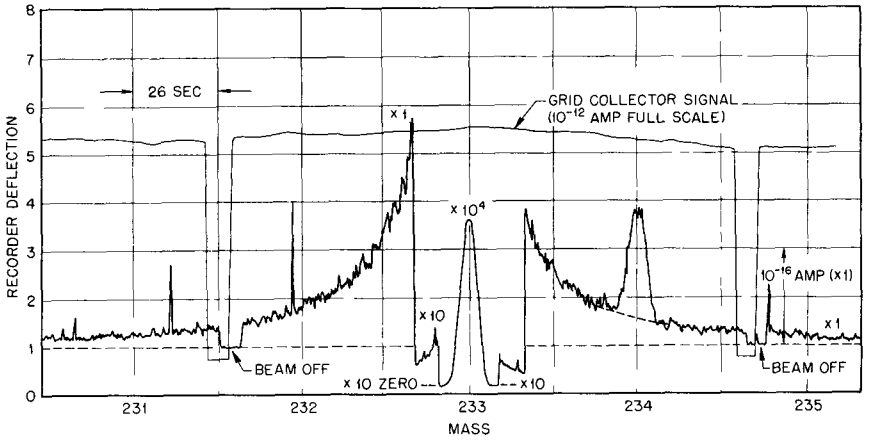


Fig. 13.16—Characteristic peak shape and scattering tails. Spectrometer, 12¾-in. radius, 44° magnet, 60° deflection; accelerating voltage, 15 kv; analyzer pressure, 1.4×10^{-7} mm mercury; electron-multiplier gain, 10^4; and U^{234}/U^{238}, 0.000063.

cent; thus it should be possible to obtain greater than 90 per cent transmission of ions from a 0.030- by ½-in. filament at a resolution of 500.

(d) *Scattering.* The peak shape of a resolved mass is shown in Fig. 13.16. The characteristic image width is made up of the source slit width; focusing aberrations, such as those due to second-order angular divergence ($r\alpha^2$) and spherical aberrations; and energy spread $r(dV/V)$. At the edges of both the low- and high-mass sides, the intensity drops off sharply owing to these effects; then it has a tail that tapers off gradually for a distance many times the image width. The tail is due principally to elastic scattering of the ion beam by the residual gas pressure in the vacuum system. Figure 13.17 shows scattering as a function of nitrogen pressure in the analyzer region originating from the source region and is analogous to the conditions resulting from source outgassing. The pressure is essentially constant throughout the analyzer region and is somewhat higher than that where the ion gauge is located. The scattering tail on the low-mass side is somewhat higher than that on the high-mass side; this shows the effect of energy loss in scattering.

For scattering to be achieved less than 10^{-5} one mass unit away at mass 235, a vacuum of less than 4×10^{-8} torr is needed. It is difficult to maintain a vacuum below 2×10^{-8} torr during a multiple-filament surface-ionization analysis because of the outgassing resulting from the 50 watts required to heat the two filaments. Where the sample requires this low scattering, the procedure is carried out with the

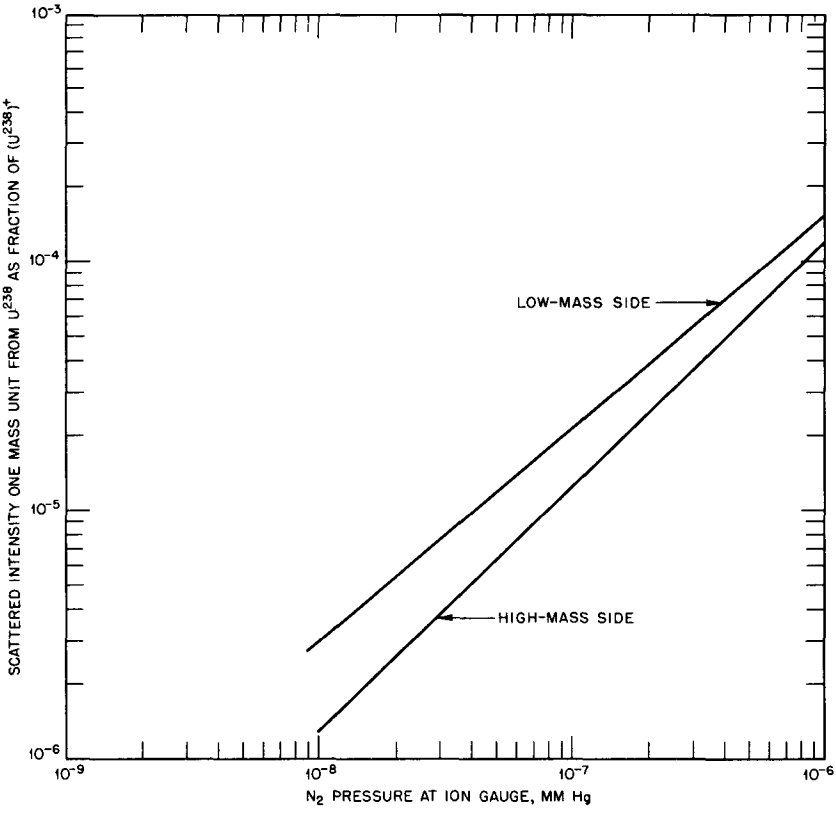


Fig. 13.17—Scattering of $(U^{238})^+$ vs. nitrogen pressure for a 14.5-kv ion beam.

source degassed as much as possible. See Sec. 13–2.4(b) for the detailed operating procedure.

With the two-stage mass spectrometer,[34] scattering can be reduced to the extent of about 10^{-8} one mass unit away at mass 235.

(e) *Mechanical Features.* The analyzer tube, source, and collector chambers are fabricated of Heliarc-welded Inconel or nonmagnetic stainless steel, and use flanges with gold-wire gaskets. The liquid-nitrogen traps and mercury diffusion pumps are of glass and are connected to the metal system by 2½-in.-diameter Kovar glass seals and gold-wire gasket flanges.

The analyzer tube (2 in. in outside diameter with a 1/16- or 3/32-in. wall) is bent to the correct curvature and angle and then flattened in the curve portion in a jig to a width 1/16 in. less than the magnet pole gap. The tube is filled with Cerrobend* for the bending operation and with paraffin for the flattening operation. The tube section, as

*Cerro de Pasco Sales Corp.

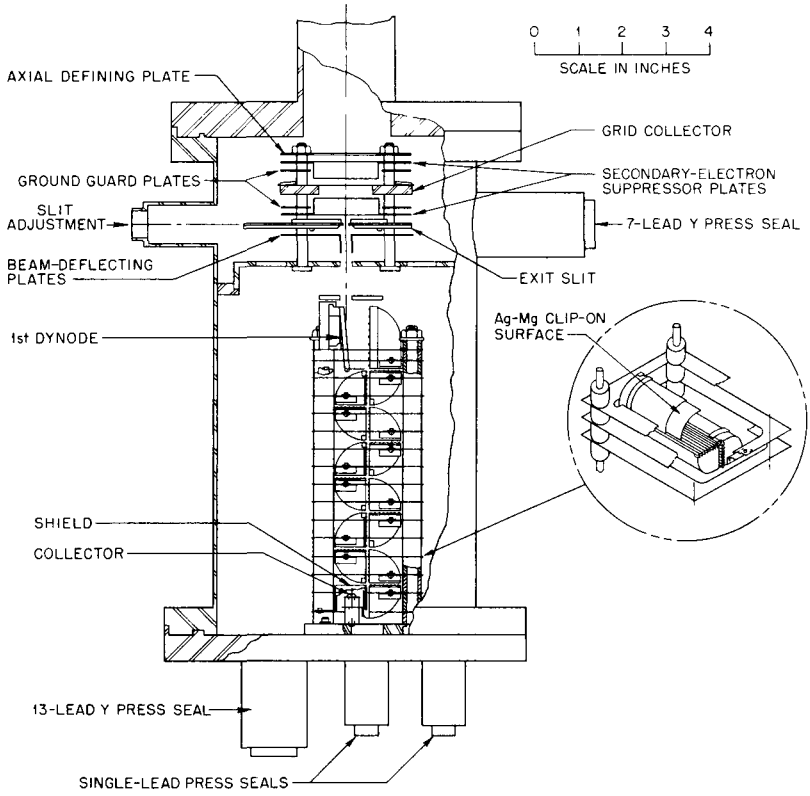


Fig. 13.18—Collector assembly with grid collector and electron multiplier.

well as all other metal parts, is stress relieved prior to final machining. Completely annealed Inconel is avoided because of its lower yield point. The tube is mounted rigidly from one main support near the source, the collector end being held by a support that permits freedom of movement in the direction of thermal expansion of the tube (see Fig. 13.9). The alignment of the source and collector slits is maintained by reference between accurately jig-bored dowel pins used for mounting the source slits and dowel pins on the flange used for attaching the collector chamber. The acceptance angle of the tube is about $\pm 1/20$ radian, which is much more than the usual divergence of the beam of less than $\pm 1/80$ radian.

Figure 13.18 shows a flange with a gold-wire gasket. This design is adapted from one described by Westinghouse. With precision doweling of the flanges, the flange can be heated and can be opened and closed as many as twenty times before the gold-wire gasket needs replacing. The gold-wire gasket (0.020 to 0.040 in.) is made by melting the ends together in a gas–oxygen flame. The entire gasket is

then annealed. The gasket is made about ⅛ in. too short, depending on the diameter, and then is stretched to fit snugly in place over the inside diameter of the groove.

Two mercury diffusion pumps are used in an arrangement that provides differential pumping of the source and analyzer regions. The only opening between these two regions is the source-defining slit, 0.006 by 0.5 in., making the differential pumping ratio for noncondensable gases about 50, assuming the pumping speed of the pump and trap combination is about 10 liters/sec. This ratio is closer to 30 in practice because of leakage at the junction of the defining slit and analyzer-tube end.

The mercury diffusion pumps are Consolidated Vacuum Corporation model GHG–15 (speed, 20 liters/sec) or Kontes Glass Co. type K–92475 size B or C (speed, 80 liters/sec). The traps are 16 in. long with a 100-mm outside diameter and a 60-mm inside diameter. The trap is sealed to a Kovar glass graded seal (2¼-in.-OD Kovar metal), and the Kovar metal tube is welded to a gold-wire gasket flange. With the GHG–15 pump, the speed for noncondensable gases is about 10 liters/sec at the trap. Both diffusion pumps are adequately backed by a 21-liter/min mechanical pump. A stopcock is put in the fore vacuum line joining the two diffusion pumps. The purpose of this is to permit introduction of a dry gas from the source chamber to the instrument up to atmospheric pressure while the mercury diffusion pumps are on without sweeping mercury vapor from the source diffusion pump into the analyzer. The mercury diffusion pumps are protected in case of water supply failure by a pressure switch. In addition, if there is a large water leak in the connections of the water system, a flowmeter on the output end of the water circuit will control a solenoid valve shutting off the water supply and diffusion pumps. The pressures in both the analyzer and source regions are indicated by ion gauges attached near both traps. The main source slit, source-collimating slit, and collector slit are all separately adjustable through bellow seals. Windows are mounted on the source chamber for observing filament and electrode alignment and filament temperatures.

(f) *Source System.* A complete multiple-filament source system is shown in Fig. 13.12. A feature of this assembly is the division of the source into two sections, a section consisting of electrodes and slits at or near ground potential, which is mounted directly on the tube for accurate alignment of the slits, and a section of electrodes at high voltage including the surface-ionizing filament section, which is mounted from the end flange with long insulators. The ion optical system is that used by Inghram and Chupka [21] with the addition of the axial beam-centering plates. Every time a sample is changed this

second section is removed by removing the end flange. The alignment between this section and the ground-slit section is not very critical, and small irregularities in alignment are adjusted for by the beam-centering plates J_4 and J_5. Gross misalignments can be determined by observing through the window the light patterns on the slit system when the filament is turned on.

The location of the filaments relative to J_2 electrodes is quite critical for proper focusing and correspondingly good sensitivity. (See enlarged view in Fig. 13.12.) A single or simple surface-ionization filament can be used with this source either by using the center filament of a multiple-filament assembly as the sample filament or by using the center filament alone with tabs mounted on J_2 to take the place of the side filaments for proper focusing action. Craig [42] has described a surface-ionization source with an electron optical system designed so that focusing is not critical to location of the filaments.

The electrodes are all constructed of stainless steel (300 series) so that they can be cleaned in 8*N* nitric acid and 0.5 per cent hydrofluoric acid. The high-voltage insulators are pyrex rods and spacers. A pyrex tube of 100 mm diameter surrounds the high-voltage section and protects the inside of the metal chamber from becoming contaminated with deposits of radioactive sample materials, such as plutonium. The chamber wall surrounding the source section is water cooled, which prevents the wall from heating up during an analysis and giving off volatile organic compounds which cause peaks at every mass and greatly limit sensitivity.

Typical operating voltages for this source are:

J_1	14,750 volts	J_7	0 to ±400 volts
J_2	14,725 volts	J_8	0 to ±400 volts
J_3	14,500 volts	J_9	Ground
J_4	11,500 volts	J_{10}	+400 to 600 volts
J_5	11,500±0 to 400 volts	J_{11}	+400 to 600 volts
J_6	Ground		

As described by Inghram and Chupka,[21] this source has the property of sharply distinguishing ions originating from the center filament from ions coming off either side filament. This is done by the short focal length lens action of J_2.

Vapor shields are mounted on J_1 to shield the insulators from the metal vapor evaporating from the center filament, which is at a temperature of 2500 to 3000°K. Rhenium filaments cause leakage more readily than tungsten, even though the rhenium filaments operate at a lower temperature.

The surfaces of the plates between which there is the large potential drop (J_4 and J_5 to first ground slit) are finished with all edges

rounded and polished smooth to prevent arcing. This treatment is sufficient to prevent arcing if the source is degassed.

The source system also incorporates a pair of parallel plates, J_{10} and J_{11} (Fig. 13.12), which center the beam in the axial direction and have a weak converging lens effect to minimize axial divergence. These plates are located between the source-defining slit and the magnet, close to the former. The field produced by these plates is at right angles to the direction in which the radial focusing properties are determined, and hence this focusing is not disturbed. The potentials on these plates needed to produce the maximum intensity are small compared to ion-beam energy.

(g) *Collector System.* Figure 13.18 shows a collector system with an electron-multiplier detector and a grid collector [25] in front of the defining slit. The assembly is all mounted in a chamber that attaches to a flange on the end of the spectrometer tube. Thus, repairs can be made to any part of the collector system without removing the spectrometer tube. For a system without an electron multiplier, a smaller chamber is used with only a simple collector plate and secondary-electron repeller mounted in place of the electron multiplier. The collector-slit width is adjustable; the adjustment method is similar to that used for the source slits except that an insulating connection is used so the collector slit may be put at a small potential from ground to prevent secondary electrons, produced by ions hitting the slit plate, from getting to the grid.

The grid plate is stainless steel with stainless-steel wires welded to it.[43] The grid wires are 0.003-in. wire wound on 0.006-in. spacing to give a 50 to 50 open-to-closed area ratio. In cases where sensitivity of detection is paramount, 0.003-in. wire on 0.012-in. spacing is used for a 3 to 1 open-to-closed area ratio. The range of mass intercepted by the grid shown on Fig. 13.18 is ± 2.5 per cent so as to monitor uranium masses 232 through 238.

Electron multipliers as ion detectors in a mass spectrometer can be used either as pulse-counting devices or as current amplifiers. White and Collins [44] describe the use of an Allen focused type for pulse counting and discuss the advantages and disadvantages of such a system.

The important characteristics of a multiplier used as a current amplifier are gain, gain stability, noise, mass discrimination, and linearity. A review of the basic characteristics of electron multipliers has been given by Inghram and Hayden.[20]

Figure 13.18 shows a large size semifocused 90°-cylinder multiplier [46, 47] featuring a large beam area acceptance. There are fifteen stages with the activated silver–magnesium dynode surfaces in the form of clip-on plates to facilitate installing new surfaces. The acti-

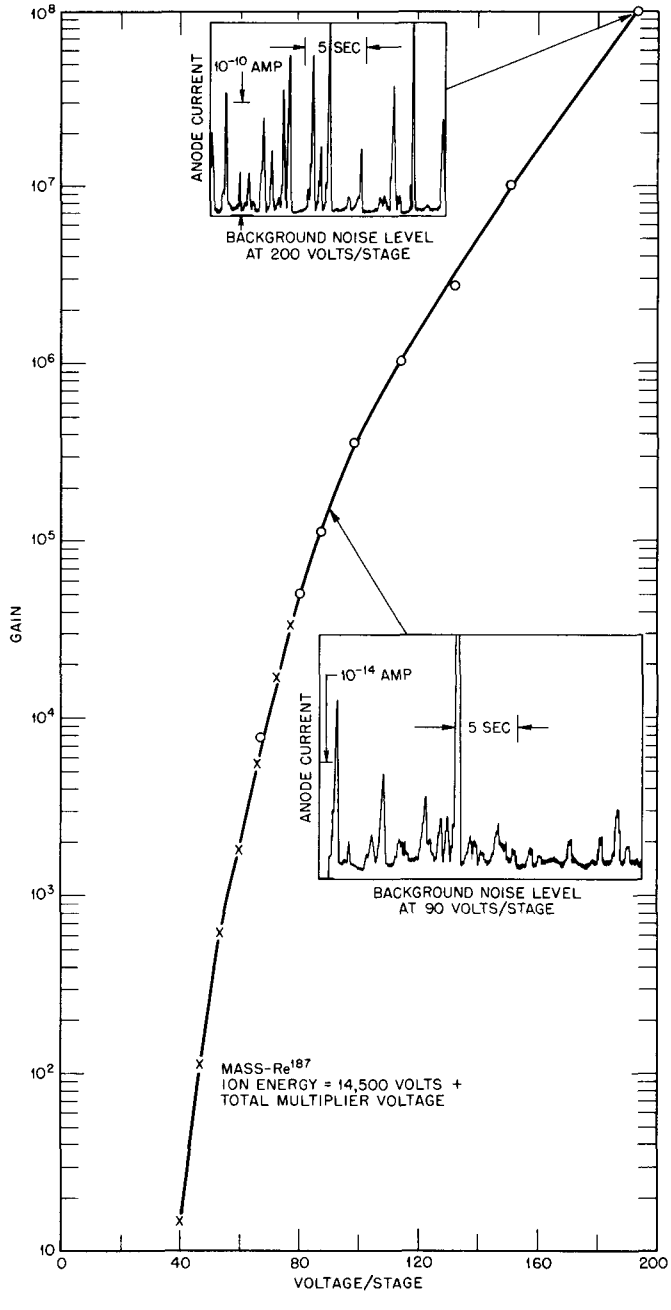


Fig. 13.19—Gain of 90°-cylinder 15-stage silver–magnesium electron multiplier.

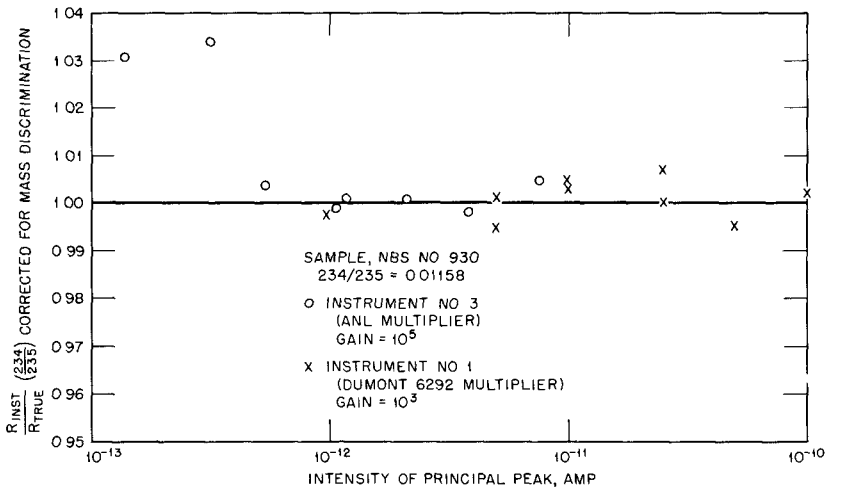


Fig. 13.20—Isotopic ratios vs. ion-current intensity for linearity check. Two examples of linear Electron Multiplier.

vation procedure, is basically the two-step procedure described by Rappaport,[48] which consists of vacuum baking at 550° C, exposure at 500°C to water at dry-ice temperature and then to oxygen at 10^{-2} torr. The first dynode is movable so that one part can be used for highly radioactive samples and another section kept clean and moved into position in cases where the highest sensitivity is desired; the section for use with radioactive samples is located behind a shield plate to prevent the activity from causing background counts in the multiplier. The gain vs. dynode voltage and noise characteristics are shown in Fig. 13.19. The mass discrimination for uranium is 0.3 per cent per mass unit at mass 238. The linearity of this multiplier for currents between 10^{-15} to 10^{-10} amp is shown in Fig. 13.20. (Note that the lowest current of 10^{-13} amp shown in the figure is for the principal peak intensity.)

The stability of the gain with time of this 15-stage silver–magnesium multipliers is as follows: Freshly activated surfaces installed in the vacuum within 4 hr have a gain as high as 10^8 to 10^9 for 300 volts per dynode but lose this gain within one week down to about 10^7. Thereafter, the gain is essentially stable for years, tolerating many periodic exposures to dry nitrogen or helium at atmospheric pressure for short periods of less than an hour. The gain is easily destroyed by exposure to low partial pressures of mercury or by sputtering caused by voltages left on with only partial vacuum. Baking does not reactivate the silver–magnesium.

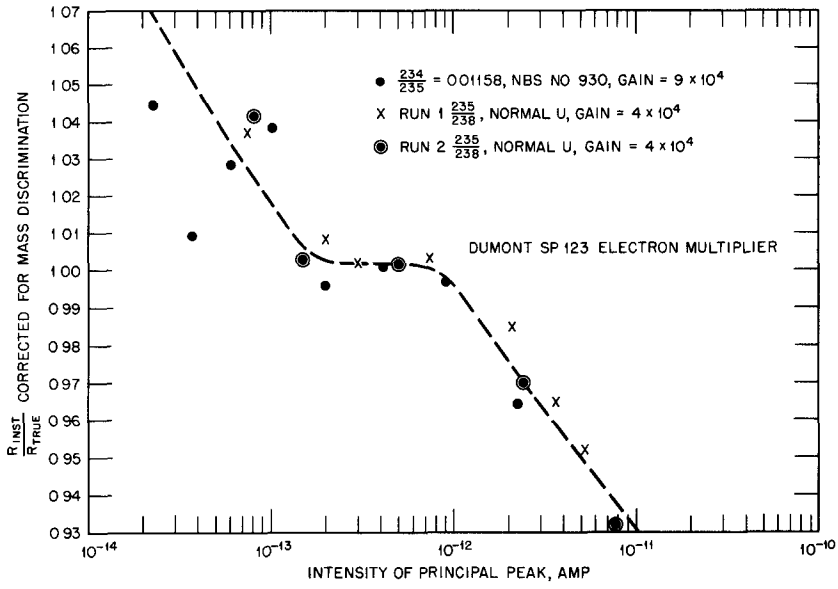


Fig. 13.21—Isotopic ratios vs. ion-current intensity for linearity check. Example of non-linear Electron Multiplier.

Other versions of this instrument have utilized commercial electron multipliers, such as the semifocused 90°-cylinder type* [46, 47] and the nonfocused venetian-blind type.†[49] These units usually come sealed in an envelope meant for photomultiplier use and can be obtained with activated silver-magnesium dynodes and without cesium activation of the photocathode. The multiplier unit is removed from the envelope and installed in the collector chamber with a shielded collector mounted and insulated separately from the other dynodes. Both types have been used with a gain between 10^4 to 10^5 over a period of several years with approximately 500 sample changes. During the sample changes the multiplier was exposed to dry nitrogen and/or helium at atmospheric pressure for from 15 min to several hours. The mass discrimination for uranium of instruments using these multipliers has usually been about 0.4 per cent per mass at mass 238.

Some multipliers exhibit a nonlinearity for high ion currents, as illustrated in Fig. 13.21. This nonlinearity is independent of gain, indicating that it is produced at the first dynode. The effect is in the direction that increases the secondary-electron emission at higher ion currents. The linearity of two other multipliers (including the large-size multiplier shown in Fig. 13.18) from 10^{-15} to 10^{-10} amp, as shown in Fig. 13.20, may be explained by the ion current in these cases hitting over a larger area.

*Allen B. DuMont Laboratories, Inc., type SP 123.
†Electric and Musical Industries, Ltd., type 9603.

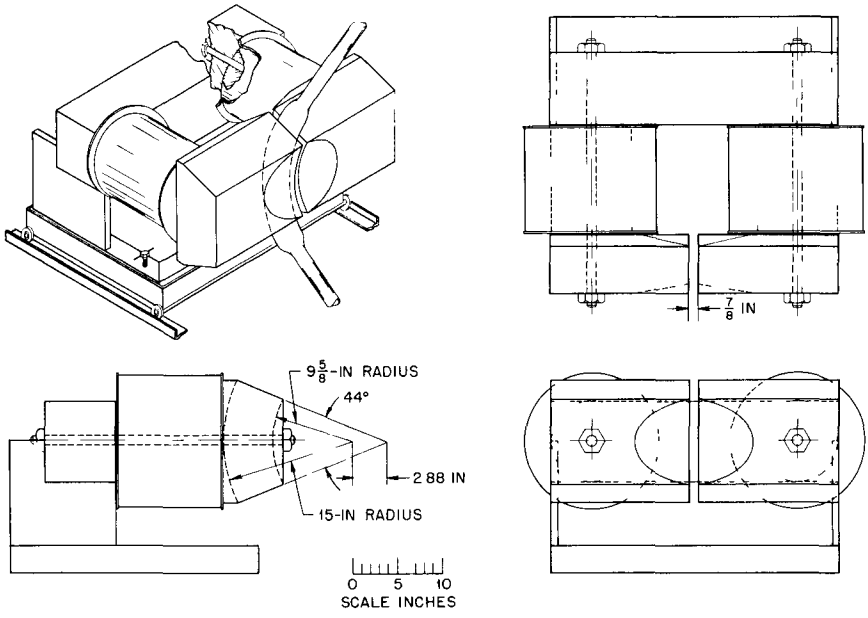


Fig. 13.22—Electromagnet with 44° sector for 12¾-in.-radius mass spectrometer (after design of M. G. Inghram).

Another nonlinearity effect occurs with most multipliers for output currents greater than 10^{-7} amp and is similar to a fatigue or saturation effect in the final high-current dynodes. This effect has time-dependent characteristics similar to thermal effects and, in general, amounts to a several per cent decrease in gain over a 5-sec interval but recovers after the high-intensity ion current is removed. When a multiplier is used for current amplification, a gain of 10^4 to 10^5 is adequate Higher gains do not give useful higher sensitivities and, because of the fatigue effect, will limit the upper limit of ion currents that can be measured.

Another important characteristic of the multiplier is that the gain be constant as the ion beam is scanned across the collector slit; that is, with a collector slit wider than the image, there should be flat-topped peaks. If this condition does not exist, the mass discrimination may be excessively variable and not reproducible in successive analyses. The ion beam is directed to the region of the first dynode, where the gain is constant with position, by the beam deflector plates shown in Fig. 13.18.

(h) *Magnet.* (1) *Electromagnet.* Figure 13.22 is a view of the electromagnet. The gap is $\frac{7}{8} \pm 0.001$ in. The pole faces, as well as the other parts of the yoke circuit, are made from Armco iron. Each

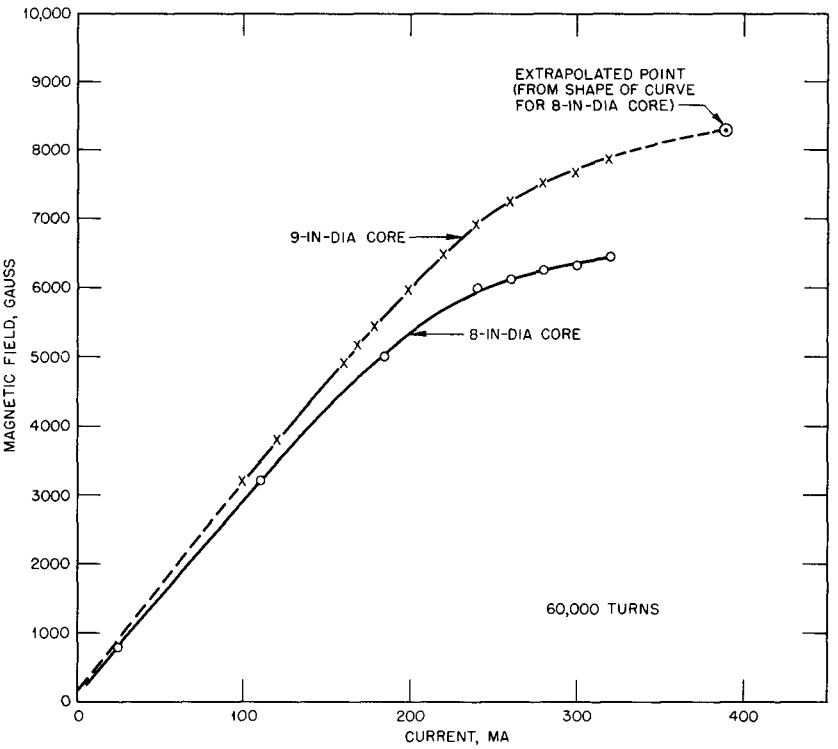


Fig. 13.23—Magnetic field vs. current for a 12-in.-radius electromagnet.

coil has 30,000 turns of No. 22 heavy Formwar wire insulated for 4000 volts. The magnetic-field strength as a function of current is shown in Fig. 13.23. The uniformity of the field across the pole face is shown in Fig. 13.24. A plot of the fringing field along the axis of the analyzer tube is shown in Fig. 13.25.

(2) *Permanent Magnet.* Figure 13.26 shows a permanent magnet designed by Inghram, Stanton, and Johnson which is used with some models of this machine.[33] This drawing shows the 8° wedges that are cemented to the pole faces to convert the magnet to a 44° sector. The maximum field is 8300 gauss. This magnet employs a shunt mechanism for varying the field down to 1400 gauss. Each of the two Alnico-V sections is made up of six pieces for a total length of 8 in. The Alnico-V area is 136 sq. in., over 5⅓ in. of the length and tapers to 120 sq. in. at the pole-face junction. Pie-wound coils, 32 in all (16 each side), are slipped over the Alnico-V sections after the magnet is partially assembled. Each coil consists of two coils, wound in parallel, of 215 turns each with No. 16 heavy Formwar (resistance 3.3 ohms) insulated for 2000 volts. For magnetizing the Alnico-V, these coils are all put in parallel across a d-c arc welder

with a current of 600 amp for 5 sec. After they have been magnetized the coils are all put in series, and a 0- to 1-amp 200-volt supply is used to vary the magnetic field electrically ± 1.5 per cent. This current can be supplied as a sweep field from 0.10 amp/sec to 0.001 amp/sec, which corresponds to 1 to 0.01 per cent of mass per second.

A plot of the fringing field along the optical axis is shown in Fig. 13.25. This field is considerably less than that of the electromagnet

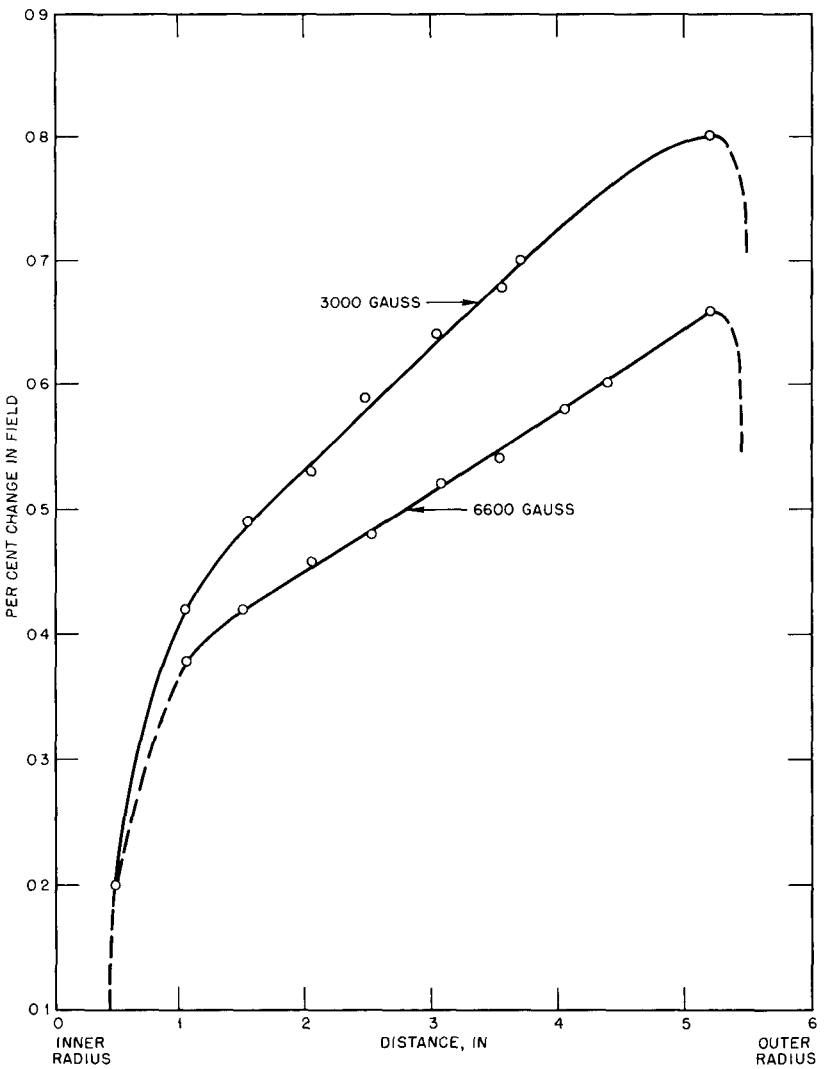


Fig. 13.24—Uniformity of the field in the air gap of a 12-in.-radius mass spectrometer.

because the magnetizing forces are located close to the pole faces and there is partial shielding by the box yoke.

(i) *Vacuum Lock.* Various types of vacuum-lock systems for introducing samples into the ion source rapidly without disturbing the vacuum are in use.[35, 50, 51]

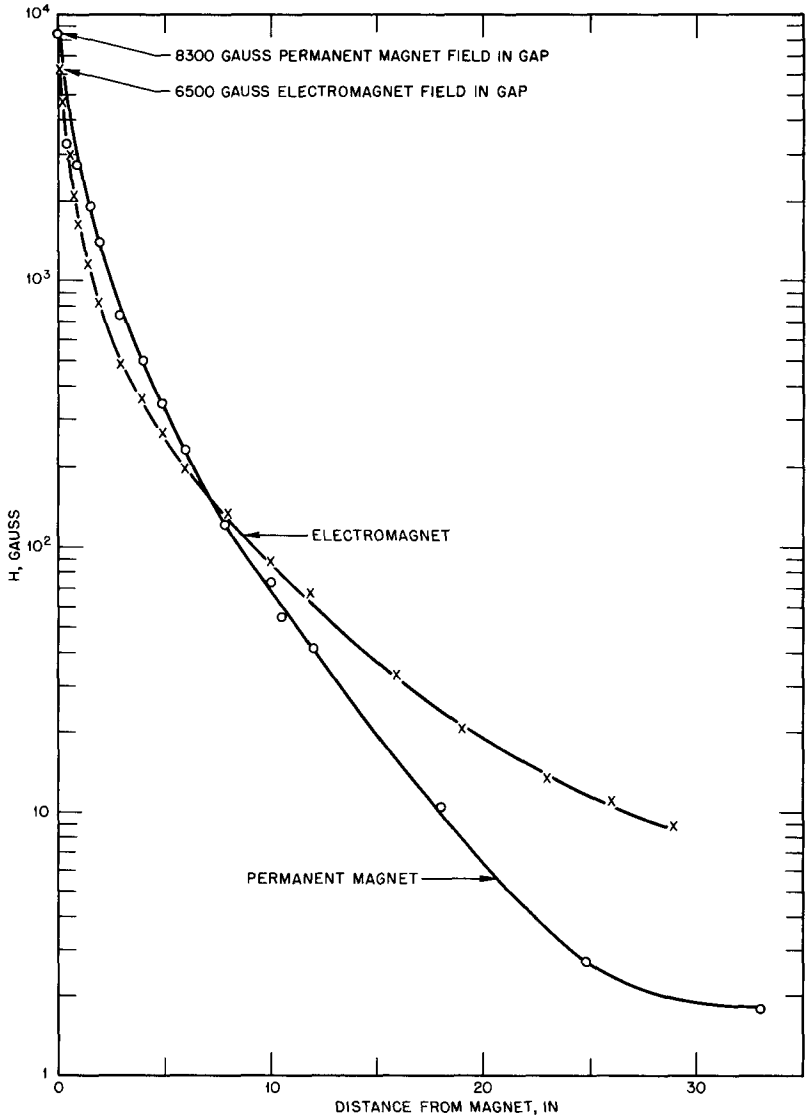


Fig. 13.25—Fringing field along the optical axis of a 12-in.-radius mass spectrometer.

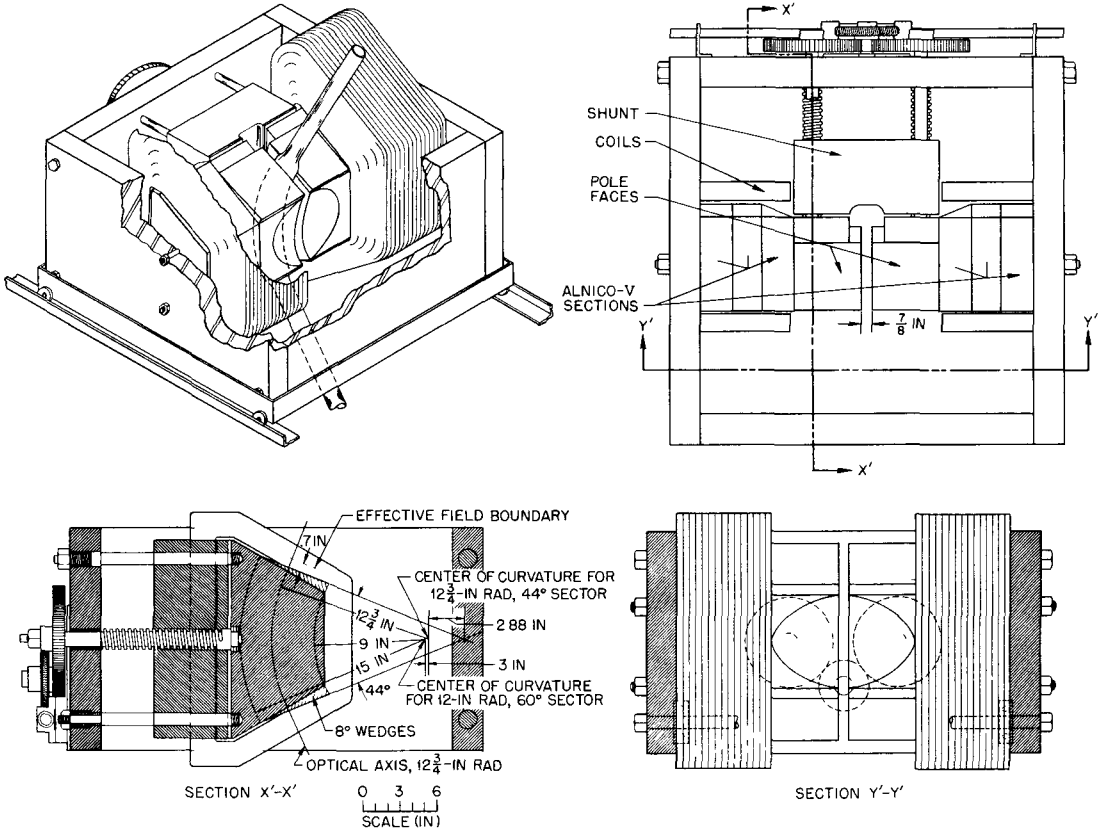


Fig. 13.26—Permanent magnet with 44° sector for 12¾-in.-radius mass spectrometer. (Modified from 60° sector after the design of M. G. Inghram, H. E. Stanton, and H. Johnson.)

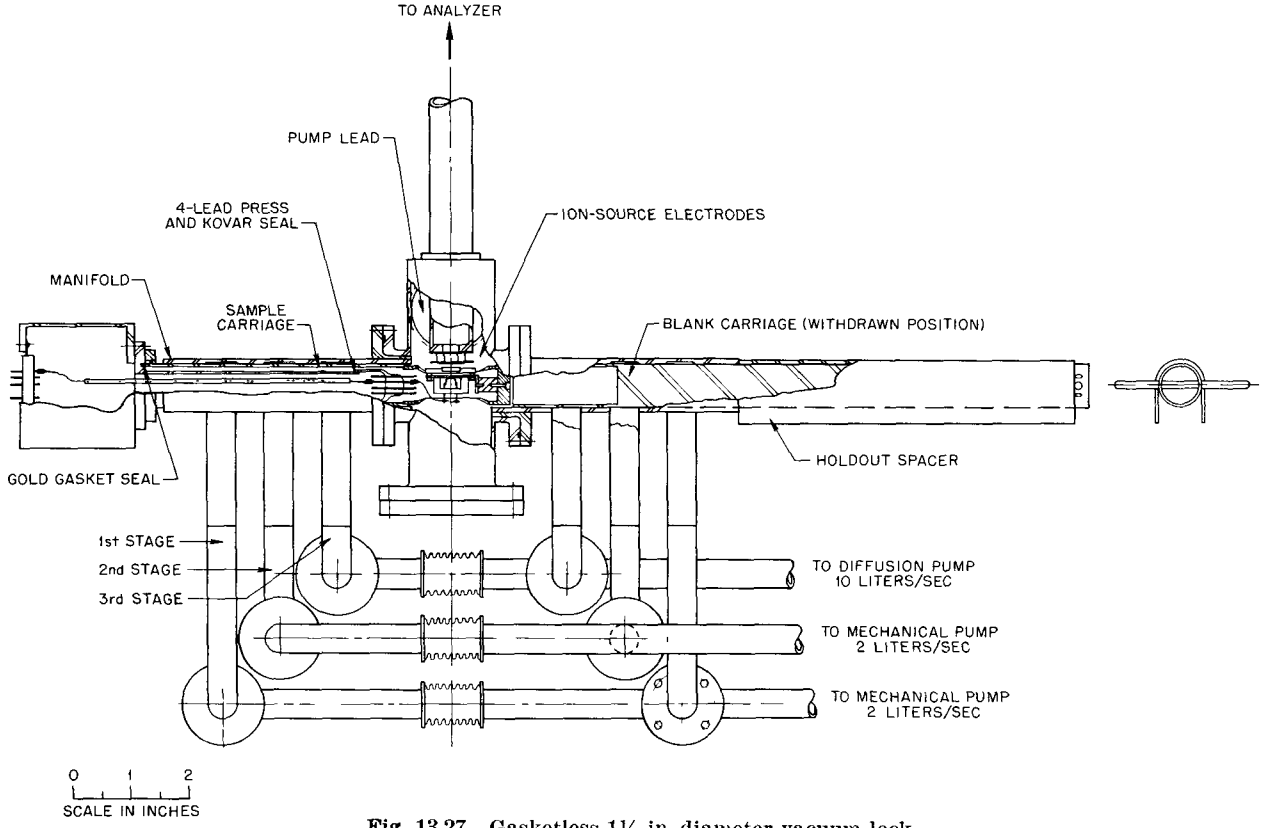


Fig. 13.27—Gasketless 1½-in.-diameter vacuum lock.

Figure 13.27 is an assembly drawing of a gasketless 1½-in.-diameter vacuum-lock system for introducing samples into a single-filament mass spectrometer. In this system the part of the ion source containing the filament on which the sample is loaded, the anode plate, and one focusing electrode are mounted on the end of a tube (carriage), which is precision machined to fit with very close tolerance (0.0005 in. to 0.0010 in.) into an opening (manifold) extending from the side of the source chamber. There are three regions of the manifold where the inside diameter is enlarged and pumping leads are attached. Another manifold, which is the mirror image of the one in which the carriage is introduced, is mounted on the opposite side of the source chamber. The first two pumping positions on each manifold are pumped by mechanical pumps, the third, by a diffusion pump. A blank rod occupies the inside of the manifold opposite the one containing the sample carriage. When a sample is to be changed, a blank carriage is inserted into the manifold opposite the sample side and is pushed in; it pushes the blank rod and sample carriage out of the unit so that the sample carriage can be removed. The blank rod now fills the opening in the sample-manifold side. The sample is changed, and the sample carriage is inserted. It pushes out the blank carriage. Both ends of the blank rod are cupped to surround the ion-source section projecting from the sample carriage so the restrictions between pumping ports will not be bypassed.

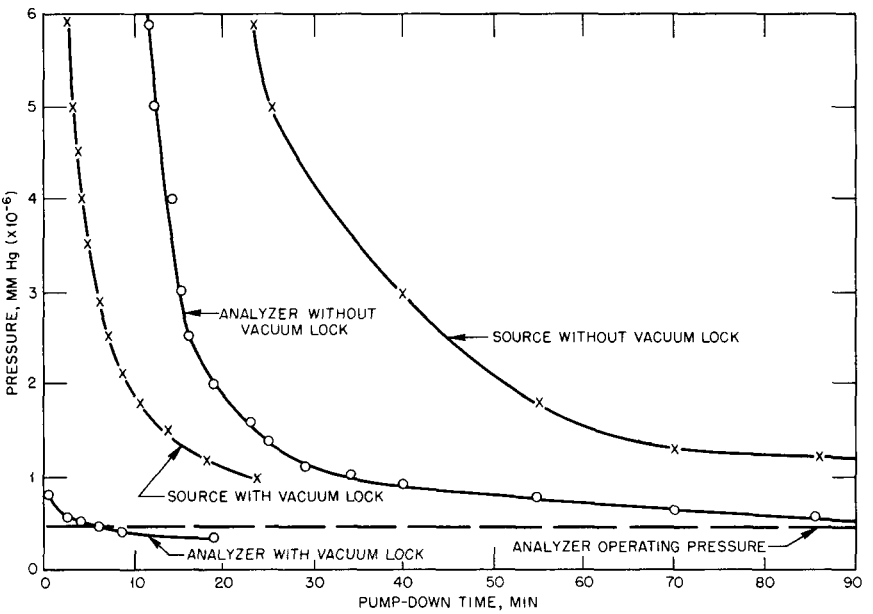


Fig. 13.28—Comparison of pump-down time with and without vacuum lock.

With very close clearance between the carriage sections and manifold (between 0.0005 and 0.0010 in.) and no gaskets, a small continuous inleakage of air is permitted. The contribution of the pressure in the ion source due to this inleakage is negligible because of the three differential pumping stages. The pressure decreases by about a factor of 10^3 between each stage.

The partial pressure in the ion-source region resulting from the inleakage is estimated at 10^{-9} torr, which is negligible compared to the contribution from outgassing. While the carriage is being inserted, there is a momentary pressure surge at each stage as the volume inside the carriage is pumped out. The pressure decrease in both source and analyzer regions after introducing a sample is shown in Fig. 13.28. The choice of materials is very important to prevent galling and seizing of the carriages with such close clearances. The manifold is made from stainless steel hardened on the inside surfaces by the Malcomizing (nitriding) process; the carriages are chromium-plated K-Monel or Inconel.

Machining procedure

Manifold

1. Rough machine.
2. Stress relieve.
3. Weld.
4. Stress relieve.
5. Finish machine to within about 0.005 in.
6. Grind to within 0.002 in. of final inside diameter; Malcomizing causes surface growth of 0.0005 to 0.002 in. and only penetrates about 0.005 in. for 300 series stainless steel.
7. Malcomize inside surface; to prevent Malcomizing on other surfaces plate with 0.003 in. fine-grain copper plate.
8. Finish grind to size.
9. Hone inside diameter with Sunnen hone machine.

Carriage

1. Rough machine.
2. Stress relieve.
3. Machine to 0.005 in.
4. Stress relieve.
5. Grind to 0.002 in. under final outside diameter.
6. Chrome plate 0.007 to 0.008 in. thick.
7. Finish grind to size.
8. Lap with size-control machine using roll laps.
9. Polish to mirror finish with Al_2O_3 and felt.

The electrical leads to the source electrodes are brought in by means of a multiple-press Kovar seal through the inside of the carriage.

Figure 13.11 is a scale drawing of the vacuum-lock source electrodes. The grounded defining slits are mounted permanently in the source chamber. The potential on the single focusing electrode is about 600 volts negative to the anode with an accelerating potential of 8000 volts; it essentially forms a cathode lens for ions emitted from the filament, with the cross-over image located at the defining slit.

This particular size of vacuum lock is adequate for simple or single-filament surface ionization but is too small for a multiple-filament source where the much greater wattage dissipation (30 to 50 watts) causes electrical leakage of pyrex insulators and arcing.

13–2.3 Single-filament or Simple Surface Ionization

(a) *Sample Preparation and Loading.* A uranium sample for a surface-ionization ion source may be easily prepared from many different chemical forms, such as the metal or oxide, or from compounds, such as nitrate, chloride, sulfate, or perchlorate. In the standard procedure a 0.05*N* to 2*N* nitric acid solution is made at a concentration of about 5 mg of uranium per cubic centimeter. If the total uranium in the sample is less than several milligrams, special care is taken to prevent the possibility of contamination of the sample with other uranium or uranium-containing material. For simple surface ionization, solutions of chloride, sulfate, or perchlorate may be loaded onto the filament as well as the nitrate; however, the nitrate is preferred if the sample is being prepared from an insoluble form, such as the metal or oxide. In some cases solutions of sulfate or phosphate cause trouble.

In general, the uranium need not be pure, and in most cases a satisfactory analysis can be obtained with up to approximately five times as much other inorganic materials present, such as aluminum and zirconium, which are common alloying metals in reactor work. In some cases difficulties are encountered with excessive amounts of other substances. These difficulties are of two types:

1. The extraneous substances cause interfering peaks in the uranium spectrum. Two known examples are: (1) calcium, which, if present in excessive amounts, will yield $CaTaO_3^+$ peaks that overlap the UO_2^+ spectrum, and (2) sodium silicates, which, if present in excessive amounts, produce peaks that interfere with the UO_2^+ spectrum.
2. Excessive amounts of some refractory materials can inhibit the surface ionization of uranium so that the sensitivity is greatly reduced. This is true of aluminum or zirconium when more than 80 per cent is present.

Where the amount of other substances present in the sample is so excessive as to cause trouble, a simple purification is made.

Two procedures in common use are described below:

Procedure 1. Ether Extraction. One to ten milligrams of the sample is transferred to a 15-ml centrifuge tube and dissolved in 1 ml of 2*N* nitric acid; then 1 ml of a saturated solution of aluminum nitrate is added. Two milliliters of diethyl ether is added, and the tube is shaken. After the solution has been centrifuged, the ether layer is drawn off with a pipet and transferred to a 1-ml centrifuge tube. The ether is evaporated to dryness, and the residue is dissolved in 0.05*N* nitric acid to give a concentration of 5 mg of uranium per milliliter.

690–457 O—64——67

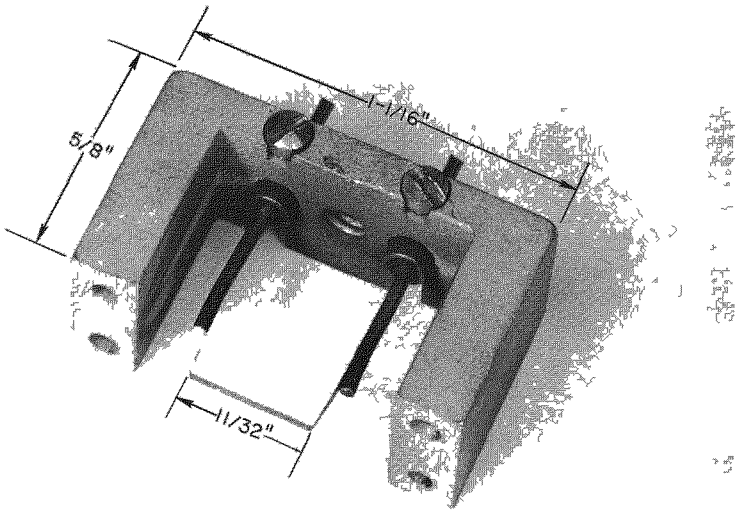


Fig. 13.29—Simple surface-ionization filament mounted in support.

Procedure 2. Ion Exchange. A ¼-in.-ID ion-exchange column is filled to a height of 6 in. with Dowex resin and is washed with water until all fine particles have been washed through. The column is then washed with 8*N* hydrochloric acid until equilibrium is reached. The sample of the aluminum–uranium alloy containing 1 to 10 mg of uranium is dissolved in 1 ml of 9*N* to 12*N* hydrochloric acid, and the solution is then run through the column. The column is treated with 25 ml of 9*N* to 12*N* hydrochloric acid to remove the aluminum. The uranium is then eluted from the column with 10 ml of 0.1*N* hydrochloric acid, and the solution is evaporated to dryness. The residue is dissolved in 0.05*N* nitric acid to give a concentration of 5 mg of uranium per milliliter

Figure 13.29 shows the filament used for simple surface ionization mounted in the filament support. A new filament with new insulating terminals is made up for each new sample. The filament holder is cleaned after every run by boiling it for 5 min in 8*N* nitric acid with 0.5 per cent hydrofluoric acid. For uranium samples a 0.001-in.-thick by 0.030-in.-wide tantalum ribbon filament is used. The filament is spot welded to insulating terminals* using the jig shown in Fig. 13.30 (filament partially bent).

After the filament has been spot welded and bent in the jig, the filament is mounted in the holder. The holder, with the filament, is

*Manufactured by The Fusite Corp., Cincinnati, Ohio

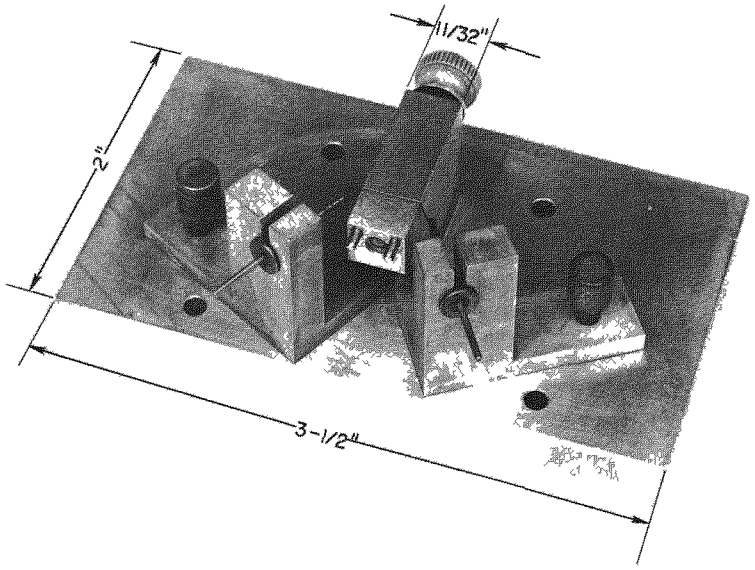


Fig. 13.30—Jig for bending tantalum ribbon.

then mounted on a plate identical to the mounting plate in the mass-spectrometer ion source, and the filament is adjusted by eye to the proper location. The filament should be flat and well centered, and its location relative to the top of the anode plate should be set correctly, as shown in Fig. 13.11. The side sections of the U-shaped filament provide for flexible elements which allow expansion of the center horizontal section without buckling when the filament is heated to the high temperatures at which ion emission occurs.

For most routine single-filament analyses, it is not necessary to pretreat the filament material. Although the filament material does contain hydrocarbon impurities, these do not cause large enough peaks to interfere with the uranium mass spectrum at the high ion intensities normally used for this type of analysis. Natural uranium is an impurity in the tantalum filament in amounts of 10^{-10} g, but this is negligible compared to the sample (10^{-4} to 10^{-5} g). It is important that the filament material be stored and handled so as not to become contaminated with uranium in the laboratory.

When the uranium sample is to be loaded on the filament, the holder containing the new prepared filament is mounted in a hood or dry box in a setup in which electrical contacts from a power supply are made to the filament (Figs. 13.31 and 13.32). A current through the filament of about 2 amp is set. A large watch glass is mounted in

between the filament and an overhead lamp; it is frequently washed to remove any uranium sprayed on it from previous loadings which might fall off and contaminate the next sample. This cleaning is especially necessary when the uranium sample being loaded has an isotopic distribution quite different from the previously loaded samples.

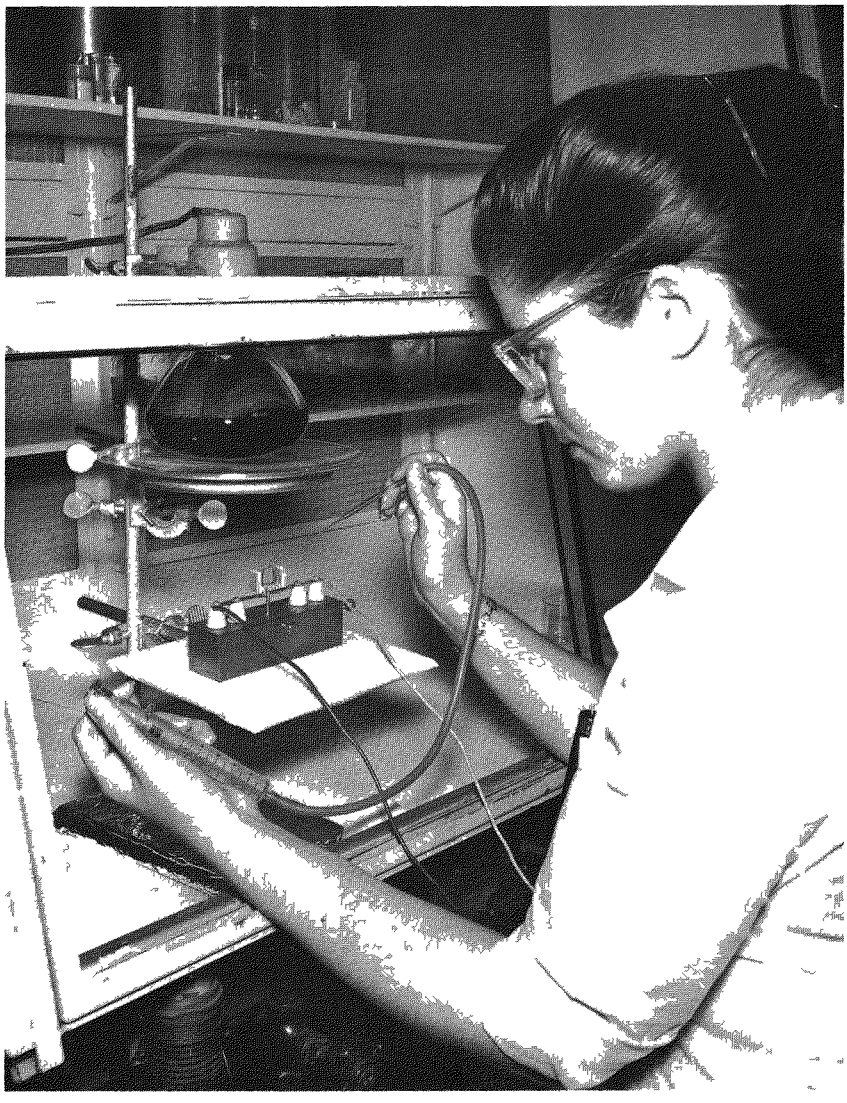


Fig 13 31—Setup for loading sample on filament

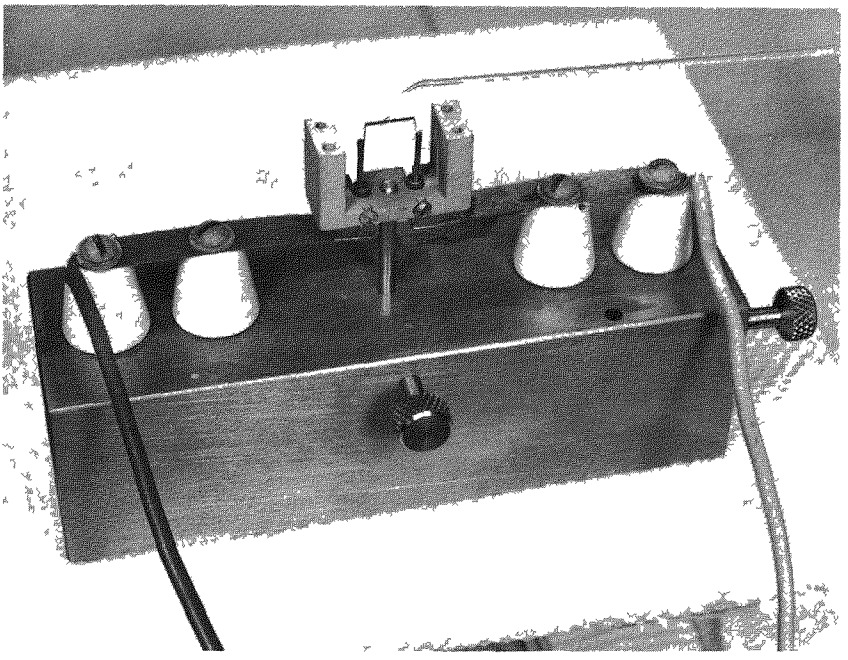


Fig 13 32—Close up of sample loading setup

About 50 to 100 μg of the uranium sample is deposited on the filament with a small throw-away pipet drawn from 5-mm pyrex tubing (Fig. 13.33). The solution is deposited in small amounts of about 2 λ at a time until the entire amount has been deposited; then it is evaporated to dryness. When the solution has evaporated, the filament current is increased to 2.5 to 3.0 amp; this current causes decomposition of the uranyl nitrate to UO_3 (red orange).

The amount of uranium sample needed for an isotopic analysis depends on two basic factors: (1) the isotopic concentration and desired range of concentration to be analyzed for and (2) instrument sensitivity, including ionization method and ion-detector sensitivity.

With a basic 12-in.-radius 60°-sector machine having a 0.006-in. source slit and 8000 volts accelerating voltage, a UO_2^+ ion beam of 5×10^{-11} amp intensity from a 50-μg sample of uranium will last for approximately 1 to 2 hr. With a standard high-current gain negative feedback amplifier, or a vibrating-reed electrometer without electron-multiplier amplification, a minimum detectable current of 10^{-15} amp corresponds to about 10^{-9} g of uranium in the sample (see Table 13.4). Ion currents of 10^{-10} amp or greater can be obtained for short periods of time; these currents enable higher sensitivities.

The loading of excessive amounts of samples (greater than 10^{-4} g) over the amount needed is avoided to minimize deposits building up

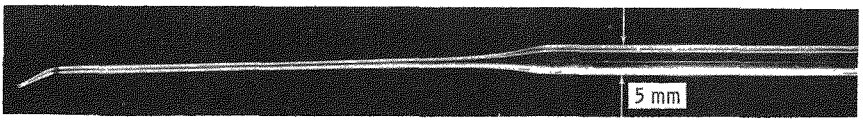


Fig. 13.33—Pipet for depositing uranium sample on the filament.

on the source plates. Heavy sample deposits cause arcing, instabilities, and possible contamination of future samples of different isotopic abundance.

Contamination is likely to occur to the extent of 10^{-5} of the total accumulated amount of a given isotope deposited in an ion source. For example, a 50-μg sample of uranium in the range of normal abundance may be analyzed with contamination less than 5×10^{-9} g following the analysis of approximately ten 50-μg samples of highly enriched U^{235}.

Where hazardous alpha radioactivity is a problem, such as with plutonium, the multiple-filament or V-filament surface-ionization technique is preferred because of their increased sensitivity (about 100). With these filaments less sample is required (see following section). The sensitivity of the simple single-filament technique for plutonium giving PuO^+ is about two to three times that for uranium as UO_2^+ ions. Thus, with a simple faraday cage detector, a satisfactory analysis can be made on 20-μg samples; with electron-multiplier detection the sensitivity is increased 100 times, and 0.2-μg samples can be analyzed.

Proper personnel protection is needed in handling plutonium samples. Samples should always be prepared and loaded in a hood with glass-front protection. For routine analysis the region where the filament is inserted in the spectrometer should be surrounded by a draft box to catch and remove any loose plutonium particles. With care an occasional sample of up to 10^7 disintegrations/min of plutonium can be analyzed without elaborate hooding of the instrument, etc. The ion-source parts should be cleaned before the accumulated amount of plutonium exceeds 0.1 to 1.0 mg. The cleaning is done by boiling parts in 8*M* nitric acid and 0.5 per cent hydrofluoric acid.

Because of the high activity of U^{232} (10^{-9} g corresponds to about 10^7 disintegrations/min) the single-filament technique without electron-multiplier detection is too hazardous to use. More sensitive techniques, such as the multiple-filament technique and electron-multiplier detection, are recommended.

On the other hand, up to 100 samples of 10^{-5} g of U^{233} (10^5-year half life) can be analyzed without hazardous conditions resulting. In the routine analysis of samples containing U^{233}, it is recommended

that the ion-source parts be cleaned after an accumulated 1 mg of U^{233} has been analyzed, or 10^7 disintegrations/min of total alpha activity if U^{232} is present to more than 0.02 per cent of the U^{233}.

Where beta or gamma activity is involved, e.g., as an isotope of an element being analyzed or from fission products from irradiated uranium, the amount of activity considered safe is that which will produce less than 1 mr/hr at 1 ft from the ion source. For fission-product impurities in a uranium sample, this level corresponds to approximately 0.004 mc of beta or 0.2 mc of gamma activity per 100 μg of uranium. Thus a sample of 100 μg of mainly U^{235}, with 10 per cent burn-up and 100-day cooling, would require at least a 10^3-fold decontamination of fission products.

(b) *Instrument Operation.* After a sample has been loaded onto the filament and evaporated to dryness, it is mounted in the instrument ion source. Before the sample can be run off, the vacuum in the ion source must be below 5×10^{-6} torr, and that in the analyzer, below 5×10^{-7} torr. The vacuum requirement of 5×10^{-7} torr in the analyzer is based on the assumption that the scattering of an 8-kv ion beam will be less than 2×10^{-4} one mass unit away at mass 235. At 15 kv a pressure of 10^{-6} torr will result in scattering less than 2×10^{-4} (see Fig. 13.17). The maximum allowable operating source pressure of 5×10^{-6} torr is a reasonable upper limit to prevent arcing with the high accelerating voltages used in the ion source. Arcing in the ion source is avoided because of the possible contamination of the sample by material deposited from previously run samples which might be volatilized in the arc. These vacuum limitations are for the average routine uranium sample. Higher or lower analyzer pressures may be tolerated as determined by the abundance sensitivity required. The analysis of samples where the ratio of U^{236}/U^{235} or Pu^{240}/Pu^{239} is very small, as in breeding gain studies, requires high abundance sensitivity and a vacuum in the 10^{-8} torr range to minimize scattering in a single-stage instrument. Analyses of this sort are done with either the multiple-filament or V-filament technique to avoid interference by oxygen isotopes.

The sample is degassed prior to running the analysis; this can be done while the instrument is being pumped down to the necessary operating vacuum. With a vacuum-lock system, the vacuum in the ion-source region decreases to a low enough value (less than 5×10^{-6}) within 10 min after the sample is installed to degas the filament and sample (see Fig. 13.28). This pretreatment is carried out for 5 min with 2 amp through the filament, and then the source is allowed to cool for 5 min with the filament off. Without a vacuum-lock system, where the instrument is let up to atmospheric pressure with helium or

dry nitrogen for sample insertion, the pressure decrease in the analyzer is slower and determines the time when the analysis can be started. While the analyzer is being pumped down, the source pressure is low enough after 20 min to degas the filament and sample at 2.0 amp. After an analyzer pressure of 5×10^{-7} torr has been reached, usually 1½ hr from sample change, the analysis can be started.

The first objective is to detect enough ions so that the focusing adjustments can be made, i.e., source-electrode voltage adjustments and mechanical alignment if a vacuum lock is used. With some instruments this can usually be done with the ion beam of the sample material itself, UO_2^+ in the case of uranium. In this case an ion beam of 10^{-13} to 10^{-12} amp will appear at a current of about 2.5 to 3.0 amp for a properly focused source.

The magnetic field or accelerating voltage is either manually or automatically scanned over a wide mass range (±5 per cent) about the expected value until ions are detected. If the source ion gun is so out of focus that ions of UO_2^+ or any other masses in this region are not detected with the filament current as high as 3.0 amp, then it is best to look for alkali ions, such as potassium, which are copiously emitted at a lower filament current of 1.5 to 2.0 amp. After an ion beam has been detected, adjustments are made for maximum intensity. Usually the first ions of UO_2^+ which are observed have poor peak shape with a large high-mass tail and come in at relatively low temperatures. These ions are believed to be formed by a tertiary process which involves, first, the copious emission of alkali impurity ions which are accelerated through the ion-source optical system and release secondary electrons from ground-potential slits which then accelerate back through the ion source and bombard the UO_2-sample filament releasing UO_2^+ with excess kinetic energy. The filament current is increased slowly until the tertiary ionization dies out. The filament current is then increased until the intensity is high enough to measure the mass spectra accurately, and the source is refocused. In the case of many samples of uranium where as many as four isotopes with widely varying abundance are present, the ratio of the two most abundant isotopes, 235 and 238, is measured first at an intensity at which the peak heights can be measured to ½ per cent precision. At this intensity the smaller abundant isotopes, 234 and 236, may be too small to measure accurately. These are measured later at higher ion currents, and additional measurements of the 235/238 ratios are made.

The measurements are made by scanning the magnetic field over the desired isotopes at a slow enough rate so that the maximum intensity is recorded; the maximum intensity is determined by the time constant of the amplifier and recorder. For most systems using 2×10^{10} ohm

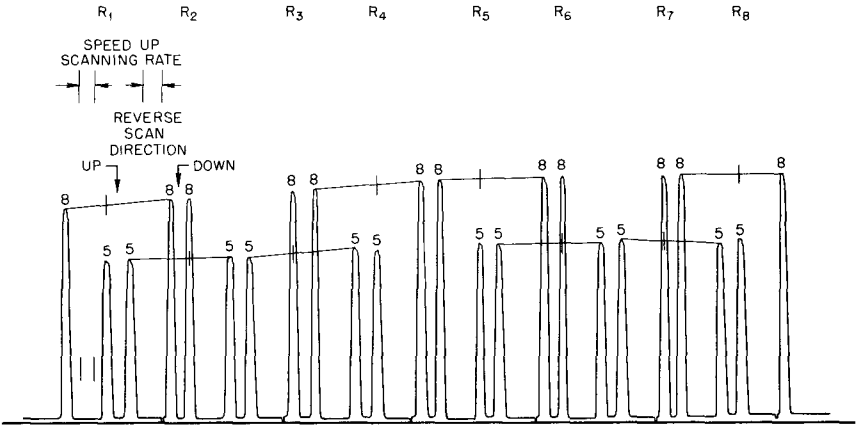


Fig. 13.34—Mass spectra of U^{238} and U^{235}.

input resistance, vibrating-reed electrometer current amplifier with a time response of less than 0.5 sec, and a 1-sec full-scale recorder, the scanning rate should be less than 4 masses per minute. Higher scanning rates are frequently used while scanning between peaks, and the rate is slowed long enough to record the peak tops. (In this connection, a wide flat-top peak is desirable such as is obtained using a 0.006-in. source slit and a 0.015-in. collector slit.) Because of the lack of regulation and the general instability of the ion intensity with time in surface ionization, the measurement of the several different isotopes as fast as possible will yield the best accuracy.

An important consideration in the scanning of the mass spectrum is that at least once during the analysis a scan is obtained of the valleys between peaks and at nearby unoccupied mass positions to determine freedom from impurities and other undesirable effects. The extent to which this is done depends on how routine the sample is.

Generally, about 12 spectra (Fig. 13.34) at a high enough intensity (greater than 10^{-13} amp for the mass in smallest concentration without an electron multiplier) and stability are sufficient to determine the ration to an internal precision of 0.1 to 0.2 per cent for one standard deviation (see Sec. 13–2.5).

13–2.4 Multiple-filament Surface Ionization

A multiple-filament ionization source [14] is shown in Fig. 13.12. The sample is deposited on one of the side filaments. The ionization process with this source is as follows: The filament on which the sample is deposited is heated to a temperature of 1500 to 2000°C; this heating causes the uranium to evaporate as UO_2 and UO. The center filament is heated to a much higher temperature (about 2500 to 3000°K for

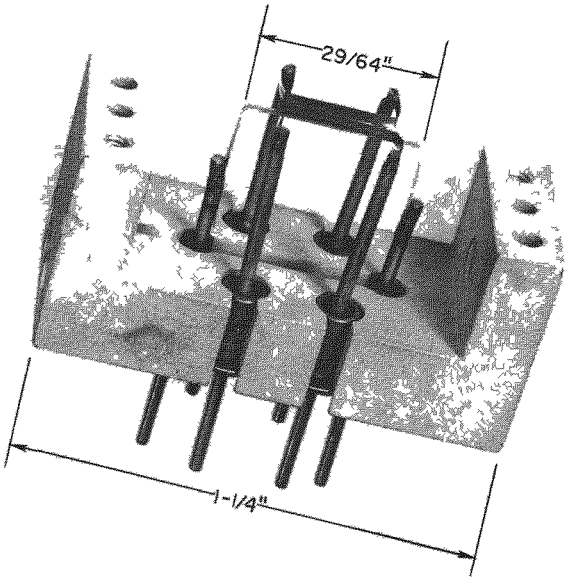


Fig. 13 35—Side view of a multiple-filament assembly.

tungsten, less than 2600°K for rhenium) than the sample filament. The molecules evaporating from the sample strike the hot center filament, and a fraction is ionized in accord with the Saha–Langmuir relation:

$$\frac{n^+}{n^o} \simeq A \exp -\left[\frac{(I-\phi)e}{kT}\right]$$

For substances with a higher ionization potential than the work function of the surface, ionization by the hot center filament is much greater than that at the temperature at which the sample is evaporated. (In addition, at this high temperature a large fraction of the UO_2 and UO molecules are reduced to the metal ions, eliminating interference by the oxygen isotopes in the uranium spectrum.)

Figures 13.35 and 13.36 are two views of a multiple-filament assembly. The filaments are made up in jigs (Figs. 13.37 and 13.38) that ensure the approximate correct shape. They are then finally adjusted by eye after they have been mounted in the holder to the positions shown in Figs. 13.12 and 13.36. The slit of the first drawing out plate, J_2, forms a fairly critical cathode lens; thus the relative positions of the filaments are quite important in obtaining the best focusing of ions coming off from the center filament and, hence, the highest sensitivity.

The most suitable filament materials are rhenium and tungsten. For the analysis of uranium, rhenium has several advantages over tungsten: (1) greater ionization efficiency because of a slightly higher work function (5.2 volts for rhenium vs. 4.58 volts for tungsten); (2) less, by several orders of magnitude, natural uranium and potassium polymer K_6, which interfere at masses 234 and 236, respectively; and (3) easier working and spot-welding (does not become brittle when

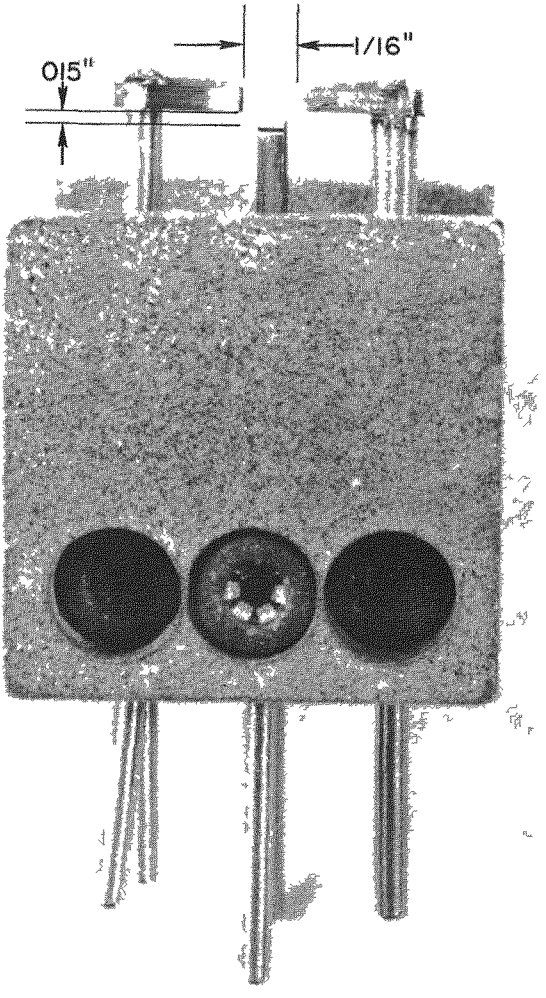


Fig 13 36—End view of a multiple-filament assembly

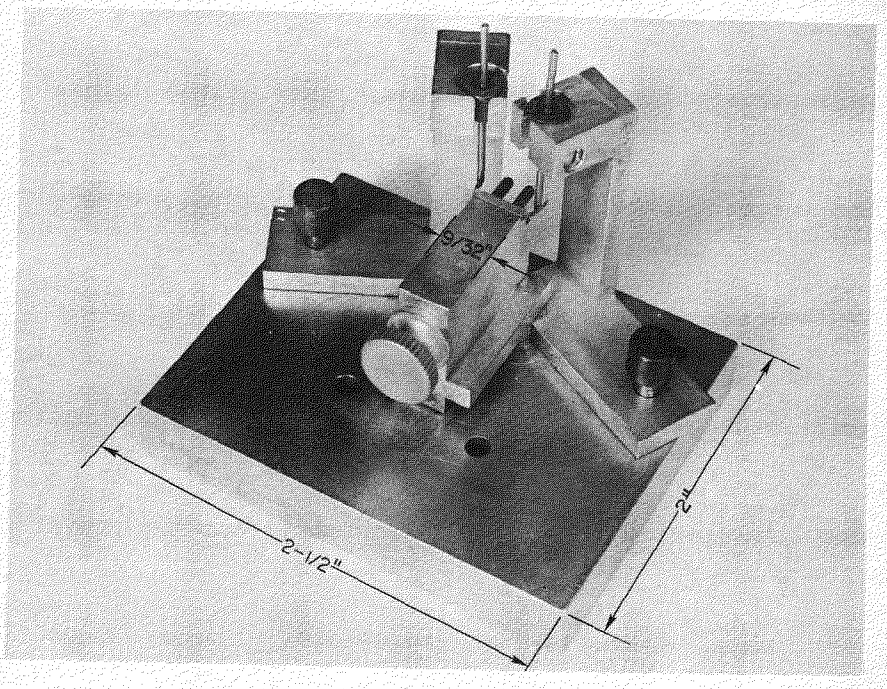


Fig. 13.37—View of side-filament shaping jig.

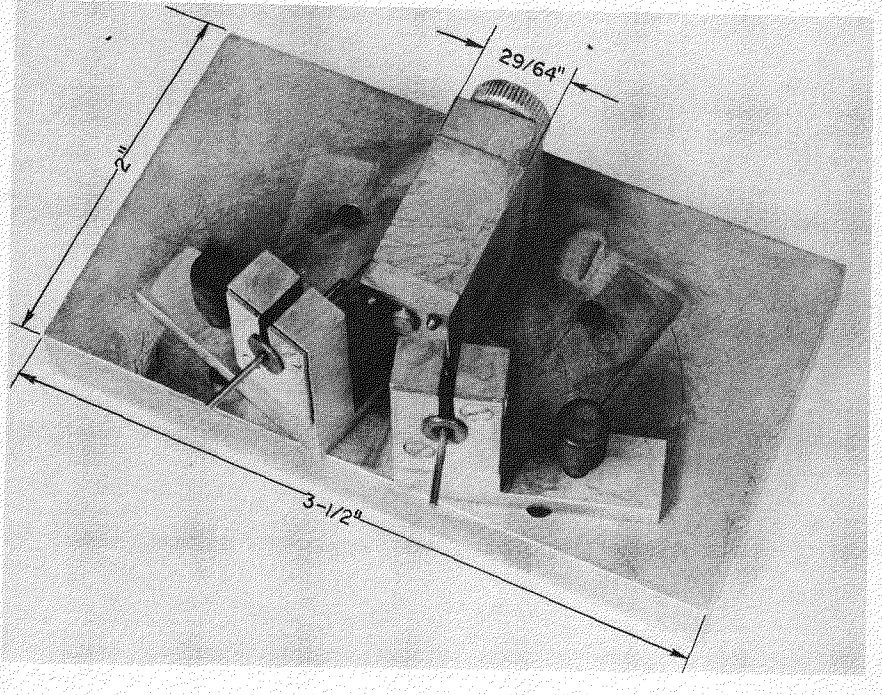


Fig. 13.38—View of center-filament shaping jig.

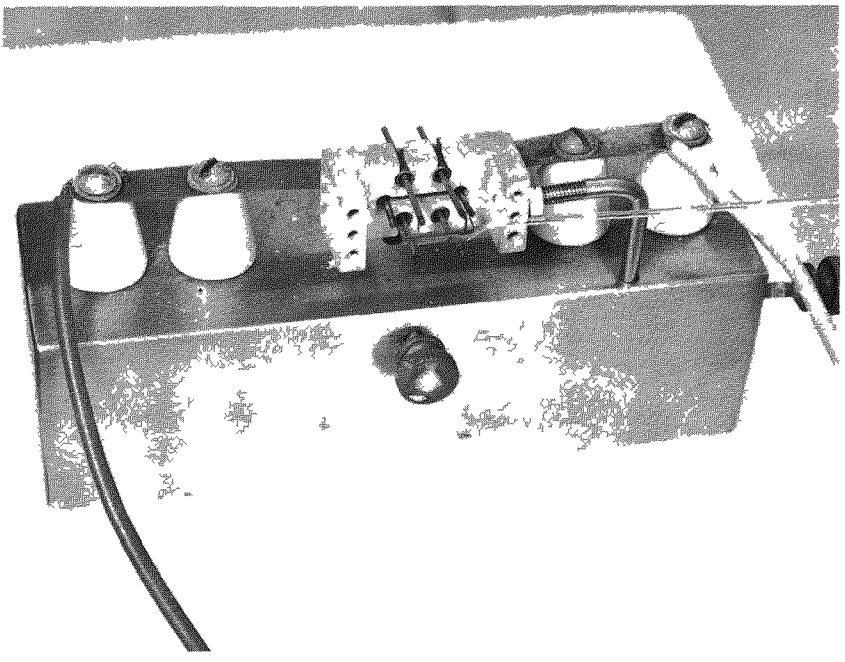


Fig 13 39—Setup for loading the sample on a multiple-filament assembly

heated). There are several difficulties with rhenium which appear to be the result of its higher vapor pressure compared to tungsten. First, at very high surface-ionization temperatures, the efficiency of ionization for uranium is reduced. This might be caused by the rhenium depositing and covering the sample and inhibiting the volatilization of uranium in some way. For this reason, rhenium center filaments should not be heated above about 2600°K. Second, the volatilized rhenium produces conducting deposits on insulators; thus the insulators must be shadowed from the center filament.

(a) *Sample Preparation and Loading.* The loading of the sample (Fig. 13.39) is similar to the procedure used in single-filament analysis, except, when the samples are very small (below 10^{-6} g) much greater precautions are taken to prevent contamination with other uranium. The reagents used to dissolve the sample must be of a high enough purity to contribute only a negligible amount of normal uranium.

The chemistry of the final steps prior to loading the sample on the filament is important in obtaining high ionization efficiency in the mass-spectrometer ion source and, hence, high-sensitivity analysis. The mechanisms of what happens to the sample in the ionization process and the effect of prior chemistry are not very well understood. Certain chemistry procedures lead to high sensitivity and others

apparently can cause the sensitivity to be less by factors of 10 to 100. A procedure that seems to work most often involves evaporation of the sample to dryness in aqua regia and dissolution of the residue in 0.05*N* nitric acid. For samples below 1 mg, a minimum quantity of both the aqua regia (200 μl) and 0.05*N* nitric acid (less than 50 μl) should be used. Loading from concentrated nitric acid should be avoided if rhenium sample filaments are used because the rhenium is readily attacked under such conditions, and this results in reduced volatilization of uranium.

In the application of the multiple-filament ion source to high sensitivity analysis, an important contamination problem is that by hydrocarbons, and special care is taken with the filament material, sample, and ion source to prevent this. The filament material as supplied always contains appreciable hydrocarbon impurities and may be pretreated before loading the sample to get rid of them. There are numerous satisfactory methods, such as vacuum baking the ribbon at 800°C or baking out the filaments in a separate vacuum system after they have been made up and mounted. It is even possible to remove these hydrocarbon impurities after the sample has been loaded and installed under high vacuum in the ion source by heating the center filament and then cooling. This cannot be done for samples of lead, thallium, or other highly volatile materials where the thermal radiation from the center filament is enough to volatilize the sample. The minimum treatment time and temperature has not been studied, but a procedure that works in most cases is:

1. Heat center filament at 3 to 4 amp for 2 to 12 hr (higher currents, shorter times).
2. Heat center filament ½ hr at 1 amp below setting for normal operating temperature (about 5.5 to 6.0 amp for 1.0-mil ribbon; current should not be high enough to appreciably shorten filament life by evaporation).
3. Cool filament ½ hr.
4. Start analysis of sample; usually hydrocarbons will still be detectable at this time, but they die out to a negligible amount when the temperature of the sample filament is high enough so that U^+ ions are observed. If the hydrocarbons do not disappear, the center filament is baked out again at normal operating temperatures (6.0 amp), and the source is allowed to cool for 1 hr.

This treatment method will require more frequent cleaning of the source, which after 20 or so samples becomes so dirty with hydrocarbon decomposition products that the treatment is no longer adequate.

Studier [31] has observed that uranium samples may be lost as volatile UO_3 if heated with as much as 10^{-6} torr of oxygen present. For this reason the elimination of hydrocarbon impurities by heating the

sample filament directly after installing it in the instrument and pumping down the equipment is avoided.

Small samples that have been through any process involving organic reagents should be treated to remove hydrocarbon material by either heating in air to 500 to 600°C or dissolving in perchloric acid and fuming to complete dryness. Heat-treatment in air may leave the sample in an oxide form that is difficult to bring into solution with nitric acid at room temperature; so a small amount of 0.05*N* nitric acid (less than 1 ml) is added, and the sample is evaporated to dryness at 100°C.

Finally, hydrocarbon peaks may result during an analysis as the result of the relatively massive wall of the source chamber warming up from the heat of the filament and giving off volatile hydrocarbons previously condensed on it. For this reason the source chamber is water cooled.

(b) *Instrument Operation.* The vacuum requirements for operation after the sample has been loaded in the multiple-filament assembly and installed in the ion source are much the same as described for single-filament operation, which is basically that a vacuum of less than 5×10^{-6} torr in the source region is necessary before any filaments can be turned on even for pretreatment or degassing of the sample. In the analyzer region a pressure of less than 5×10^{-7} torr is needed. Certain samples with very small concentrations of isotopes adjacent to principal mass peaks will require better vacuums. The pressure will rise during the course of the analysis because the heat of the filament will cause degassing; degassing will occur much faster than it does with single-filament ionization because the total wattage of the two filaments normally used in a multiple-filament source amounts to about five times that of the single filament.

Even if pretreated filaments are used, it is necessary to go through a degassing procedure before the sample can be run. This procedure serves to clean up any hydrocarbons not destroyed in the chemical treatment. A minimum treatment is to heat the center filament to a current of 0.5 amp less than the normal operating current, usually about 6.0 amp for 10 min. Then, the filament is turned off, and the source is allowed to cool for 10 min.

An important feature of the multiple-filament source is that the instrument can be focused and adjusted and the sensitivity can be checked with ions of the center filament material, such as rhenium or tungsten, without risking the sample as in single-filament operation. Figure 13.40 shows the intensity to be expected from rhenium and tungsten filaments as a function of filament current. (Note: This checking of ions from the center filament cannot be done for samples of lead, thallium, or other highly volatile materials where

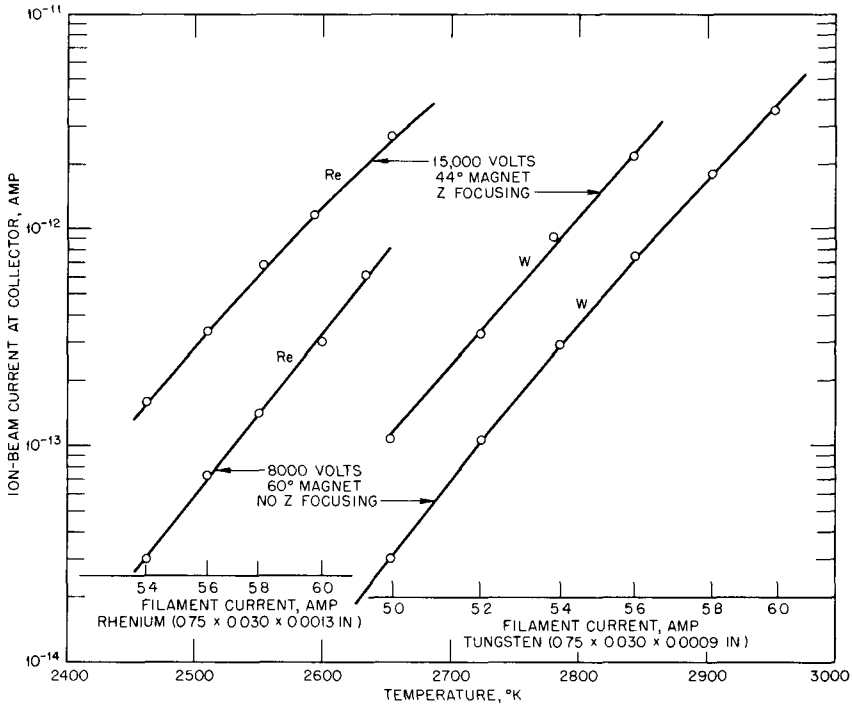


Fig. 13.40—Intensity of Re^+ and W^+ vs. temperature and filament current.

the thermal radiation from the center filament at temperatures above 1500°K is enough to volatilize the sample.) The preliminary focusing should be done fairly rapidly (5 to 10 min) and with the center filament at less than 2600°C to prevent excessive evaporation of rhenium, which may cover the sample and reduce the sensitivity.

In addition to focusing the source for maximum intensity, the presence of hydrocarbons can be checked. The defocusing action of this source, previously described, is checked. This property of the source is mainly dependent on the voltage on J_2 and on the voltage difference between J_4 and J_5. The grid collector facilitates this adjustment in that the instrument is set on a hydrocarbon peak in the vicinity of the rhenium spectrum so that the latter is monitored by the grid; then the J_2 and J_4–J_5 potentials are adjusted for minimum resolved peak intensity, at the same time a maximum grid signal is maintained. Many times the sample contains a small amount of hydrocarbons that give rise to impurity peaks before and during the preliminary heating of the sample which are too large to defocus completely; these disappear fairly soon before the uranium intensity reaches normal operating level. In general the treatment required

when hydrocarbon contamination is present depends on the amount present and the particular requirements of the sample.

After the necessary pretreatment and focusing have been carried out, the magnetic field and voltage are set to bring in the U^+ masses. With the center filament set at 5.0 to 6.0 amp, and while scanning, the current of the sample filament is increased in small increments of about 0.2 amp until the U^+ ions are observed. When the intensity is high enough (about 10^{-16} to 10^{-15} amp using electron-multiplier detection), the focusing of the source is checked. From here on the operation is much the same as described under single-filament operation. The spectra of the most abundant isotopes are obtained first, i.e., when the intensities are low, yet are high enough to give adequate precision. The less abundant isotopes are measured later when the intensity is high. This selection is a matter which the operator judges beforehand, based on the sample size, information needed, and special problems of impurities which may be present, etc.

The measurement of isotopic ratios over extremely large intensity ranges, i.e., the ratio of a very small concentration isotope to a principal peak, can involve difficulties if electron-multiplier detection is used. Electron multipliers can be nonlinear for primary-ion currents greater than 10^{-12} amp or amplified ion currents greater than 10^{-7} amp [see Secs. 13–2.2(g) and 13–2.5]. Where it is necessary that the intensity of the major peak be this high to have the intensity of a minor isotope large enough to measure, it is better, if possible, to compare the small peak to another isotope of smaller concentration than the major peak such as U^{234}/U^{235} in normal uranium.

The grid collector [25] is profitably used where the sample is very limited in quantity and the ion intensity of the low-concentration isotopes cannot be made high enough for long enough periods of time to apply the interpolative method with sufficient accuracy. The grid monitors a fraction (25 to 50 per cent) of the ion intensities of all masses within a small percentage mass range of the mass number going by the single-slit collector. With uranium the range of the grid is made to record the intensity of all uranium isotopes as well as any other ± 6 masses from the mass being recorded by the single-slit sytem. If no other peaks than uranium are present, this then provides a continuous monitor of the intensity of all uranium isotopes at all times. Where the sample size is limited, the intensity of the uranium sample may be boosted for a short period just prior to the time the small peak of interest, such as Pu^{242}, is scanned (Fig. 13.41). Although the sample decays fast and nonlinearly, the ratio of the small-concentration isotope to the grid signal is accurate to about 5 per cent. The grid signal is calibrated earlier when the principal

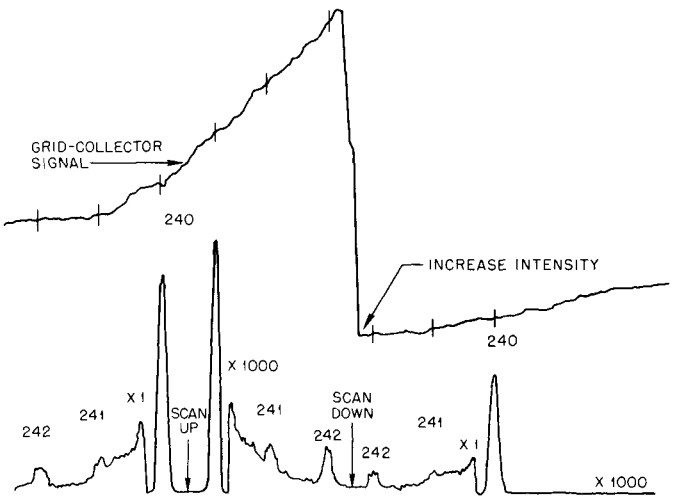


Fig. 13.41—Mass spectrum of a plutonium sample.

peaks, such as Pu^{239} and Pu^{240}, are at a lower intensity and when the intensity is not rapidly decaying. This technique is subject to several sources of error. First, the time response of the ion-measuring system for the grid collector is usually slower than that of the resolved mass-detector system, and for rapidly changing intensities this must be taken into account. Second, the grid system does not always record a constant fraction of the total ion intensity independent of the mass but may have mysterious dips or a changing fraction from one end of the spectrum scan to the other.

If tungsten filaments are used, there are impurity peaks at masses 234, 236, and 238 due to the K_6 polymer.[50, 52] Barton [52] indicates that these can be eliminated by using high-purity tungsten filaments prepared by reduction of tungsten carbonyl on a tantalum-base filament.

The masses of the K_6^+ peaks are sufficiently different from the uranium masses (0.25 mass unit) to resolve with the 12-in.-radius instrument but with reduced intensity. Figure 13.42 shows an impurity peak along with the uranium spectrum. These K_6^+ peaks originate from the center filament at extremely high temperature. They are not present at considerably lower temperatures; however, the uranium-ion intensity is also decreased.

With the multiple-filament ion source using rhenium filaments, the maximum total ionization efficiency for uranium is about 2.4×10^{-3} (2.4×10^{-2} over a solid angle of 0.1) (table 13.4); thus, with a total transmission of about 60 per cent, the fraction of the uranium reaching the collector system is 1.5×10^{-3}. Considering 2×10^{-17} amp as the minimum detectable ion current and an average emitting time of

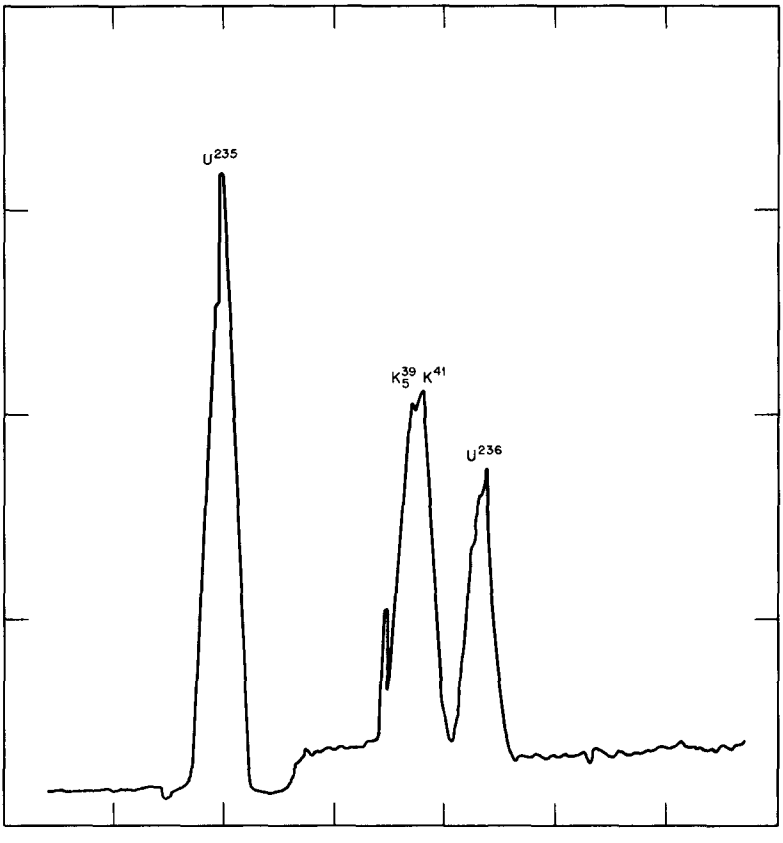


Fig. 13.42—Mass spectrum of uranium from a 12-in.-radius instrument with a multiple-filament source.

1000 sec, this corresponds to about 8×10^{7} atoms (3×10^{-14} g) as the minimum detectable quantity of any uranium isotope by this method. This sensitivity is for a high-transmission instrument (44°-sector magnet, 15,000 volts acceleration) and pure samples of uranium. The sensitivity may be lower by factors of 5 to 50 for impure samples or lower transmission instruments. The analysis of the major abundant isotopes can be carried out at much reduced ion intensity over a period of 20 to 60 min, and the bulk of the sample can be emitted at high intensity over a short time of about 100 sec to obtain the most sensitivity for a small concentration isotope.

With the multiple-filament technique, the UO^{+} spectrum as well as U^{+} ions can be obtained; the ratio UO^{+}/U^{+} being dependent on the temperature of the center filament and the oxygen and hydrocarbon background present. Usually the UO^{+} is much smaller than the U^{+} intensity, but it can be increased to the same intensity as U^{+} by the

admission of oxygen to 10^{-6} torr. This spectrum is useful for checking the 235/238 ratio where a mass 235 impurity peak other than U^{235} in the U^+ spectrum is under suspicion. Also the UO^+ may be used to obtain U^{234}/U^{235} ratios (but not U^{236}/U^{235} because of O^{17} interference) to avoid the K_6 impurity peaks in the U^+ region.

13–2.5 Accuracy

In the isotopic analyses of solids by the surface-ionization technique, the accuracy of the analysis is primarily determined by two characteristics of the method which result in errors 10 to 100 times larger than those obtained in gas-ionization methods, and as a consequence the most suitable methods for calibration and determination of accuracy become quite different. These two characteristics are the instability of the instrument bias and the instability of the ion-beam intensity.

In any mass-spectrometric isotopic analysis, the ratio of the ion currents of a given mixture of isotopes is seldom the same as the ratios of the concentrations in the sample. The various factors contributing to bias in surface ionization can be classified mainly into two independent factors: (1) nonlinearity of ion-current measuring system and (2) mass discrimination in the surface-ionization process, in source and analyzer transmission, and in ion detection.

Memory and impurities, two other general causes of bias, are not included in this discussion because they are negligible in most instances of the surface-ionization isotopic analysis of uranium.

For two isotopes, A and B, of mass m_A and m_B and concentration C_A and C_B in the sample, the measured ion-current ratio is

$$\frac{i_A}{i_B}=\frac{C_A}{C_B}\left(1+b\,\frac{m_B-m_A}{m_A}\right)f\left(\frac{i_A}{i_B}\right) \tag{13.8}$$

where $1+b[(m_B-m_A)/m_A]$ = the mass discrimination term
b = the mass discrimination factor
$f(i_A/i_B)$ = the nonlinearity term.

The calibration of any mass-spectrometric method involves either determination of these correction factors or elimination of their effect by one means or another.

In the surface-ionization isotopic analysis of solids, the mass discrimination may vary from sample to sample and may even vary during any one analysis. Therefore an unknown cannot be compared with a standard to the same precision as in gas analysis. These variations could be due to changing conditions in the complex process of surface ionization or to the nonreproducible conditions, such as distri-

bution of sample, warping of the filament, and focusing variations, which cause discrimination in ion transmission, or to changing conditions of electron-multiplier characteristics, such as variation of average angle of incidence on first dynode. The calibration and accuracy problem then amounts to analyzing known isotopic standards and measuring the mass-discrimination coefficient for a given type of instrument with a specific ionization technique, scanning method, and detector system under as nearly reproducible conditions as possible and for a significant number of calibration samples to determine the normal distribution of the correction factor.

Because of the possibility of having both mass discrimination and intensity nonlinear, the calibration standard should not be one in which both the mass difference and concentration ratio are large, such as normal abundance uranium, because it can be difficult to unravel the two error terms. When correction factors that can be applied to a multiple mixture of isotopes over a wide concentration range are being determined, the two bias factors are measured separately.

For a determination of the mass-discrimination coefficient, a 1 to 1 mixture of isotopes with a large mass difference is used. For a determination of the linearity of the ion-current measuring system, a mixture of two isotopes in the ratio of 1 to 100 and with minimum mass difference, such as U^{234} and U^{235}, is run over a wide range of intensities.

In the surface ionization of solids, the ion intensity cannot be maintained as constant as it can in gas analysis; usually it drifts up to 10 per cent per minute. With a single-collector ion-current measuring system, this requires multiple scans of the mass spectrum to average out these intensity variations by interpolation (Fig. 13.34). The standard deviation of a single ratio due to this intensity instability, sometimes referred to as internal measurement error, usually is 0.3 to 1.0 per cent (see Table 13.6). In the analysis of extremely small samples requiring electron-multiplier ion detection, the ion currents can be so small that the statistical error becomes an important error in the measurement of the ion currents.

A null method or simultaneous comparison of two or more isotope intensities would reduce considerably the error due to intensity fluctuation. Some methods using such techniques are described elsewhere.[24-26] However, they have not found extensive use in surface-ionization analysis because of the difficulty of comparing an unknown and a standard under nearly identical conditions which these techniques require to reduce the error due to variable instrument bias.

(a) *Intensity Nonlinearity.* Nonlinearity of the ion-current measuring system is another possible source of instrument bias which, with gas-analysis methods using standards and null methods, cancels out but in surface ionization can become a serious source of error. Deter-

mination of this bias is not so straightforward as that for mass discrimination. Usually a calibration of the amplifier input resistor linearity and sensitivity scale factors is sufficient in a simple type of system without electron multiplication, but this still is not a direct determination of linearity for ion beams of different intensity. With an electron multiplier it is necessary to use a more direct method of measurement. The most satisfactory method is to use an isotopic standard in which there are two isotopes with a minimum mass difference to reduce mass-discrimination effect. For uranium a very suitable standard is National Bureau of Standards standard No. 930 in which the U^{234}/U^{235} ratio has been determined as 0.01158 to high accuracy by isotopic dilution techniques with U^{233} such that the U^{233}/U^{234} ratio is about unity.

Figures 13.20 and 13.21 show the ratio of the measured ratio of U^{234}/U^{235} ion currents corrected for mass discrimination to the true concentration ratio ($U^{234}/U^{235}=0.01158$) over a wide range of ion intensities, 10^{-16} to 10^{-10} amp, and for three instruments. Two of the instruments (Fig. 13.20) show a good overall linearity, within 0.2 per cent, from 10^{-14} amp to 10^{-10} amp, and the correct ratio. In both cases, below 10^{-14} amp, the precision decreases because of statistical error, and the ratio is high because of possible impurities and nonlinearity of the vibrating-reed amplifier at very small currents. In one case (Fig. 13.21) there is a definite nonlinearity above 10^{-12} amp independent of the gain between 4×10^4 to 9×10^4. The electron multiplier in this case is an 11-stage magnetically shielded semifocused 90° cylindrical silver–magnesium dynode manufactured as type SPA–123 by Dumont. Because this nonlinearity occurred at the same primary-ion current, independent of the gain, it indicates the effect is in the first few dynodes, i.e., in the primary multiplication process by the positive ions at the first dynode.

At electron-multiplier output currents greater than about 10^{-7} amp, a fatigue type of effect occurs which is manifested by a decrease in gain of several per cent over a period of several seconds after the signal appears. After the signal has been removed, the gain recovers.

Some other causes of nonlinearity effects which have been observed are (1) nonlinear recorder slide wire, (2) nonohmic or nonlinear input resistor, and (3) filament-current changes correlated with a given mass peak being measured (caused by line-voltage decrease when switching solenoid to change input resistor while measuring a high-intensity peak).

A current-measuring system should not exhibit any nonlinearity over the range 10^{-15} to 10^{-11} amp even with an electron multiplier. If it does, such as shown in Fig. 13.21, then it is best either to replace the nonlinear unit or to avoid operating in the nonlinear region because

the corrections can be quite involved as a result of the usual variations in ion intensity with surface-ionization sources.

(b) *Calibration for Mass Discrimination.* It is possible to calibrate an instrument for the analysis of unknown samples over a concentration range of 0.01 to 100 per cent of all uranium isotopes using one standard for the mass discrimination factor and making checks on the linearity of the ion-current measuring system. Uranium isotopic standards can be obtained from the U.S. National Bureau of Standards. Table 13.5 shows the concentrations in mole per cent of the 14 standards that are available. These have been measured against reference standards prepared gravimetrically by blending high-purity U^{235} and U^{238} primary and secondary standards. The U^{235}/U^{238} ratio measurements were made by the UF_6 gas method. The U^{234}/U^{235} ratio measurements were made by isotopic dilution of the standard with U^{233} to a U^{233}/U^{234} concentration of about unity. The U^{233}/U^{234} ratio was then measured as accurately as possible with a multiple-filament surface-ionization instrument.

The NBS standard No. 500 (not shown in Table 13.5) with a U^{235}/U^{238} ratio of about unity is probably the most suitable for measuring the mass discrimination. The other standards may be used when the linearity characteristics of the instrument are known or when the unknown samples are compared with a standard of very similar composition under the same operating conditions, i.e., ion intensity, shunt factors, etc.

Table 13.5—ISOTOPIC COMPOSITION OF URANIUM STANDARDS*

(NBS Best Estimates From Pooled Data)

	U^{234}	U^{235}	U^{236}	U^{238}	$235/238$
U005	0. 0023	0. 4894	0. 0046	99. 5037	0. 004918
U010	0. 0056	1. 0031	0. 0065	98. 9848	0. 010134
U015	0. 0085	1. 531	0. 0163	98. 444	0. 01555
U020	0. 0124	2. 037	0. 0162	97. 934	0. 02080
U030	0. 0189	3. 046	0. 0202	96. 915	0. 03143
U050	0. 0280	5. 006	0. 0481	94. 918	0. 05274
U100	0. 0672	10. 189	0. 0372	89. 707	0. 11358
U150	0. 09901	15. 296	0. 0662	84. 539	0. 1809
U200	0. 1247	20. 005	0. 211	79. 659	0. 2511
U350	0. 2493	35. 177	0. 167	64. 407	0. 5462
U750	0. 5914	75. 360	0. 249	23. 800	3. 166
U800	0. 6559	80. 276	0. 246	18. 823	4. 265
U850	0. 6429	85. 142	0. 371	13. 844	6. 150
U900	0. 7771	90. 198	0. 332	8. 693	10. 375
U930	1. 0813	93. 335	0. 204	5. 380	17. 348
	234 by 233 dilution 0. 5%			OR Cert. 0. 1%	

*Concentrations are given in mole %; ratios are mole ratios.

For each calibration three separate samples of the standard are analyzed and four sets of data are taken in each analysis. The instrument is refocused to maximum intensity of the U^{235} peak between each set of data. Each set consists of approximately eight independent ratios, R_{ij}, of U^{235}/U^{238} which are obtained by alternate interpolation, *a–b–b–a–a–b–b–a*, as in Fig. 13.34. If the long-term intensity drift is not too nonlinear, these ratios will have a normal distribution curve for which the usual estimates of standard deviation can be made and the standard tests of consistency can be applied. From the set of data the mass-discrimination factor b is determined.

$$b=\frac{m}{\Delta m}\left(\frac{\bar{\bar{R}}}{R_T}-1\right) \tag{13.9}$$

where $\bar{\bar{R}}=\frac{1}{n}\sum_{j}^{n}\bar{R}_j$

$$\bar{R}_j=\frac{1}{k}\sum_{i}^{k}R_{ij}$$

R_T=the true value of the isotope ratio

In this case $R_T=U^{235}/U^{238}$ as obtained from the standard values.

Normally the mass-discrimination factor can be considered as fairly constant; the principal source of error in its determination is the internal precision of the calibration measurement, which is the result of the intensity instability inherent in surface ionization. Any variation in the mass-discrimination factor is accounted for in the external or overall precision measurement, as discussed in the section on precision and shown in Tables 13.7 to 13.11.

Under certain circumstances the mass discrimination may vary between different analyses and different times of the same analysis by an amount several times the internal precision. These variations have usually been traced to the different mass peaks having different transmissions either through the source or analyzer. An example of this is the so-called "voltage effect," which is the change in transmission with accelerating voltage when the transmission is less than 90 per cent. The transmission of the low-mass ions is greater because of the higher accelerating voltages. This condition can be worse if fixed voltages are used for any of the source focusing plates or if the beam is not focused at maximum intensity.

There is no such effect with essentially complete transmission (>95 per cent) such as results with the almost point-source emission of the V-filament or with special high-resolution instruments permitting very wide slits. Otherwise the effect is minimized if all voltages are proportional to the accelerating voltage and the source focusing is adjusted for maximum intensity.

Without high source transmission the mass discrimination is minimized by magnetic-field scanning. The principal disadvantage of this method is the effect of the changing magnetic field on the gain of unshielded electron multipliers. For this reason electron multipliers should be well shielded from magnetic fields. Another effect with magnetic scanning is the change of the focusing of the main magnet with magnetic field. This only causes mass discrimination if the collector slit is smaller than the focused ion-beam images.

(c) *Precision.* A set of calibration data will serve to determine the precision of the method, taking into account such external variable factors as different sample loadings, filament assemblies, and focusing conditions as well as the fluctuations within individual sets of data due mainly to intensity instability. The precision of the method, σ_T, is defined as the best estimate of the standard deviation for the average of a set of approximately ten ratios and is determined from the internal and external variances. The internal variance, S_j^2, of each set is derived from the individual ratios that enter into $\overline{R}_j$ and is a measure of the statistical variations within the set.

$$S_j^2=\frac{\sum_i^k [(\overline{R}j-R_{ij})/\overline{R}_j]^2}{k(k-1)} \tag{13.10}$$

The external variance, S_{ex}^2, is derived from the variation in the $\overline{R}_j$ values corresponding to different sets and different analyses of the same standard, and, in comparison with the internal variances by an F consistency test, it will indicate any differences between sets that the internal variance does not take into account, whether statistical or not, such as variable mass discrimination owing to focusing conditions, sample location, filament position, contamination, etc. In general, for any set of analyses for any given pair of isotopes using standard samples,

$$S_{ex}^2=\frac{\sum^n(\Delta/R_T)^2}{n-1} \tag{13.11}$$

where n is the number of sets of data and R_T is the known ratio corresponding to the sample for which Δ is the difference between the measured ratio corrected for mass discrimination and the true ratio

$$\Delta=\frac{\overline{R}_j}{(1/n)\sum(\overline{R}_j/R_T)}-R_T \tag{13.12}$$

The n different sets may include several sets of data for each analysis, i.e., at different intensities, but also should include several different analyses including sample changes.

If the mass-discrimination factor is determined from another set of data, for example, in the determination of S_{ex} for U^{234}/U^{235} using one-third of the mass-discrimination factor measured from U^{235}/U^{238} calibration results, then

$$S_{ex}^2=\frac{\sum^{n}[(\Delta/R_T)-\text{Bias}]^2}{n-1} \tag{13.13}$$

where

$$\text{Bias}=\frac{\sum^{n}(\Delta/R_T)}{n} \tag{13.14}$$

If S_j^2 and S_{ex}^2 are consistent by an F test, then

$$\sigma_T^2=\frac{(1/n)\sum^{n}S_j^2+S_{ex}^2}{2} \tag{13.15}$$

If they are not consistent

$$\sigma_T^2=(1/n)\sum^{n}S_j^2+S_{ex}^2 \tag{13.16}$$

The calibration for mass discrimination will provide the data for determining the precision of measuring the ratio U^{235}/U^{238}. For the minor isotopes U^{234} and U^{236}, the precision is considered in terms of measuring the ratios U^{234}/U^{235} and U^{236}/U^{235}. Measurement of the precision in these cases can be carried out the same as is done for the calibration for mass discrimination using U^{235}/U^{238}.

(d) *Analysis of an Unknown.* In the analysis of an unknown uranium sample, a set of spectra of U^{235} and U^{238} and of U^{234}, U^{235}, and U^{236} are obtained, preferably more than 12, always with the U^{235} intensity maximized. The ratios $R_{85}=U^{238}/U^{235}$, $R_{45}=U^{234}/U^{235}$, and $R_{65}=U^{236}/U^{235}$ are then calculated in each case by first taking the average of eight independent ratios taken by alternate interpolation and then correcting for mass discrimination, using the mass discrimination factor as determined in the above calibration.

$$R_T=R_{\text{meas.}}(1+b\epsilon)\ (1\pm 2.3\sigma) \tag{13.17}$$

where

$$\epsilon=\frac{\Delta m}{m} \tag{13.18}$$

noting that

$$\epsilon_{85}=\frac{3}{238},\ \epsilon_{45}=-\frac{1}{235},\ \epsilon_{65}=\frac{1}{235} \tag{13.19}$$

and the factor 2.3 is Student's t value for the 95 per cent confidence limits with seven degrees of freedom. For the accuracy, σ, the standard deviation of the overall precision of the method, σ_T is used, providing the internal precision, S_j, is consistent with σ_T by the chi-square test,

$$S_j < 1.4\sigma_T \tag{13.20}$$

for seven degrees of freedom (eight ratios). If S_j is greater than $1.4\sigma_T$, then the value of S_j is used for σ. If the UO_2 spectrum is used, the ratios are then corrected for the presence of oxygen isotope.

(e) *Results.* Table 13.6 summarizes the results of five series of calibrations carried out on two instruments at Argonne National Laboratory over several years. Three of the calibrations involve the use of a single NBS uranium isotopic standard in determining the mass discrimination, and two involve the entire range of available NBS standards. The accuracy for analysis of mixtures containing U^{234}, U^{235}, U^{236}, and U^{238} is considered in terms of the accuracy in measuring the three independent ratios U^{235}/U^{238}, U^{234}/U^{235}, and U^{236}/U^{235}.

Table 13.6—ACCURACY IN URANIUM SURFACE-IONIZATION ISOTOPIC ANALYSIS

Series No.	Method of ionization	Isotope ratio	Accuracy (single analysis), %	Bias, %	Remarks
1	Single filament.	235/238	±0. 37	--------	Instrument 2, single standard.
2	Single filament.	235/238	±0. 18	--------	Instrument 2, single standard.
3	Multiple filament.	235/238	±0. 68	--------	Instrument 1, single standard.
4	Single filament.	235/238	±0. 53	--------	Instrument 2, multiple standards.
		234/235	±1. 8	−0. 14	
		236/235	For 235/238 >0. 05		
			±1. 0	+0. 66	
			For 235/238 <0. 05		
			±2. 9	+6. 7	
5	Multiple filament.	235/238	±0. 51	--------	Instrument 1, multiple standards.
		234/235	±1. 4	−0. 25	
		236/235	±1. 1	+0. 62	

(1) U^{235}/U^{238}. The accuracy of measuring U^{235}/U^{238} concentration ratios is obtained directly from the variances in the calibration runs for determining mass discrimination. Table 13.6 summarizes these results for both the single- and multiple-filament surface-ionization methods, which are shown in more detail in Tables 13.7 to 13.9 for the single-standard sets and in Tables 13.10 and 13.11 for the multiple-standard sets.

The values for the standard deviation, σ_T, using the single-standard method, are based on the analysis of three samples for four sets of data each with eight ratios for each set. The value for σ_T is the best esti-

Table 13.7—CALIBRATION AND ACCURACY IN SINGLE-FILAMENT SURFACE IONIZATION OF URANIUM USING A SINGLE NBS STANDARD

Run	Set	$\bar{R}_i$ Meas. U^{235}/U^{238}	$S_i \times 10^{-4}$	$\Delta/R_T \times 10^{-4}$
1	a	1.0287	±20	+42
	b	1.0264	±27	+29
	c	1.0243	±14	+8
	d	1.0248	±17	+13
2	a	1.0276	±58	+49
	b	1.0240	±16	+5
	c	1.0151	±26	−84
	d	1.0173	±92	−62
3	a	1.0233	±11	−2
	b	1.0236	±15	−1
	c	1.0221	±15	−14
	d	1.0254	±14	+29

$$\bar{\bar{R}} = 1.0235$$

$$\text{Mass discrimination} = \frac{\bar{\bar{R}}}{R_T} = 1.0235$$

$$\bar{S}_i = \left(\frac{\sum S_i^2}{12}\right)^{1/2} = 0.0035$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R_T}\right)^2}{11}\right]^{1/2} = 0.0039$$

$\sigma_T = 0.0037$ (average of 8 ratios)

Notes: 1. 12-in.-radius 60° mass spectrometer, ANL instrument 2.
2. Single filament, tantalum.
3. Electron multiplier, 9 stage, 90° cylinder, unshielded.
4. NBS U-500 standard, $U^{235}/U^{238} = 1.000$.
5. Focusing only on mass 235.
6. Analyst A.

mate of variance for the average of one set of eight ratios for one analysis considering both internal and external precision.

The values of σ_T for the cases involving the multiple standards are based on one analysis of each standard with an average of four sets per analysis each set containing on the average about 20 of all possible interpolated ratios and taken at different ion intensities and grid resistors. The final U^{235}/U^{238} raw ratio for each standard is the grand average of all ratios. The errors given in column 4 in these series are mean deviation and correspond to 0.8 times the standard deviation.

The values of σ_T in all five series show consistent agreement about an average value of ± 0.5 per cent indicating no significant difference

Table 13.8—CALIBRATION AND ACCURACY IN SINGLE-FILAMENT SURFACE IONIZATION OF URANIUM USING A SINGLE NBS STANDARD

Run	Set	$\bar{R}_i$ Meas. U^{235}/U^{238}	$S_i \times 10^{-4}$	$\Delta/R_T \times 10^{-4}$
1	a	1.0251	±10	19
	b	1.0238	±13	1
	c	1.0182	±14	50
	d	1.0196	±13	36
2	a	1.0238	±16	6
	b	1.0239	±13	7
	c	1.0244	±11	12
	d	1.0244	±24	12
3	a	1.0252	±10	20
	b	1.0242	±12	10
	c	1.0230	±14	2
	d	1.0235	±12	3

$$\bar{\bar{R}} = 1.0232$$

$$\text{Mass discrimination} = \frac{\bar{\bar{R}}}{R_T} = 1.0232$$

$$\bar{S}_i = \left(\frac{\sum S_i^2}{12}\right)^{1/2} = 0.0014$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R_T}\right)^2}{11}\right]^{1/2} = 0.0021$$

$\sigma_T = 0.0018$ (average of 8 ratios)

Notes: 1. 12-in.-radius 60° mass spectrometer, ANL instrument 2.
2. Single filament, tantalum.
3. Electron multiplier, 9 stage, 90° cylinder, unshielded.
4. NBS U-500 standard, $U^{235}/U^{238} = 1.000$.
5. Focusing only on mass 238.
6. Analyst B.

between calibration with a single standard and calibration with different standards. Different series on each instrument yield consistent mass-discrimination values, 1.023 for instrument 2 and 1.012 to 1.015 for instrument 1.

The results in Table 13.10 show a small dependence of mass discrimination with concentration. This indicates most likely a small nonlinearity in the ion-current measuring system, such as the electron multiplier or grid resistor.

(2) U^{234}/U^{235}. The accuracy of measuring U^{234}/U^{235} is determined by comparing the results that are obtained in the analysis of NBS standards after correcting the raw ratios for mass discrimination based

Table 13.9—CALIBRATION AND ACCURACY IN MULTIPLE-FILAMENT SURFACE IONIZATION OF URANIUM USING A SINGLE NBS STANDARD

Run	Set	$\bar{R}_j$ Meas. U^{235}/U^{238}	$S_i \times 10^{-4}$	$\Delta/R_T \times 10^{-4}$
1	a	0.5602	±10	+57
	b	0.5559	±14	+12
	c	0.5574	±5	+19
	d	0.5546	±8	+1
2	a	0.5592	±8	+47
	b	0.5554	±6	+9
	c	0.5536	±10	−9
	d	0.5553	±7	+8
3	a	0.5531	±11	−14
	b	0.5524	±5	−21
	c	0.5498	±13	−47
	d	0.5472	±14	−73

$$\bar{\bar{R}} = 0.5545 \qquad \bar{S}_i = \left(\frac{\sum S_i^2}{12}\right)^{1/2} = 0.0018$$

$$\text{Mass discrimination} = \frac{\bar{\bar{R}}}{R_T} = 1.015 \qquad S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R_T}\right)^2}{11}\right]^{1/2} = 0.0065$$

$$\sigma_T = 0.0068 \text{ (average of 8 ratios)}$$

Notes: 1. 12-in.-radius 60° mass spectrometer, ANL instrument 1.
2. Multiple-filament ion source, rhenium filament.
3. Electron multiplier, 11 stage, 90° cylinder, shielded.
4. Alternate-focusing on mass 235 and 238.
5. NBS standard No. 350, $U^{235}/U^{238} = 0.5462$.
6. Analyst C.

on a value of one-third the U^{235}/U^{238} mass discrimination as described in the outlined method. These corrected results are compared with the NBS best estimates in Tables 13.12 and 13.13, which are then tests of the calibration method in which only the mass discrimination of U^{235}/U^{238} is determined. The average bias values are obtained in each case as well as the accuracy of the method.

Table 13.10—CALIBRATION FOR MASS DISCRIMINATION AND ACCURACY IN SINGLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS of U^{235}/U^{238} USING FIFTEEN NBS ISOTOPIC STANDARDS

Uranium isotopic standard	U^{235}/U^{238} mole ratio					$\frac{\Delta}{\overline{R}}=\left(\frac{\overline{R}_i}{1.023\,R_T}-1\right)$
	R_T (NBS best estimate)	$\overline{R}_i$	$S_i/1.25$*	Corrected $=\overline{R}_i/1.023$	$\frac{\overline{R}_i}{R_T}$	
U005	0. 004918	0. 005022	±0. 0032	0. 004919	1. 021	−0. 002
U010	0. 010134	0. 01043	±0. 0096	0. 01020	1. 029	+0. 006
U015	0. 01555	0. 01584	±0. 0013	0. 01548	1. 019	−0. 004
U020	0. 02080	0. 02106	±0. 0028	0. 02059	1. 013	−0. 010
U030	0. 03143	0. 03188	±0. 0016	0. 03116	1. 014	−0. 009
U050	0. 05274	0. 0538	±0. 0037	0. 0526	1. 020	−0. 003
U100	0. 11358	0. 1164	±0. 0043	0. 1138	1. 025	+0. 002
U150	0. 1809	0. 1864	±0. 0021	0. 1822	1. 030	+0. 007
U200	0. 2511	0. 2550	±0. 0020	0 2493	1. 016	−0. 007
U350	0. 5462	0. 5600	±0. 0009	0. 5474	1. 025	+0. 002
U750	3. 166	3. 247	±0. 0052	3. 174	1. 026	+0. 003
U800	4 256	4. 371	±0. 0046	4. 273	1. 025	+0. 002
U850	6 150	6. 313	±0. 0032	6. 171	1. 027	+0. 004
U900	10 375	10. 69	±0. 0037	10. 45	1. 030	+0. 007
U930	17. 348	17. 74	±0. 0034	17. 34	1. 023	0

$$\text{Mass discrimination}=\frac{\sum \frac{\overline{R}_i}{R_T}}{15}=1.023$$

$$\overline{S}_i=\left(\sum \frac{S_i^2}{15}\right)^{1/2}=0.0050$$

$$S_{ex}=\left[\sum \left(\frac{\Delta}{\overline{R}}\right)^2\right]^{1/2}=0.0056$$

$$\sigma_T=0.0053$$

Notes 1. ANL instrument 2
2 Single tantalum-filament surface-ionization source
3 Accelerating voltage, 8000 volts
4 Electron-multiplier detector

*S_i is normalized internal precision, values shown are mean deviations, hence factor 1 25 to obtain root mean square or internal precision of $\overline{R}_i$

As in the case of the U^{235}/U^{238} data in these two series, there is one analysis of each standard with an average of four sets per analysis, each set containing on the average about 20 of all possible interpolated ratios taken at different intensities and grid resistors. The final U^{234}/U^{235} raw ratio is the grand average of all ratios, and the errors given in column 4 are the mean deviations.

Table 13.11—CALIBRATION FOR MASS DISCRIMINATION AND ACCURACY IN MULTIPLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS OF U^{235}/U^{238} USING FIFTEEN NBS STANDARDS

Uranium isotopic standard	U^{235}/U^{238}, mole ratio				$\frac{\overline{R}_i}{R_T}$	$\frac{\Delta}{\overline{R}} = \left(\frac{\overline{R}_i}{1.0125\,R_T} - 1\right)$
	R_T (NBS best estimate)	$\overline{R}_i$	$S_i/1.25$*	Corrected $= \overline{R}_i/1.0125$		
U005	0 004918	0. 004986	±0. 0100	0. 004924	1. 014	+0. 001
U010	0. 010134	0. 01025	±0. 0078	0 01012	1. 011	−0. 002
U015	0. 01555	0. 01576	±0. 0051	0. 01557	1. 014	+0. 001
U020	0. 02080	0. 02096	±0. 0014	0. 02070	1. 008	−0. 005
U030	0. 03143	0. 03179	±0. 0035	0. 03140	1. 011	−0. 002
U050	0. 05274	0. 05314	±0. 0038	0. 05248	1. 008	−0. 005
U100	0. 11358	0. 1153	±0. 0043	0. 1139	1. 015	+0. 002
U150	0. 1809	0. 1826	±0. 0038	0. 1803	1. 009	−0. 004
U200	0. 2511	0. 2547	±0. 0047	0. 2516	1. 014	+0. 001
U350	0. 5462	0. 5515	±0. 0022	0. 5447	1. 010	−0. 003
U750	3. 166	3. 220	±0. 0043	3. 180	1. 017	+0. 004
U800	4. 265	4. 322	±0. 0093	4. 269	1. 013	0
U850	6. 150	6. 223	±0. 0032	6. 146	1. 012	−0. 001
U900	10. 375	10. 57	±0. 0080	10. 44	1 019	+0. 006
U930	17. 348	17. 56	±0. 0034	17. 34	1. 012	−0 001

$$\text{Mass discrimination} = \frac{\sum \frac{\overline{R}_i}{R_T}}{15} = 1.0125$$

$$\overline{S}_i = \left(\frac{\sum S_i^2}{15}\right)^{1/2} = 0.0070$$

$$S_{ex} = \left[\frac{\sum \left(\frac{\Delta}{\overline{R}}\right)^2}{14}\right]^{1/2} = 0.0032$$

$$\sigma_T = 0.0051$$

Notes 1 ANL instrument 1
2 Multiple tungsten-filament surface-ionization source
3 Accelerating voltage, 8000 volts
4 Electron-multiplier detector

*S_i is normalized internal precision, values shown are mean deviations, hence factor 1 25 to obtain root mean square or internal precision of $\overline{R}_i$

The values for the U005 and U010 standards in Table 13.13 (multiple filament) were not included in the final determination of average bias and accuracy of the method because these were outside the normal distribution of the others. These are cases where the U^{235} concentration is very small, making the U^{234} concentration extremely small.

Table 13.12—ACCURACY IN SINGLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS OF U^{234}/U^{235} USING CALIBRATION BASED ON U^{235}/U^{238}

Uranium isotopic standard	U^{234}/U^{235}, mole ratio					
	R_T (NBS best estimate)	$\bar{R}_i$	$S_i/1.25$*	Corrected $= \bar{R}_i/1.0077$	Corrected / R_T	$\frac{\Delta}{\bar{R}} =$ Corrected / R_T -1
U005	0. 004700	0. 004498	±0. 0200	0. 004464	0. 950	−0. 050
U010	0. 005583	0. 005543	±0. 0198	0. 005501	0. 985	−0. 015
U015	0. 005552	0. 005722	±0. 0070	0. 005678	1. 023	+0. 023
U020	0. 006087	0. 006173	±0. 0032	0. 006126	1. 006	+0. 006
U030	0. 006205	0. 00629	±0. 0032	0. 00624	1. 006	+0. 006
U050	0. 005593	0. 005650	±0. 0035	0. 00561	1. 003	+0. 003
U100	0. 006595	0. 006639	±0. 0012	0. 006588	0. 999	−0. 001
U150	0. 006473	0. 006590	±0. 0106	0. 006540	1. 010	+0. 010
U200	0. 006233	0. 00634	±0. 0047	0. 00629	1. 009	+0. 009
U350	0. 007087	0. 007100	±0. 0014	0. 007045	0. 994	−0. 006
U750	0. 007848	0. 007933	±0. 0038	0. 007872	1. 003	+0. 003
U800	0. 008171	0. 008245	±0. 0073	0. 008182	1. 001	+0. 001
U850	0. 007551	0. 007577	±0. 0026	0. 007519	0. 996	−0. 004
U900	0. 008615	0. 00863	±0. 0463	0. 00856	0. 994	−0. 006
U930	0. 01159	0. 01168	±0. 0034	0. 01159	1. 000	0

$$\bar{S}_i = \left(\frac{\sum S_i^2}{15}\right)^{1/2} = 0.019$$

$$\text{Bias} = \frac{\sum\left(\frac{\Delta}{\bar{R}}\right)}{15} = -0.0014$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{\bar{R}} - \text{Bias}\right)^2}{14}\right]^{1/2} = 0.016$$

$$\sigma_T = 0.018$$

Notes

1 ANL instrument 2
2. Single tantalum-filament surface-ionization source
3 Accelerating voltage, 8000 volts
4 Electron-multiplier detector

*$\bar{S}_i$ is normalized internal precision, values shown are mean deviations, hence factor 1 25 to obtain root mean square or internal precision of $\bar{R}_i$

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The bias is negligible in both series, being less than 0.25 per cent. The accuracy of the method, σ_T, is ± 1.6 per cent for the single filament and ± 1.2 per cent for the multiple filament. This is considerably more error than was obtained for U^{235}/U^{238} and is probably caused by a combination of random statistics and scattering background from

Table 13.13—ACCURACY IN MULTIPLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS OF U^{234}/U^{235} USING CALIBRATION BASED ON U^{235}/U^{238}

Uranium isotopic standard	U^{234}/U^{235}, mole ratio				Corrected / R_T	$\frac{\Delta}{R}$ = Corrected / R_T − 1
	R_T (NBS best estimate)	$\overline{R}_i$	$S_i/1.25$*	Corrected = $\overline{R}_i/1.0042$		
U005	0. 004700	0. 004364	±0. 0069	0. 004346	9. 025	†−0. 075
U010	0. 005583	0. 005424	±0. 0111	0. 005401	0. 969	†−0. 033
U015	0. 005552	0. 005633	±0. 0089	0. 005609	1. 010	+0. 010
U020	0. 006087	0. 006117	±0. 0098	0. 006091	1. 001	+0. 001
U030	0. 006205	0. 006154	±0. 0049	0. 006128	0. 988	−0. 012
U050	0. 005593	0. 005809	±0. 0344	0. 005785	1. 034	+0. 034
U100	0. 006595	0. 006638	±0. 0075	0. 006610	1. 002	+0. 002
U150	0. 006473	0. 006475	±0. 0093	0. 006448	0. 996	−0. 004
U200	0. 006233	0. 006287	±0. 0064	0. 006261	1. 004	+0. 004
U350	0. 007087	0. 006990	±0. 0049	0. 006961	0. 982	−0. 018
U750	0. 007848	0. 007920	±0. 0152	0. 007887	1. 005	+0. 005
U800	0. 008171	0. 008282	±0. 0193	0. 008247	1. 009	+0. 009
U850	0. 007551	0. 007588	±0. 0026	0. 007556	1. 001	+0. 001
U900	0. 008615	0. 008631	±0. 0046	0. 008595	0. 998	−0. 002
U930	0. 01159	0. 01167	±0. 0103	0. 01162	1. 003	+0. 003

$$\overline{S}_i = \left(\frac{\sum S_i^2}{15}\right)^{1/2} = 0.016$$

$$\text{Bias} = \frac{\sum\left(\frac{\Delta}{R}\right)}{13} = +0.0025$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R} - \text{Bias}\right)^2}{12}\right]^{1/2} = 0.012$$

$$\sigma_T = 0.014$$

Notes: 1. ANL instrument 1.
2. Multiple tungsten-filament surface-ionization source.
3. Accelerating voltage, 8000 volts.
4. Electron-multiplier detector.

*S_i is normalized internal precision; values shown are mean deviations, hence factor 1.25 to obtain root mean square or internal precision of $\overline{R}_i$.

† Not included.

Table 13.14—ACCURACY IN SINGLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS OF U^{236}/U^{235} USING CALIBRATION BASED ON U^{235}/U^{238}

Uranium isotopic standard	U^{236}/U^{235}, mole ratio					
	R_T (NBS best estimate)	$\overline{R}_i$	$S_i/1.25$*	Corrected $= \overline{R}_i/1.0077$	Corrected / R_T	$\frac{\Delta}{R} =$ Corrected / R_T -1
U005	0. 0094	0. 01020	±0. 0245	0. 01028	1. 094	+0. 094
U010	0. 0065	0. 00705	±0. 0099	0. 00710	1. 092	+0. 092
U015	0. 0106	0. 01100	±0. 0018	0. 01108	1. 045	+0. 045
U020	0. 00795	0. 00841	±0. 0083	0. 00847	1. 065	+0. 065
U030	0. 00663	0. 00682	±0. 0088	0. 00687	1. 036	+0. 036
U050	0 00961	0. 00952	±0. 0021	0. 00959	0. 998	−0. 002
U100	0 00365	0. 00369	±0. 0081	0 00372	1. 019	+0. 019
U150	0 00433	0 00429	±0. 0093	0. 00432	0. 998	−0. 002
U200	0 0105	0. 01043	±0. 0096	0. 01051	1. 001	+0. 001
U350	0 00475	0. 00475	±0. 0023	0. 00479	1. 008	+0. 008
U750	0. 00330	0. 00331	±0. 0060	0. 00334	1. 012	+0. 012
U800	0. 00306	0. 00308	±0. 0032	0. 00310	1. 013	+0. 013
U850	0. 00436	0 00434	±0 0023	0. 00437	1. 002	+0. 002
U900	0. 00368	0. 00368	±0. 0082	0. 00371	1. 008	+0. 008
U930	0. 00219	0. 00219	±0. 0046	0. 00221	1. 009.	+0. 009

$$\overline{S}_i = \left(\frac{\sum S_i^2}{15}\right)^{1/2} = 0.011$$

For $U^{235}/U^{238} > 0.05$

$$\text{Bias} = +0\ 0066$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R} - \text{Bias}\right)^2}{9}\right]^{1/2} = 0.0086$$

$$\sigma_T = 0.010$$

For $U^{235}/U^{238} < 0.05$

$$\text{Bias} = +0.067$$

$$S_{ex} = \left[\frac{\sum\left(\frac{\Delta}{R} - \text{Bias}\right)^2}{4}\right]^{1/2} = 0.027$$

$$\sigma_T = 0.029$$

Notes 1 ANL instrument 2
2 Single tantalum-filament surface-ionization source
3 Accelerating voltage, 8000 volts
4 Electron-multiplier detector

*S_i is normalized internal precision, values shown are mean deviations, hence factor 1 25 to obtain root mean square or internal precision of $\overline{R}_i$

U^{238} in the case of the lower U^{235} concentration standards, plus U^{235} scattering background in all standards.

(3) *U^{236}/U^{235}*. The accuracy of measuring U^{236}/U^{235} is determined in a similar manner to that described for U^{234}/U^{235} based on U^{235}/U^{238}

Table 13.15—ACCURACY IN MULTIPLE-FILAMENT SURFACE-IONIZATION ISOTOPIC ANALYSIS OF U^{236}/U^{235} USING CALIBRATION BASED ON U^{235}/U^{238}

Uranium isotopic standard	U^{236}/U^{235}, mole ratio					
	R_T (NBS best estimate)	$\bar{R}_i$	$S_i/1.25$*	Corrected $= \bar{R}_i/1.0042$	Corrected / R_T	$\frac{\Delta}{R} =$ Corrected / R_T -1
U005----	0. 0094	0. 009909	±0. 0172	0. 009951	1. 059	†+0. 059
U010----	0. 0065	0. 006934	±0. 0043	0. 006963	1. 071	†+0. 071
U015----	0. 0106	0. 01070	±0. 0065	0. 01074	1. 013	+0. 013
U020----	0. 00795	0. 008001	±0. 0087	0. 008035	1. 011	+0. 011
U030----	0. 00663	0. 006711	±0. 0045	0. 006739	1. 016	+0. 016
U050----	0. 00961	0. 009525	±0. 0094	0. 009565	0. 995	−0. 005
U100----	0. 00365	0. 003718	±0. 0048	0. 003734	1. 023	+0. 025
U150----	0. 00433	0. 004313	±0. 0116	0. 004331	1. 000	0
U200----	0. 0105	0. 01043	±0. 0019	9. 01047	0. 997	−0. 003
U350----	0. 00475	0. 004699	±0. 0085	0. 004719	0. 993	−0. 007
U750----	0. 00330	0. 003318	+0. 0090	0. 003332	1. 010	+0. 010
U800----	0. 00306	0. 003082	±0. 0162	0. 003095	1. 011	+0. 011
U850----	0. 00436	0. 004374	±0. 0023	0. 004392	1. 007	+0. 007
U900----	0. 00368	0. 003699	±0. 0027	0. 003715	1. 010	+0. 010
U930----	0. 00219	0. 002167	±0. 0091	0. 002176	0. 994	−0. 006

$$\bar{S}_i = \left(\frac{\sum S_i^2}{15}\right)^{1/2} = 0.011$$

$$\text{Bias} = \frac{\sum\left(\frac{\Delta}{\bar{R}}\right)}{13} = +0.0062$$

$$S_{ex} = \left(\frac{\sum\left(\frac{\Delta}{\bar{R}} - \text{Bias}\right)^2}{12}\right)^{1/2} = 0.010$$

$$\sigma_T = 0.011$$

Notes: 1. ANL instrument 1.
2. Multiple tungsten-filament surface-ionization source.
3. Accelerating voltage, 8000 volts.
4. Electron-multiplier detector.

*$\bar{S}_i$ is normalized internal precision; values shown are mean deviations, hence factor 1.25 to obtain root mean square or internal precision of $\bar{R}_i$.

† Not included.

mass discrimination. These results are shown in Tables 13.14 and 13.15.

The amount of data and the method of averaging are the same as described for U^{234}/U^{235}.

The values for the U005 and U010 standards in Table 13.15 (multiple filament) were not included in the final determination of bias and accuracy of the method because these were outside the normal distribution of the others.

The bias for the multiple filament set is ± 0.6 per cent with an accuracy of ± 1.0 per cent. The amount of bias is probably not significant because the values used for the NBS standards are only given to three significant figures; the first significant figure is 2 to 3 in most cases.

In the case of the single-filament results shown in Table 13.14, there was a much larger positive bias for the five standards with lowest U^{235} concentration as compared with the results on the other standards.

For a U^{235}/U^{238} ratio less than 0.05, the bias is ± 6.7 per cent with an accuracy of ± 2.7 per cent. Above a U^{235}/U^{238} ratio of 0.05, the bias is ± 0.66 per cent with an accuracy of ± 0.9 per cent.

(f) *Summary.* These results demonstrate the accuracy obtained for the single- and multiple-filament surface-ionization methods described in this procedure relative to the NBS best estimates of the composition of NBS uranium isotopic standards and for the range of composition of these standards. For all isotopes the method demonstrates less error than the NBS certified accuracy for these standards. Therefore the bias values given above in the U^{234}/U^{235} and U^{236}/U^{235} measurements cannot be ascertained at this time as significant. Also, the measurements of error for these minor isotopes, although higher than for U^{235}/U^{238}, are less than the error limits of 2.0 per cent which the NBS will certify at this time.

The U^{234}/U^{235} and U^{236}/U^{235} ratios are small (<0.01) and usually involve measuring U^{234} and U^{236} peaks on top of a scattering tail from the U^{235} peak as well as from the U^{238} peak in the case of U^{235} concentrations less than 2 per cent. This may vary in different instruments and, because of possible error from reading the zeros for the small peaks, a calibration check of the U^{234}/U^{235} and U^{236}/U^{235} bias should be performed as outlined for the U^{235}/U^{238} bias determination or as shown in Tables 13.12 to 13.15.

Table 13.16 gives the mass discrimination for a number of 12-in.-radius sector mass spectrometers using NBS uranium isotopic standards. The discrimination values given are the ratios of the measured ion-current ratios of U^{235}/U^{238} to the concentration ratios and are therefore, the quantity $1+b[(238-235)/238]$ in Eq. 13.8.

Table 13.16—MASS DISCRIMINATION IN SURFACE-IONIZATION ISOTOPIC ANALYSIS OF URANIUM FOR 9 DIFFERENT 12-IN.-RADIUS MASS SPECTROMETERS

Instrument*	Location	Ionization method	Ion detector	Number of runs	Date	Mass discrimination† of U^{235}/U^{238}
1	NBS	Multiple filament	Direct	10	1958	1.002 ±0.004
2	ANL 1	Multiple filament	Venetian blind, unshielded	15	July 1958	1.012 ±0.003
3	ANL 1	Multiple filament	Dumont SP 123, shielded	20	Oct. 1960	1.015 ±0.003
4	ANL 3	Multiple filament	ANL, 15 stage, 90° cylinder dynodes, shielded	12	Dec. 1960	1.012 ±0.004
5	ANL Idaho	Multiple filament	NAA, 15 stage, 90° cylinder dynodes, shielded	5	Dec. 1960	1.015 ±0.003
6	Westinghouse Idaho	Multiple filament	NAA, 15 stage, 90° cylinder dynodes, shielded	6	1959	1.000 ±0.005
7a	Phillips Petr. Idaho	Single filament	Direct	7	July 1958	1.013 ±0.004
7b	Phillips Petr. Idaho	Single filament	Direct	5	Jan. 1961	0.999 ±0.002
8	ANL 2	Single filament	Dumont 6292, 9 stage, not shielded	15	July 1958	1.023 ±0.006
9	KAPL	V-filament	Allen, 15 stage, pulse counting	26	1960	1.0054±0.002

*Instrument 9 used voltage scanning; all others used magnetic scanning.
†Error is standard deviation for a single determination.

It is not possible from the results in this table to make definite conclusions about the mass discrimination of the separate factors of ionization, transmission, or electron multipliers. Some general characteristics, however, are distinguishable.

First, there is some tendency for instruments with direct ion detection to show no discrimination. This would indicate no discrimination in the surface-ionization process. For instrument No. 7 the discrimination was different at different times, which could be because of a change in transmission discrimination, the transmission being low (10 to 50 per cent) in these cases and, hence, more critical with regard to discrimination than when transmission is high.

Second, instruments with electron multipliers used as current integrators give a discrimination between 1.010 and 1.025. The factor for five cases with magnetically shielded multipliers is between 1.012 and 1.015.

In all cases involving the single- and multiple-filament techniques, the total transmission is estimated as 10 to 50 per cent, whereas the transmissions with the V-filament instrument is of the order of 95 per cent or more because of the small area of ion emission and low temperature. With such high transmission as in the V-filament, the transmission discrimination would be expected to be very small even with voltage scanning, which usually produces appreciable discrimination (ion-source voltage effect) when the transmission is not high. It may be this factor which causes the discrimination of lower transmission instruments to change from time to time.

Figure 13.43 shows the results of analyzing several samples of uranium with the multiple-filament technique for long periods of time and shows an apparent but very small time fractionation effect. These samples were large for the high-sensitivity multiple-filament technique and therefore lasted many hours.

In uranium surface-ionization isotopic analysis, the mass-discrimination effects in the ionization process, whether single-, multiple-, or V-filament technque, are probably small. Transmission normally does not introduce discrimination, and electron multipliers used as current amplifiers and magnetically shielded or of the nonfocused type usually produce discrimination of 1.2 to 1.5 per cent per 3 mass units. There are exceptions to all these generalizations. Even two identical instruments, 5 and 6 in Table 13.16, both using the same ionization technique, source optical system, shielded electron multiplier, and magnetic scanning have different mass discrimination. Thus every instrument must be calibrated even though the techniques used normally produce no discrimination.

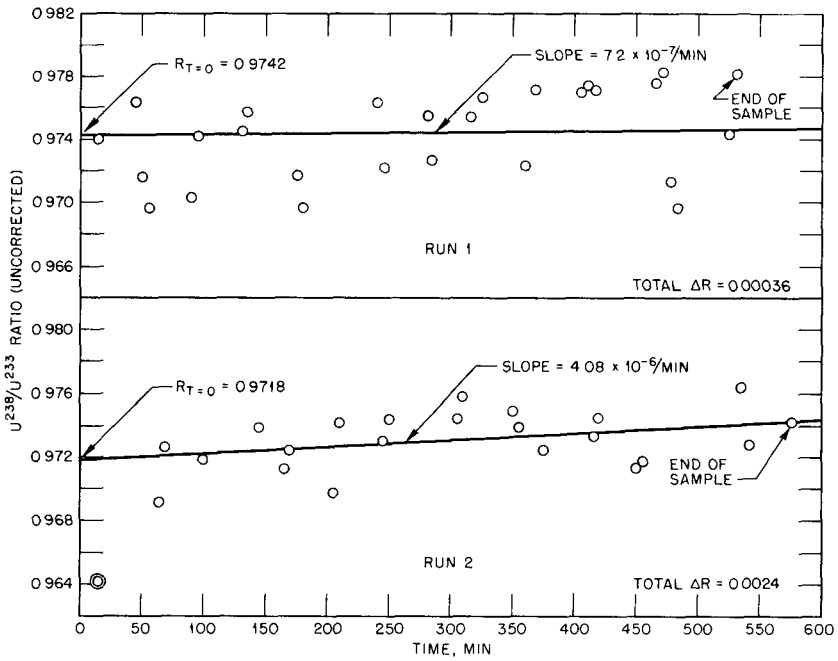


Fig. 13.43—Graph of the U^{238}/U^{233} ratio plotted against time for a multiple-filament surface-ionization source.

13.3 MASS SPECTROMETRY OF BORON

A. E. Cameron

Boron is an element of great importance in reactor technology because of the large neutron-capture cross section of the B^{10} isotope. Boron is used both in normal composition and in the form of highly enriched B^{10} for neutron detection, for neutron absorption in shielding, and as a burnable poison for control of reactor reactivity. The reaction $B^{10}(n,\alpha)Li^7$ has been used for flux measurement by following the production of the lithium isotope. Boron trifluoride counter tubes are much used for neutron detection. The capture follows the $1/v$ (v=velocity) law, and the cross section of approximately 4000 barns makes sensitive detectors possible.

When boron is used for shielding, control rods, or burnable poison, a specification may be set to establish the content of the B^{10} isotope. The reliance will then be upon mass spectrometric measurement, and at the present time most workers in the field do not feel as confident about boron measurements as about determining the isotopic composition of many other elements. There has been a strong suspicion, based largely upon the measurements of Thode et al.,[53] that boron in nature is subject to variation in composition. More recent measurements by

Osberghaus [54] and Parwel et al.[55] do not confirm the variations observed by Thode.

Most workers have used readily volatile boron compounds: BF_3; BCl_3; or diborane, B_2H_6. Extreme care must be taken to ensure that memory is not affecting the answers because of exchange of the sample gas with the material adsorbed in the sample system and the mass spectrometer from previous runs. As is shown in the discussion to follow, the use of borax (sodium tetraborate) and the production of ions by thermal emission from a hot filament appear to make the measurements much less dependent upon memory effects and may well provide a reliable method of measurement.

In all cases, regardless of the form in which the sample is measured, it is of great importance that any chemical operations be quantitative and that no steps be taken in the preparation which could lead to isotope separation. The high percentage mass difference between the two nuclides makes boron nearly as susceptible to isotope separation effects as is lithium.

13–3.1 Abundance Measurements

Inghram [56] ionized boron trifluoride (BF_3) and trimethyl borate [$B(OCH_3)_3$] by electron impact in a 60° 6-in.-radius mass spectrometer, using gas techniques since both compounds are readily volatile. He reported a B^{11}/B^{10} ratio of 4.31 ± 0.04. Thode, Macnamara, Lossing, and Collins [53] also used boron trifluoride in 90° and 180° mass spectrometers and reported a variation among the samples measured of from 4.27 to 4.42 for the B^{11}/B^{10} ratio. Osberghaus [54] used both boron trifluoride and boron trichloride in a gas instrument. Six minerals were investigated, and no difference was observed within an experimental error reported to be ± 0.5 per cent. His reported B^{11}/B^{10} ratio was 4.11 ± 0.02.

Schütze [57] used electron bombardment of boron trichloride and boron trifluoride and observed no variation in the isotopic composition during the measurements when the compounds were prepared by methods that gave 100 percent yield. If, however, potassium fluoborate (KBF_4) or sodium fluoborate ($NaBF_4$) were heated to produce boron trifluoride in a container in the ion source, it was observed that the $KB^{11}F_4$ appeared to decompose more readily and an isotopic fractionation occurred. Boron oxide (B_2O_3) and anhydrous sodium tetraborate ($Na_2B_4O_7$) were also evaporated in the ion source and the B^+ abundances were measured. Measurements on these two compounds were less precise than on the gaseous materials. He concluded that there was a difference in borons of two different origins. Boron from Italy showed a B^{11}/B^{10} ratio of 4.10 ± 0.02, and that from central Asia, 4.25 ± 0.05.

Palmer and coworkers [58] at Harwell found boron trifluoride to be a satisfactory sample form if multiple flushes were used to eliminate effects of memory. A glass sample system was preferred to metal, either because of lower sorption or quicker exchange with the new sample. A short glass-capillary viscous-flow leak was used. The volume of the sample system was held to about 10 ml behind the leak. They also described a solid-sample technique using fused sodium tetraborate on a tungsten filament. Ions were observed at masses 88 and 89 corresponding to $Na_2B^{10}O_2^{16+}$ and $Na_2B^{11}O_2^{16+}$. A correction to the mass-89 peak can be made for the $Na_2B^{10}O^{16}O^{17+}$ ion if desired, although this is very small.

Parwel et al.[55] investigated borons of various origins very carefully and found no differences except for boron derived from sea water, and here the discrepancy was small. They used BF_3 in a gas instrument. Panchenkov and Moissev [59] reported a B^{11}/B^{10} ratio of 4.43 for commercially prepared boron trifluoride. Semenov and Zonov [60] found boric acid and boric oxide to be preferable to boron trifluoride because the preparation of the more volatile compound was avoided. The oxide was fused on a platinum filament ribbon, and ions were obtained by heating to 1000 to 1200°C. The $B_2O_3^+$ and B^+ ions were measured. Two mass spectrometers were used, and measurements were also made by decomposing fluoroborate in the ion sources and ionizing the boron trifluoride liberated. They concluded that the boron oxide measurements were satisfactory. Their observed B^{11}/B^{10} ratio for presumed normal boron was 4.18.

Bentley and Hamer [61] reported blending boron trifluoride, highly enriched and impoverished in the B^{10} isotope, to determine mass-spectrometer bias. Bentley [62] described the procedure in detail and gave the precautions taken to remove the effects of memory. A heated metal-sample system was used to aid in desorbing boron trifluoride and to speed up exchange with the next sample. The molecular leak was made of glass. The effects of memory could be completely eliminated in 8 hr even going from fully enriched to fully impoverished material. Samples were stored in boron-free glass tubes with breakseals.

The standards were blended by measuring boron trifluoride in a fixed volume at controlled temperature and measured pressure. The measured discrimination in the mass spectrometer was such that the B^{11}/B^{10} ratio was too small by 3 to 4 per cent. The indication was that either discriminations in ion lenses or an isotope effect in the ionization were the cause of the error. A sample of boron was obtained from Herr von Ubisch which had been shown to be identical with other natural samples. The B^{11}/B^{10} ratio measured and corrected for discrimination was 4.19, or a B^{10} content of 19.27 ± 0.13 per cent.

Flushing the sample system and spectrometer with various gases, such as water vapor, ammonia, hydrogen, and helium, has been suggested, but none of these treatments has proven very successful.[63] Boron trichloride has been demonstrated to aid significantly in the removal of boron trifluoride from glass sample-handling systems.[64] The boron trichloride must have nearly the same isotopic composition as the sample which is to be introduced.

Lehmann [65] reported measurements upon diborane in a conventional gas mass spectrometer. He proposed a B^{11}/B^{10} ratio of 4.00 for naturally occurring boron.

Workers at Knolls Atomic Power Laboratory [66] have investigated the reliability of the boron isotopic measurements using the thermal ions from sodium tetraborate. They very carefully prepared standards from materials containing 99.85 and 1.45 per cent B^{10}. These were then run as borax in a 6-in.-radius 60°-deflection mass spectrometer with thermal ionization source. The ions at masses 88 and 89 were counted by a secondary-electron multiplier and pulse-counting equipment. Since scanning was done by variation in the accelerating voltage, a correction was applied for the voltage effect as well as for counting loss and the contribution of O^{17} to the mass 89 ion. No statistically significant bias was observed between the values calculated for the standards and those observed.

An article by McMullen, Cragg, and Thode [67] reports the preparation of gravimetric standards in the form of borax from highly enriched B^{10} (96.6 per cent) and impoverished material containing 1.0 per cent B^{10}. These standards were used to establish the discrimination factor in the thermal-ionization mass spectrometer used to measure four borax samples from the Searles Lake deposit. The instrumental bias observed was 0.5 per cent per mass unit. The four Searles Lake samples ranged from B^{11}/B^{10} ratios of 4.040 ± 0.008 to 4.072 ± 0.012 on an absolute basis. The writers state that the results of a new study on a suite of samples recently obtained from various geological settings again confirm variations in the abundance of the boron isotopes. These results will be published later.

13–3.2 Types of Mass Spectrometers

(a) *Gas-analysis Instruments.* Mass spectrometers that are adapted for the analysis of gases can also be used for the determination of the isotopic composition of boron since a number of volatile compounds exist. It is preferable, however, that the instrument used be somewhat modified if boron trifluoride is to be used as the sample gas. The method of introduction of a sample into a gas mass spectrometer involves the attachment of the sample in an appropriate container and evacuation of the connection before the sample valve is opened or be-

fore the glass breakseal is broken, if this is the sample-handling device. The sample is then expanded into an appropriate volume so that a fixed pressure is obtained back of the leak through which the sample flows into the ionization region. A suitable manometer is usually provided on this expansion volume so that the pressure can be adjusted to be approximately the same for different samples. This necessity could be avoided by the use of an adjustable leak as is done with uranium hexafluoride measurements.

The properties of the leak will be either fractionating or nonfractionating, depending upon whether the gas flows through by molecular or viscous flow. The molecular leak is generally to be preferred, although Palmer [58] used a viscous leak made from a small glass capillary for his boron trifluoride measurements. A possible objection to an adjustable leak, unless it is followed by a capillary to make it definitely viscous in flow characteristics, is that the fractionation characteristics may change with setting.

Pyrex glass is to be avoided if boron trifluoride is used because of isotopic exchange between the sample gas and the boron in the glass system. A metal system avoids the worry about exchange but will show severe memory effects unless it is adapted to be heated and pumped thoroughly as well as flushed with the fresh sample.

Ion-source life may be uncertain with a potentially corrosive material like boron trifluoride. The convenient ion for boron trifluoride measurements is the BF_2^+, which is the most abundant. Since fluorine is anisotopic, the B^{11}/B^{10} ratio is obtainable directly from the ions at masses 48 and 49. The boron trifluoride gas should be free from silicon tetrafluoride, and contact with water should be avoided. Reaction with water vapor can produce compounds that give interfering ions at masses 48 and 49. These ions are $B^{11}FH_2O^+$ and $B^{10}F_2H^+$. The ionization of silicon tetrafluoride also gives ions at these masses corresponding to $Si^{29}F^+$ and $Si^{30}F^+$. Monitoring the SiF_3^+ and SiF_2^+ ion positions indicates the presence of this contaminant.

When boron trichloride is used, it is better to use the B^+ ions and avoid the necessity of correcting for the chlorine isotopes in the BCl_2^+ ion and interference with $B^{10}Cl^{35+}$ at mass 45 from $C^{13}O^{16}O^{16+}$ and $C^{12}O^{17}O^{16+}$ and at mass 46 from $C^{12}O^{18}O^{16+}$. Corrections for these ions can be made from the size of the peak at mass 44 produced by $C^{12}O^{16}O^{16+}$.

All the ions involved are of low mass, and thus there is no resolution problem. Gas-analysis instruments of 60° 6-in.-radius or 180° 5-in.-radius are quite satisfactory. A gas-analysis instrument of different ion optical type is commercially available from the Consolidated Elec-

trodynamics Corp. This is a cycloidal focusing instrument using a permanent magnet. It shows unit resolution at mass 200, and so more than adequately covers the range necessary for boron measurements. The sample system is metal and is adapted to be heated to 150°C.

(b) *Solid-sample Mass Spectrometers.* Mass spectrometers adapted for solid samples and producing ions by thermal emission from a hot filament are discussed in Sec. 13–2. For boron measurements, using borax as the sample form and measuring the ions at masses 88 and 89 of the composition $Na_2B^{10}O_2^{16+}$ and $Na_2B^{11}O_2^{16}$, adequate resolution is obtainable with a small-radius instrument. The instrument must make provision for breaking vacuum in the ion-source region or in the entire analyzer tube for installation of a new sample and filament assembly. If an instrument fitted with a vacuum lock for introducing triple filaments is available, it is adaptable to the single-filament measurements. Vacuum requirements for solid-sample measurements are, in general, not as stringent as those for gas work. Measurements can usually be made satisfactorily at pressures on the order of 10^{-6} mm of mercury without interferences.

The use of boric oxide with thermal ionization will be essentially the same as the use of borax, with the measurement of different ions.[60] If, however, this oxide, borax, or other solid boron compound is to be evaporated in the ion source and ionized by electron impact, a hybrid instrument is required. The ion source will be essentially that of a gas instrument, but provision must be made for introduction of the solid sample in a filament or in a small furnace from which vapor can be produced. This again will require breaking vacuum for each sample or the use of a vacuum lock. The vacuum lock can be somewhat simpler than for handling filaments because it may be possible to avoid changing electrical connections along with the sample.

13–3.3 Ion Detection

Most measurements have been made with a direct-current detection scheme which uses a single receiver and in which the two ion beams are brought alternately upon the exit slit. It is preferable that this be accomplished by varying the magnetic field to avoid changing voltage discrimination in the ion source and a consequent voltage correction. The magnitude of the signals from the two isotopic beams may be indicated by the trace on a recorder chart or may be measured by a galvanometer and decade potentiometer arrangement, as described for uranium hexafluoride measurements in Sec. 13–1.2.

Hass et al.[66] have detected the ion beams with a secondary-electron multiplier and pulse-counting equipment. Corrections were necessary for counting loss, which is a function of the speed of the scaling equipment and of the counting rate. A correction was also made for the voltage effect since they did not scan by changing the

magnetic field. It is necessary to establish this correction by measuring the same peak at two different accelerating voltages to determine the effect upon intensity which is caused by the changed voltages in the source region. The magnetic field must be changed to bring the ion beam onto the receiver slit for the second voltage. This correction is, unfortunately, a function of the geometry in the part of the ion source where the ions obtain their initial acceleration and may vary somewhat from filament to filament because the geometry cannot be reproduced perfectly.

Parwel et al.[55] made their comparisons between samples of boron of natural origin with a mass spectrometer with a dual collector. They were attempting to observe differences between samples, rather than to make an absolute measurement. The arrangements described in Sec. 13–1.2 would function equally well for B^{11}/B^{10} ratio measurements and would permit fairly precise comparisons to standard materials if the need arose for determining small differences and if standards were available.

13–3.4 Gas vs. Solids Measurement

The advantage would appear to be all with the measurement of isotopic ratio by thermal production of ions. The boron trifluoride method is subject to difficulty because of the memory effects, which can be removed or minimized only by heating and by flushing with the next sample to be introduced. If glass is used for the sample container or for the sample introduction system, it must be boron free. The flushing procedure is wasteful of sample, and relatively large amounts must therefore be prepared. This is not always convenient. It may be necessary to prepare many milligrams of boron trifluoride to make a reliable measurement. Furthermore, the work of Bentley[62] indicates that the mass spectrometer shows a 3 to 4 per cent bias in the boron trifluoride measurements.

The production of thermal ions from borax by the method described by Palmer et al.[58] has been shown by Haas et al.[66] to be without significant bias. Memory effects can be eliminated by using a new filament and a cleaned mount for each sample and by ensuring that no parts of the ion source on which borax may have deposited by evaporation become hot enough to cause re-evaporation. The sample required in this type measurement is on the order of fractions of a milligram, and no gas-handling apparatus is required.

13–3.5 Sample Preparation

In the preparation of boron samples for mass spectrometry, it is of extreme importance that recovery of boron and its conversion to

another chemical form be complete. It is possible that many of the discrepancies observed in boron isotopic measurements are the result of incomplete chemistry rather than variations in the sample composition.

The solubility of boric acid in diethyl ether is sufficiently great that this compound can be completely extracted from an acid solution. If the starting material is refractory, like some minerals, fusion with potassium hydroxide may be required. Preliminary purification to remove materials that would extract along with the boric acid may be necessary. Fluoride, phosphate, sulfate, and nitrate ion and some cations must be removed.

The boric acid is readily made into the sodium salt for loading on a filament for thermal ionization. If, however, boron trifluoride must be prepared, larger amounts of material are required. Potassium fluorobrate is prepared from boric acid by the following reaction:[68]

$$H_3BO_3 + 3HF + KF \rightarrow KF \cdot BF_3 + 3H_2O$$

The potassium salt is precipitated by the addition of potassium hydroxide. It is dried and stored at elevated temperature or sealed to prevent attack by moisture.

Samples of boron trifluoride for mass-spectrometer use are prepared from the potassium fluoborate by heating a few milligrams of the salt in a metal tube connected to the sample system. A temperature of 800°C will give complete decomposition. Traces of silicon trifluoride can be removed by freezing with dry-ice slush at −80°C. The boron compound boils at −101°C; therefore it is not condensed.

Boron trichloride must be prepared either by heating the element in chlorine or in dry hydrogen chloride gas. Boric acid can be converted to boron trichloride by mixing with carbon and heating in a stream of elemental chlorine. The compound is readily hydrolized and must be kept from contact with moisture.

Direct fluorination of the elemental boron, the oxide, or carbide can be accomplished in the manner described in Sec. 13–1.3. In this case, however, a metal reaction tube is much to be preferred to glass to avoid production of silicon trifluoride and also possible isotopic contamination of the sample by boron in the glass. Finely divided carbide would be required for the reaction to go with cobalt trifluoride as the fluorinating agent. The boron trifluoride should be trapped at liquid-nitrogen temperature; the temperature should be raised to −80°C with dry-ice slush; and the boron trifluoride should be transferred to the sample tube, leaving hydrogen fluoride and silicon tetrafluoride behind.

13–3.6 Precision and Accuracy

The best precision obtained in boron measurements is that reported by Parwel et al.[55] for the intercomparison of samples of boron trifluoride in a gas instrument with dual collection. The writers made no claim for the accuracy of the results, but they report a precision of ±0.2 per cent for the intercomparisons. By using standards mixed from boron trifluoride highly enriched and highly impoverished in the B^{10} isotope, Bentley [62] was able to correct for discriminations in the mass spectrometry. He reported the B^{10} abundance in the normal boron with an accuracy of ±0.7 per cent.

Haas et al.[66] evaluated the accuracy of a single analysis by the borax method at ±1.3 per cent of the B^{11}/B^{10} ratio at the 95 per cent confidence level. This corresponds to an accuracy of ±1.0 relative per cent uncertainty in B^{10} abundance in natural boron.

It is thus safe to say that with the present state of the art of boron isotopic abundance measurements, an accuracy of 1 per cent of the B^{10} abundance is obtainable by thermal ionization using borax. Any improvement in this determination would require use of standards and, preferably, gas techniques with extreme precautions being taken to eliminate the effects of memory. All chemical procedures must give 100 per cent yield to avoid isotope-separation effects.

13–4 MASS SPECTROMETRY OF LITHIUM

A. E. Cameron

Lithium is not an element of major importance to reactors. There are, however, some unique uses of this element, and its mass spectrometry assumes some importance. The two isotopes of masses 7 and 6 occur in a ratio of approximately 12.5 for the 7/6. A variation of this ratio in nature has been demonstrated [69] with the fluctuation between about 12.4 and 12.7, depending upon the mineral and its geological origin. This variation corresponds to a variation in the atom per cent of Li^6 of from 7.30 to 7.46 per cent. Greater variations than this will be observed in commercial chemicals since any purification process, such as partial precipitation or partial crystallization, may produce an appreciable isotope fractionation. The purchaser of lithium compounds must also beware of securing material that is substantially depleted in the light isotope since a large amount of lithium has been returned to the general market after having gone through a separation process for the production of enriched Li^6. For any purpose in which the content of Li^6 is important, as, for instance, in the growing of lithium iodide crystals for neutron detection, it would be advisable to verify the isotopic composition before use.

The major use of lithium in reactors has thus far been in the production of tritium by the (n,α) reaction on the Li^6 isotope. A potentially large use for the Li^7 isotope as metal is as a heat-transfer medium, for which it possesses excellent properties. Because of the 950-barn cross section of the light isotope, the Li^6 content must be reduced by a factor of about 400, however, in order that the total neutron absorption be equivalent to that of sodium. The same isotopic purity would be required if the fluoride were to be used as a component of a fused-salt fuel mixture. Mass spectrometry of the lithium would be a requirement in the case of such uses.

The light isotope of boron, B^{10}, undergoes an (n,α) reaction to give Li^7. This isotope is much used as an neutron detector, and neutron-flux measurements have been made by exposing rods of known boron content to the reactor flux and then determining the Li^7 produced. Because a pure isotope is produced, a simple determination of the total lithium by flame photometry may suffice to determine the extent of the reaction. However, an isotope-dilution procedure in which a known amount of very pure Li^6 (obtainable from electromagnetic separations) is added to the sample and the Li^7/Li^6 ratio determined with a mass spectrometer is capable of yielding analytical results of higher precision. It it also adaptable to working with very small quantities and may frequently be more satisfactory than flame photometry.

13–4.1 Ion Production

There is no stable compound of lithium which has sufficient vapor pressure at or near ordinary temperatures to permit satisfactory measurements to be made with a gas mass spectrometer. The two general approaches available are (1) ionization by electron bombardment of some kind of vapor produced by heating a lithium compound in a retort contained in or near the ion source and (2) thermal ionization in which the sample is coated on a filament that is heated to produce ionization or in which the sample is evaporated from one filament and impinges on another one that is much hotter. In this latter technique the processes of evaporation and of ionization are separated, and certain discriminations observed with a single filament may be minimized.

Friedman [72] has studied the vapors produced by heating single crystals of lithium iodide and has determined the thermodynamic relation between the various species in the vapor. The reliable ion that Cameron reports is formed by electron bombardment of the dimer Li_2I_2 causing removal of one iodide atom. This ionization would be expected to proceed without isotope effect and could account for the

690–457 O—64——70

highly reliable character of this ion. The LiI^+ ion, if formed by removal of an electron from the monomer, should also be reliable; but, if formed by the removal of a lithium atom or ion from the dimer, it might show an isotope effect.

The bromide, chloride, and fluoride are sufficiently volatile at readily obtainable source-furnace temperatures to be useful in an electron-bombardment source. Here, however, if a molecular ion is measured, a correction must be made for the isotopic composition of the chlorine or the bromine and corrosion effects with bromide appear to be somewhat greater than desirable. The iodide offers the unique advantage that iodine is anisotopic. The nitrate and sulfate have both been used in double- or triple-filament work with thermal ionization, as will be discussed below, but do not appear to have been used in electron-bombardment measurements.

The amount of material that must be sublimed to secure an adequate signal at the collector is large compared to that which is required in thermal-ion production. The efficiency of electron ionization is low and may differ from surface ionization by a factor of 10^{-5} to 10^{-7}; therefore milligrams, instead of microgram or submicrogram amounts of material, are required. This means that a considerable amount of material deposits in the ion source, which gives rise to difficulties from deposits on ion lens elements or on insulators. The resulting disturbance of the ion or electron beam or potentials on the source elements caused by insulator leakage leads to unstable operation. A further complication arises if any surface upon which lithium-bearing material has been deposited is subsequently heated enough to allow re-evaporation. This leads to memory and affects the next samples measured. It is not possible to measure normal and highly enriched material in the same ion source without an intervening cleaning operation. Various source structures that have been designed to avoid the effect are discussed below.

(a) *Electron Bombardment.* The vapor of a lithium-bearing compound is ionized by slow electrons, about 75-volt energy, in an ion source that is not too different from that used in a gas instrument. Measurements have been made using metal,[70] but a correction must be made for the isotopic fractionation caused by preferential evaporation of the light isotope from the liquid. This correction factor is proportional to the inverse ratio of the square roots of the atomic masses; but, since an ideal separation process is not likely to occur, the correction may be somewhat uncertain, and a drifting value for the isotopic ratio may be observed.

The possibility exists of using a compound containing lithium which will have a high molecular weight and in which the evaporative

discrimination between light and heavy molecules can be eliminated or at least minimized. The sublimation of molecules from crystalline surfaces occurs without isotopic discriminations. If, in addition, the molecule is a heavy one, reliable results should be obtained. White and Cameron,[71] for instance, sublimed $LiAlCl_4$, bombarded the vapor with slow electrons, and made measurements at masses 6 and 7. Although the results appear to be reliable, this compound is not too readily prepared, is very hygroscopic, and sublimes in only a very narrow temperature range without dismutation. Lithium iodide avoids the dismutation difficulty but is also hygroscopic. It is, however, quite readily prepared and sublimes with sufficient vapor pressure at reasonable temperatures.

Cameron [69] has made measurements by electron bombardment of lithium iodide vapor and has compared the results obtained by measuring the Li^+, LiI^+, and Li_2I^+ ions. Measurements of the LiI^+ ions at masses 133 to 134, and LiI^+ at masses 139 to 141 avoid the possibility of severe mass discriminations in the ion lenses and appear to be more reliable than measurements made upon the light metal ion. Cameron concluded that only measurements with the Li_2I^+ ion currents were reliable since no change in the isotopic ratios was observed in spite of the fact that measurements were made with two mass spectrometers over a considerable period of time and with many changes in the operating parameters of the instruments.

(b) *Thermal Ionization.* Lithium ions can be produced in very high yield from lithium compounds that are in contact with a hot surface of a material of high work function, like tungsten, tantalum, or rhenium. A dull-red heat suffices to produce positive ions. If, however, the lithium compound is applied to the surface and it is heated sufficiently to cause evaporation of positive ions, a simultaneous evaporation of the lithium compound occurs. Not only are the light-isotope ions, Li^{6+}, produced preferentially, which would lead to a bias, but the evaporation of uncharged molecules also proceeds with the light component preferred and a drifting ratio is observed.

An immediate improvement is made by using a double- or triple-filament ion source in which the sample is deposited upon an evaporating surface capable of being heated either by direct resistance heating or by radiative heating from the ionizing filament. It is assumed that molecules striking the hot surface are ionized without discrimination. The remaining bias effects will be found in the primary process of evaporation in which the isotope effect can be minimized by using a compound of high molecular weight and in discriminations caused by aberrations in the ion lenses because the Li^+ ions have such a high proportional mass difference.

The sample size for this technique may be quite small, a microgram or less, compared to the milligram sample size required for electron bombardment. The amount of material evaporated in the ion source is thus reduced, and the problems of cross contamination and of memory can be controlled more readily. It is possible to design a filament mount that can be changed, together with all the pertinent surroundings, to eliminate the possibility of re-evaporation of deposits from a previous sample. The small size of the sample does, however, introduce an additional problem because most materials are found to contain some lithium and the ionizing filaments require prebaking and checking to ensure freedom from lithium.

13–4.2 Sample Preparation

The intention here is not to provide a complete manual for the preparation of samples but rather to indicate some precautions that must be taken. Isotope fractionation readily occurs, and it is particularly important that all the lithium in a sample be recovered. It has been shown by Wagner, Pelz, and Higatsberger [73] that a shift in the 7/6 ratio from 12.48 to 14.03 was produced by many repetitive partial precipitations of lithium carbonate from a chloride solution. The presence of silicate or phosphate can introduce a discrimination because of preferential segregation of one isotope in the insoluble compound.

Lithium is very readily separated from other elements and from its neighbors in the alkali metal series by charging the neutral solution on a cation resin column and then eluting it with hydrochloric acid of about 0.5 normality. The lithium is the first of the alkali metals to appear. The elution process can be conveniently monitored with a simple flame test or by a flame photometer. The resolution of the column can be varied by changing the ratio of length to diameter; a longer column spreads the peaks farther apart. It is feasible to separate lithium from a very high concentration of sodium by using a relatively long column of small diameter. The diameter will be determined by the amount of material to be handled. For samples to be analyzed for isotopic content by surface ionization, relatively small amounts of lithium are required, and a column of 1 cm inside diameter packed with purified Dowex-50 for a length of 12.5 cm is quite satisfactory. Care must, of course, be taken to prevent cross contamination of samples in the use of the exchange column.

For handling small samples, it is also necessary to investigate the reagent blank to ensure that contamination is not occurring because of lithium present in the chemicals. Even supposedly pure materials, like clear fused quartz, are found to contain enough lithium to interfere

with critical measurements when low amounts of the element are being handled. Where larger amounts are available, precautions can be less stringent.

Lithium iodide is conveniently prepared from most lithium compounds except the silicate and phosphate by adding purified hydriodic acid and evaporating. The higher boiling hydriodic acid will displace the other halogen acids and will reduce sulphate and nitrate. Several additions of acid should be made if any appreciable amount of sulphate is being reduced. The iodide will, however, undergo hydrolysis and reaction with water to produce iodate. This is inhibited by an excess of hydriodic acid and can be further suppressed by adding ammonium iodide. Lithium iodide is very soluble in absolute ethanol or acetone, and this frequently provides a convenient way of transferring the sample to the sample carrier for installation in the ion source.

Hydriodic acid as commonly supplied contains a small amount of hypophosphorous acid (H_3PO_2) as a stabilizer. The acid must be distilled to separate it from this, and such distillation should be carried out in an inert atmosphere. The acid should then be stored in darkness, but even then decomposition to yield free iodine will proceed. It is better to prepare small amounts of the acid more frequently when routine measurements are being made.

The handling of the solutions or of solids for installation in the mass spectrometer depends upon the exact type of ion source being used. For sources in which a region is heated to vaporize the lithium compound, it may prove very convenient to use a porous substrate, such as alundum, fine nickel gauze, or a suitable porous metal. A solution that has already been prepared in appropriate concentration may be applied to the porous sample carrier and then dried. Alternatively, the final preparation in the desired chemical form may be carried out on the sample carrier itself just before installation in the ion source.

13–4.3 Types of Mass Spectrometers

Most workers in the field have made measurements on the metallic ions (Li^+) at masses 6 and 7. There is thus no resolution difficulty, and even a spectrometer of small radius will suffice. In general, in the United States the instruments that have come to be known as the "standard Nier spectrometer" have been used. This instrument is a 15-cm-radius 60° magnetic deflection apparatus. In such an instrument the ion beams are separated by 25 mm at the receiver position. The workers who have been faced with the problem of making isotopic measurements upon lithium have usually modified equipment they had available. Bishop, Briercliffe and Bentley [74] have described the conversion of a Metropolitan-Vickers MS–3 for lithium measurements,

and Bishop and Bentley [75] have described the conversion of the Metropolitan-Vickers MS–1 and MS–2 for the same purpose. These were originally gas instruments and were more elaborate than was necessary for this type measurement. Some workers have, therefore, built instruments specifically for the measurement of lithium isotopic ratios. Higatsberger [76] used a mass spectrometer of 30 cm radius but with only a 15° deflection for measurements of the Li^6/Li^7 ratio. Adequate resolution was secured with this instrument.

A mass spectrometer designed specifically for the isotopic analysis of lithium has been described by Bentley, Bishop, and Davidson.[77] An outline drawing of the arrangement of this instrument is shown in Fig. 13.44. It is, in effect, a double mass spectrometer. The tube

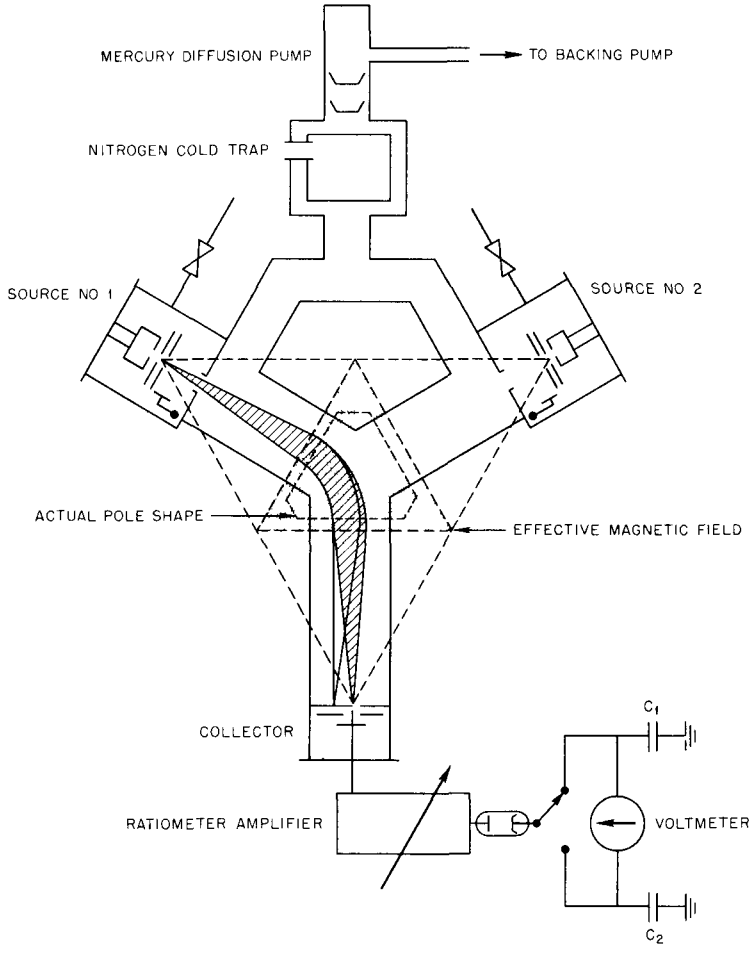


Fig. 13.44—Dual mass spectrometer for lithium isotopic measurements.

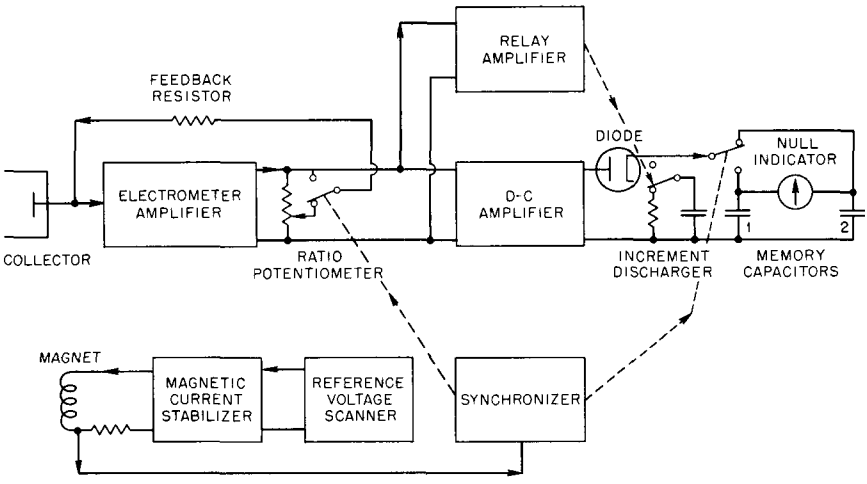


Fig. 13.45—Block diagram of measuring circuits for the dual mass spectrometer.

is built in the form of a Y with two ion-source regions, a common magnetic field in the form of an equilateral triangle, and a common collector and read-out mechanism. The radius of curvature is 10 cm. The ion sources are mounted on flanges that can be removed for cleaning and for installation of new samples. The source chambers are isolated from the analyzer regions by a gate valve in each chamber. It is thus possible to remove the ion sources without losing the vacuum in the analyzer region. This reduces pump-down time.

Two ion sources can be installed; the system is then pumped down, and the two samples can be measured. It is necessary, of course, to reverse the magnetic field between samples to bring the ion beams onto the collector. The ion source is a relatively simple structure, and the filament, sample mount, and its surrounding ion box can readily be removed for cleaning between samples.

The two ion beams to be compared follow identical paths through the magnetic field. Magnetic scanning is used to bring the beams alternately upon the collector slit, and ratios are determined semi-automatically and read from a potentiometer dial. The block diagram of the measuring circuits is shown in Fig. 13.45. The operation is as follows: The limit controls on the reference voltage scanner are set so that the magnet current is swept repetitively to move the mass 6 and mass 7 ion beams just past the collector slit. The electrometer amplifier, which is a vibrating reed with associated amplifier (somewhat modified), has a fixed minimum gain for the larger of the two peaks; its gain is variable for the smaller peak by changing the setting of the ratio potentiometer. Memory capacitors 1 and 2, which are isolated from the d-c amplifier by the diode, store the maximum

amplifier output produced by the scanning of the two ion beams across the collector slit. These capacitors, and the ratio potentiometer are switched at the proper time by the synchronizer, which is triggered by the magnet current. Equality of the stored voltage on the two condensers is indicated by the null indicator, a vacuum-tube type balance indicator. The setting of the ratio potentiometer is varied manually as the scanning proceeds automatically until the null indicator shows that the stored voltages are equal. For readings to be made on a falling ion current, it is necessary to discharge the condensers partially before each ion peak is stored. This is accomplished by the incremental discharger driven by the relay amplifier. This discharge removes a portion of the charge before each storing cycle.

The time required with the special lithium mass spectrometer for a single determination was 1¼ hr of machine time and 2¾ hr of operator time. This included cleaning source A, loading source B, running the sample introduced on B, and outgassing and checking source A preliminary to loading the next sample on it. This time was found to be about half of the time that had been required for making one measurement with the modified MS–1, –2, or –3. The precision and the estimated accuracy compared favorably with the other instruments.

A spectrometer designed specifically for the rapid analysis of the isotopic content of alkali metals has been described by Pavlenko, Rafal'son, and Shereshevskii.[78] A simplified diagram of the instrument is given in Fig. 13.46. The radius of curvature of the ion beam is 10 cm, and a 90° magnetic deflection is used. The article states that the mass range of the instrument is from 4 to 40; so it would seem intended for lithium work or possibly for potassium. The magnetic field is produced by a permanent magnet, and the ion beams are brought onto the collector by varying the accelerating voltage.

A Ferris wheel arrangement carries 24 filaments on which the substances being measured are placed. The entire assembly is then installed, and the filaments are brought into operating position one after the other. Thus, it is possible to analyze 24 separate samples without breaking vacuum. Disadvantages of this instrument are the single-filament technique and scanning with accelerating voltage, both of which introduce discriminations of considerable magnitude for light elements. It would be necessary to compare unknown samples to a series of standards. The instrument appears to employ a single ion-collector device. Some improvement would be made by using dual collection, although this would not eliminate the discriminations of the single-filament source.

A mass spectrometer built expressly for the measurement of the isotopic composition of lithium is described by Ridley and Silver.[79]

This instrument uses a 60° deflection on a 4.6-in. radius. Dual collectors are used, one of which is movable to secure the best operating conditions. A single filament is used with side flags on which lithium nitrate is deposited. These sample tabs are heated by radiation from the ionizing filament to vaporize the lithium salt. The ion beam is pulsed at 25 cycles/sec with 10-msec pulses. A pair of electrometer tubes with 10-megohm input resistors detects the ion currents from the collector pockets. The inputs to a pair of amplifiers are taken from calibrated attenuators, which are the cathode-follower loads for the electrometer tubes. One of the amplifiers inverts the signal it receives. The positive and negative pulses that result are displayed on an oscilloscope screen. The attenuator in the output of the larger signal is adjusted until the displayed pulses cancel, and the ratio is then read directly from the dials of the attenuators. Ratios are

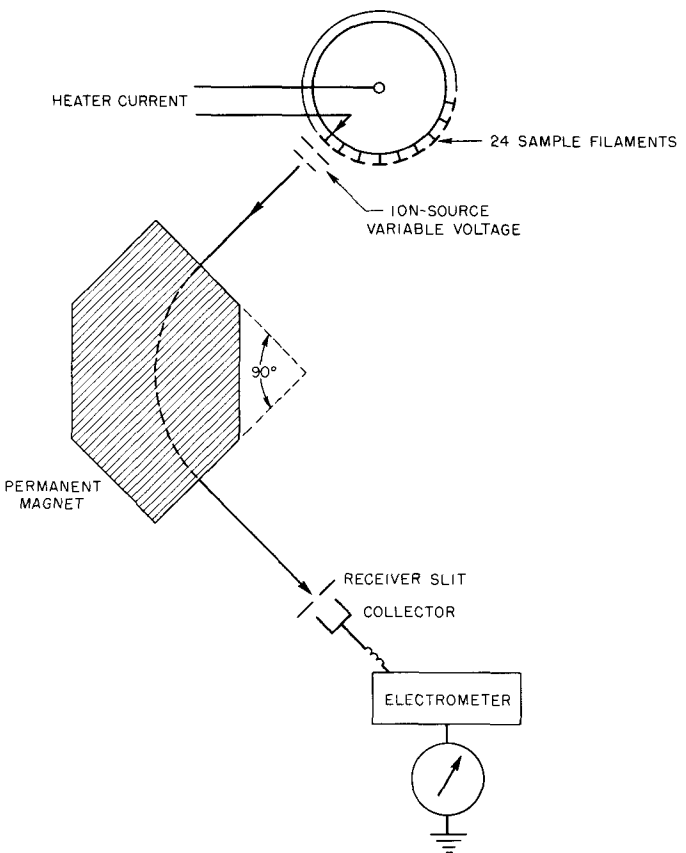


Fig. 13.46—Light-element mass spectrometer with 24 single filaments.

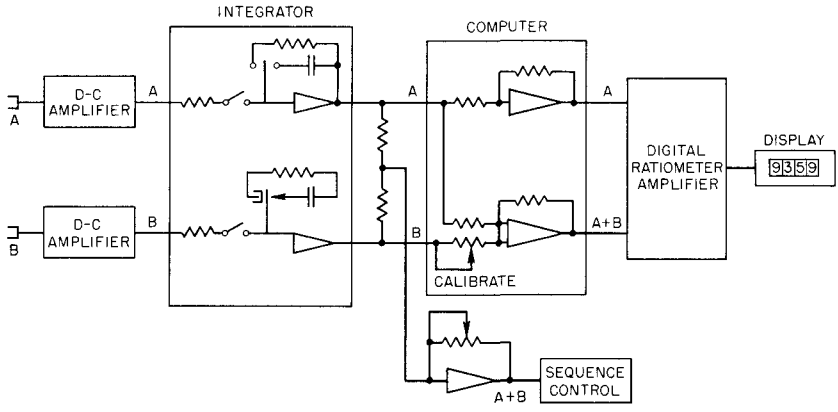


Fig. 13.47—Schematic diagram of ratiometer for dual-collection mass spectrometer.

quoted to 2 per cent accuracy only because of unknown discriminations in the spectrometer.

A rather extensive and elaborate mass-spectrometer installation was constructed in the Y–12 laboratory for monitoring the operation of a lithium-isotope separation plant.[80, 81] Several mass-spectrometer tubes and vacuum systems are linked to one set of electronics. The tubes themselves are 15 cm radius and have 60° deflection. The source envelopes are fitted with vacuum locks to permit sample changing without loss of vacuum. Dual collector pockets are placed on the focal plane at the receiver end of the instrument. The read-out system of the instrument is shown schematically in Fig. 13.47.

The ion currents collected by A and B are amplified through identical d-c amplifiers, integrated, and fed to the computer panel. This unit sums the outputs of A and B and feeds this output and output A to the digital ratiometer amplifier, where the ratio of the outputs of A/A+B is calculated and the results are displayed as atom per cent. The output sum, A+B, taken ahead of the computer panel is fed to a sequence control, which instructs the ratiometer to display at a predetermined value of the ion currents.

The samples are prepared directly in 0.22-caliber long-rifle cartridge cases made of copper-plated mild steel. Hydriodic acid is added to the lithium salt in the container, and it is then dried on a hot plate. The cartridge is grasped with the handling rod, which passes through the removable Lucite cover for the vacuum lock shown in Fig. 13.48. With the rod fully retracted, the cover is placed on the vacuum-lock chamber, the rough vacuum valve is opened until the chamber is pumped to about 200 μ pressure, and then the flapper is operated through a vacuum seal.

The rod is extended, and the sample container is placed in the stainless-steel cylinder of the ion source. The rod is then withdrawn, and the flapper is closed. The tungsten heater around the stainless-steel cylinder is in steady operation. As soon as the pressure in the main tube has recovered sufficiently, the ionizing filament is turned on, and the operation is then automatically controlled by the sequence controller. It has been found more satisfactory to repeat samples than to take data for a longer time on any individual sample. The ioniza-

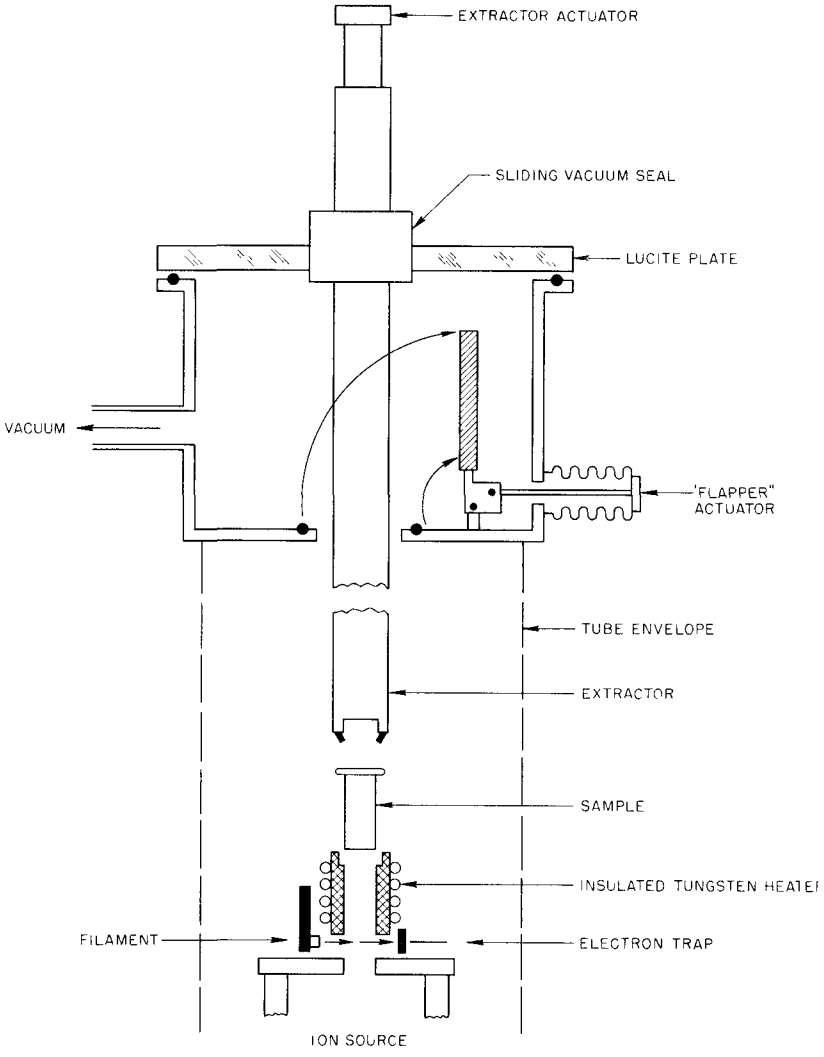


Fig. 13.48—Vacuum lock and sample changer for lithium mass spectrometer.

tion is presumed to be by electron impact; however, it would appear that there might be some thermal contribution since the temperature of the sample carrier reaches 800 to 900°C and the work function of copper is given as 4.61 volts,[82] which seems high enough to give some production of ions from lithium. With this arrangement in good operating condition, it is possible to make a determination in less than 5 min, not including the sample preparation time. This installation is calibrated against standards to maintain control quality.

At least one attempt has been made to measure the isotopic composition of lithium by ion-counting techniques. Collins and Rourke [83] attempted to use single filaments coated with lithium hydroxide or lithium sulfate and kept the ion currents below 10^{-14}. The ions were detected with a secondary-electron multiplier, and the counts were recorded with appropriate scaling and registering equipment. They concluded that this method was unreliable, not because of the method of ion detection, but because of difficulties associated with the production of ions from a single filament. They assign a large portion of the troubles to warping of the filament and the consequent changes in ion source geometry. Subsequent to the work reported above, they used this technique for the measurement of lithium isotopic composition with a 30-cm-radius instrument in which the magnetic fields necessary to bring the two ion peaks upon the collector are set by nuclear magnetic resonance probe controls. With this arrangement it is possible for them to go rapidly between masses 6 and 7 and to be assured that the ion beam will fall precisely upon the collector slit. No claim is made, however, that the technique is applicable to other than relative measurements.

13–4.4 Ion Sources

An ion source for electron-bombardment ionization of the vapors of inorganic materials, in which the ionization chamber is readily substituted, has been described by Cameron.[84] This source was used with lithium iodide in the measurements of lithium isotopic abundances. The Y–12 source discussed above is a variant of this kind of assembly. It has an advantage in that most of the surfaces that come in contact with the sample are changed and the memory effects are minimized although there was found to be some slight effect in going from highly enriched material back to normal or near normal.

Palmer and coworkers at Harwell have used a triple-filament source.[85] The central filament is the ionizing surface, and the sample is coated on both the side filaments or upon only one. These need not be adapted for heating, other than by radiation from the ionizing filament. They have used lithium nitrate, a salt which is volatile under the conditions of operation, and have agreed closely with Cam-

eron's figures for the iodide measurements on samples of the same material. The rather complicated assembly may be replaced by an ionizing filament and a simple metallic flag of nickel or nichrome V suitably positioned to be heated by radiation. This was the arrangement used by Bentley et al.[77] This arrangement would be suitable for work with nitrate, bromide, and iodide and possibly other compounds, depending upon the heat dissipation of the ionizing filament and upon the spacings of the elements.

The three-filament assembly has been used by Schutten [86] to compare lithium samples that differed only slightly in isotopic composition. The two samples were coated on the side filaments, and the center filament was operated at a low enough temperature that no evaporation took place without deliberate heating. One side filament was then raised in temperature until adequate signal was obtained. This filament was then turned off, and current was applied to the other. He observed about a 1 per cent cross contamination from evaporation from one sample filament to the other. For studying processes in which the separation factors were between 0.90 and 1.10, the error from cross contamination was smaller than the error in the mass-spectrometer measurement. Ratios were measured to an accuracy of about 0.2 per cent.

Ivanov and Kykavade [87] have described a two-filament arrangement for which they claim excellent sensitivity in the rare-earth region. A planer zigzag ionizing filament was mounted in close proximity to a tungsten ribbon, which served as the sample carrier and from which neutral molecules were evaporated. On contact with the ionizing filament, these neutral molecules were decomposed and ionized with high efficiency. A modification of this arrangement has been used in the Oak Ridge National Laboratory for measurements of lithium isotopic abundance. The flat ionizing filament was replaced with a helix of tungsten wound on a 0.5-mm mandrel. For convenience the ribbon sample carrier mounted behind this may be of nickel. Preliminary outgassing removed contaminating lithium. The sample form was lithium bromide. The source showed high sensitivity and appeared to give very reproducible results although a bias existed between the ratios measured and those observed with the lithium iodide method using electron bombardment. The cause of this bias has not been investigated.

Any improvement that one can make in the rigidity and reproducibility of geometry of a thermal-ionization source appears to add to the precision of the measurements. At Iowa State University, H. Svec (private communication) has developed a mass spectrometer with dual collection and has adapted it to the measurement of lithium

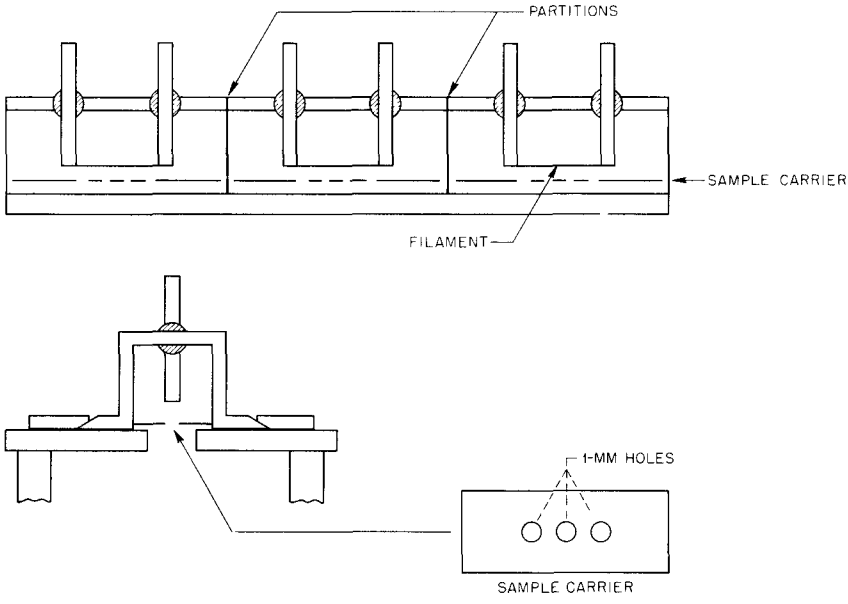


Fig. 13.49—Triple-sample carrier.

isotopic ratio. The principal improvement seems to have been in the design of the ion source. Figure 13.49 is a sketch of the operating principle. The sample is coated on a nichrome V strip, which is snapped into a holder so that the geometry is very reproducible. The filaments, supported on ⅛-in.-diameter legs for extreme rigidity, are made of tungsten ribbon 0.040 by 0.001 by 5 mm long. Ions are extracted through three holes 0.040 in. in diameter and spaced 0.080 in. center to center. The sample is coated around these holes as lithium sulfate, lithium nitrate, or lithium iodide. The sample carrier holds three samples and can be slid in accurately machined ways by a vacuum linkage to position each of the three in turn. Thus a standard and two unknown samples can be loaded and measured without breaking vacuum. Each sample is completely isolated from the others, and no cross contamination has been observed.

The spectrometer itself is of 5 cm radius. Ion currents are of the order of 10^{-10} amp maximum, and sample size is, in general, 10 to 50 μg. Direct-current amplifiers are used, and no ratio determinations are made according to the method described by Nier, Ney, and Inghram.[88] Under favorable conditions a precision of measurement of 0.2 per cent is obtainable at the 95 per cent confidence level. With carefully made standards the accuracy also approaches this value.

13–4.5 Precision and Accuracy

The hydrogen-deuterium pair and boron and lithium provide the worst cases of discrimination which can be found for mass spectrom-

etry. The high proportional mass difference between the isotopes causes discriminations in the ion lenses. Since any process that involves evaporation may introduce a separation, it is difficult to assign an absolute accuracy to any mass-spectrometric measurements unless it is possible to compare the unknown sample to a standard or standards that have been prepared by careful gravimetric mixing of highly purified separated isotopes.

The iodide method, using electron bombardment, would seem to be less susceptible to bias, but one should hesitate to claim an accuracy of greater than 1 per cent of the ratio. Comparison of samples, one to another, can probably be done with a precision of 0.5 per cent at the 95 per cent confidence level. Bishop and Bentley [75] quote ±2 per cent for absolute accuracy and 0.6 to 0.7 per cent for precision at the 95 per cent confidence level. The method used by Svec permits comparison of samples to a precision of 0.2 per cent.

The procedure followed in the Y–12 laboratory is to calibrate the mass spectrometers with standard material. Standards are mixed gravimetrically from very pure Li^6 and Li^7 prepared from batches of electromagnetically separated isotopes. These primary standards are used to establish the Li^6 content of larger amounts of material, which are used for frequent calibration of the instruments. At four different levels the limits of error (LE) at 95 per cent confidence for a single determination are:

Li^6, wt. %	*LE, %*
95	±0.15
35	±0.60
7.5	3.0
2.3	7.5

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CHAPTER 14

RADIOCHEMICAL AND NUCLEAR METHODS

S. A. Reynolds*

Radiochemical analysis [1-4] is concerned with the determination of the radioactivity associated with the elements in a sample. Such measurements may subsequently be used to compute masses or concentrations, but the activity measurement is the primary one. The radiochemist must be familiar with the chemistry of many elements, including the rarer ones, and must know something of the physics of radioactive decay and radiation detection. Radiochemistry became of great importance over 20 years ago with the beginning of the Manhattan Project,[5] and this importance has increased with the establishment of the U.S. Atomic Energy Commission (AEC) programs, the widespread use of radioisotopes, the worldwide construction of reactors, and the development of radioactivation analysis.

14–1 TECHNIQUES AND APPARATUS

14–1.1 Separation Methods

Radiochemical separation methods [6-11] include precipitation, solvent extraction, distillation, ion exchange, and chromatography. Published methods, such as those described in sec. 14–4 and in various chapters of this book, furnish many examples. Since radioelements are often present in very low chemical concentrations, effects such as sorption on surfaces, anomalies in solvent extraction, etc., must be guarded against. These effects may be eliminated by the addition of an acid, a complexing agent, or a carrier to a radioelement solution. A carrier is a material chemically similar to, or identical with, a given radionuclide. An isotopic carrier is the ordinary stable element with which the radioactive species is isotopic.

In separations employing an isotopic carrier, the interchange of the carrier and the radioelement is an essential first step (Refs. 1, 4, 5, and 12). This interchange is achieved by acidification, by the formation of a complex, or by oxidation and/or reduction. Once the interchange has been achieved, losses of carrier and radionuclide are proportional; therefore the radioactivity ultimately measured can be simply corrected for yield or recovery. Later steps in a typical analysis include separation from other activities and inactive species,

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Table 14.1—INSTRUMENTS USED FOR VARIOUS TYPES OF RADIOACTIVITY

Instrument*	Radiation			
	Alpha	Beta ($\beta^- + \beta^+$)	Gamma	X-ray†
Windowless proportional counter	X	X		
Thin-window proportional counter	X	X		
Solid scintillation detector	X	X		
NaI(Tl) [15]			X	
Thin NaI(Tl) wafer				X
Liquid scintillation counter [16]	X	X (especially for low-energy beta)		
Semiconductor detector [17]	X	X		
End-window or glass-wall Geiger counter		X	X	X
Ionization chamber		X		
With high-pressure gas			X	

*Text references apply except for ones specifically noted in this table.
†For example, from electron-capture decay.

measurement of recovery (by gravimetric, colorimetric, or other method), and activity determination.

14–1.2 Measurement

Instruments used for measuring various types of radioactivity are summarized in Table 14.1 (Refs. 1, 2, 4, 13, and 14). For testing reproducibility of instrument performance, a reference standard is used. This standard is a long-lived source of the type of radiation measured by a given instrument. Thus Pu^{239} or Am^{241} is a suitable alpha standard; Pa^{234} (UX_2) in equilibrium with U^{238} (natural uranium) is satisfactory for beta; and Cs^{137} or Ra^{226} can be used for gamma detectors. For absolute measurements, standards are used to calibrate measuring devices. Such standards are usually prepared by 4π counting, coincidence counting, and defined-geometry techniques.[12, 18, 19] Standards are supplied in the United States by the National Bureau of Standards and private companies. Calibrations must be made under the conditions encountered in the use of the instruments, with respect to the size and positioning of the source, solids content (especially for alpha and beta counting), etc.

14–1.3 Instrumental Analysis

The half life and the type and energy of radiation of a nuclide can be used to identify it and to make quantitative analyses of mixtures (Refs. 1, 2, 4, 14, and 15). In a mixture of nuclides, an analysis can be made by resolving decay data by graphical or analytical means,

provided the half lives are short and sufficiently different. Mixtures of beta emitters can be resolved in a similar way by taking absorption data in aluminum.

The most important instrumental methods involve the use of spectrometers. Mixtures of alpha-emitting nuclides are frequently analyzed by spectra obtained from gridded ionization chambers [14] or diode detectors.[17] Beta spectro are obtained by scintillation spectrometry with organic solid or liquid phosphors. Much use is made of gamma spectrometry in which cylindrical sodium iodide detectors are employed. The principles and applications of the method have been discussed extensively elsewhere (Refs. 1, 2, 4, 14, 15, 20, and 21). It is sufficient to note that data are available for converting observed counting rates under photopeaks to absolute photon-emission rates (hence to disintegration rates), that techniques (at present largely graphical) are available for resolving spectra of mixtures to obtain quantitative activities of individual components, and that many instruments (both simple and complicated) are commercially available. Table 14.2 lists a number of nuclides commonly measured by gamma spectrometry, along with their principal energies and intensities of gamma radiation.[21]

14–1.4 Statistics

All measurements are subject to random error since the measurement of radioactive decay is itself a statistical process. At low activity (few counts) large errors occur, and at high activity dead-time losses become important. Such errors have been discussed in Refs. 1, 2, 14, 22, and 23. It should be noted that any radiochemical method has an inherent error, independent of the random error in measurement, which may range from a fraction of one percent to several percent. Properly, the method error should be combined with the counting error (root-mean-square combination) to estimate the error in a particular analysis.

14–1.5 Sources of Nuclear Data

Properties of radionuclides, such as half lives, radiation energies, and intensities, etc., can be found in various tabulations (Refs. 15, 21, and 24 to 27). In preparing one of these tabulations, Ref. 21, an attempt was made to select the best values of half lives and absolute gamma intensities. In gamma spectrometry it is essential that the absolute gamma intensities be known.

14–2 ACTIVATION ANALYSIS

In radioactivation analysis the elemental content of radioisotopes induced by nuclear-particle bombardment is measured (Refs. 1 to 4, 9, 10, and 28 to 31). Several different types of bombarding particles have

Table 14.2—IMPORTANT GAMMA-RAY EMITTERS

Nuclide*	Half life	Decay mode	Major gammas	
			Energy	Intensity †
Ar^{41}	110 min	β^-	1. 30	0. 99
$Ag^{110m,\ 110}$	253 days	β^-	0. 66	0. 9
			‡0. 90	1. 0
Am^{241}	460 years	α	0. 060	0. 40
Au^{198}	2.69 days	β^-	0. 41	0. 95
Ba^{140}	12.8 days	β^-	0. 54	0. 25
Br^{82}	36 hr	β^-	0. 77	0. 83
Ca^{47}	4.5 days	β^-	1. 30	0. 71
Ce^{141}	33 days	β^-	0. 145	0. 43
Ce^{144}	285 days	β^-	0. 134	0. 11
Co^{60}	5.27 years	β^-	1. 17	1. 00
			1. 33	1. 00
Cs^{134}	2.05 years	β^-	0. 60	0. 97
Cs^{137}–Ba^{137m}	30 years	β^-	0. 66	0. 85
Fe^{59}	45 days	β^-	1. 10	0. 56
			1. 29	0. 44
Hg^{203}	46 days	β^-	0. 28	0. 83
I^{131}	8.08 days	β^-	0. 36	0. 81
K^{42}	12.5 hr	β^-	1. 52	0. 18
Kr^{85}	10.6 years	β^-	0. 52	0. 0040
La^{140}	40 hr	β^-	1. 60	0. 95
Mn^{54}	314 days	§ϵ	0. 84	1. 00
Mn^{56}	2.58 hr	β^-	0. 84	0. 99
Na^{22}	2.6 years	$\beta^+\epsilon$	¶0. 51	1. 80
			1. 27	1. 00
Na^{24}	15.0 hr	β^-	1. 37	1. 00
			2. 75	1. 00
Nb^{95}	35 days	β^-	0. 76	0. 99
Ru^{103}	40 days	β^-	0. 50	0. 90
Ru^{106}–Rh^{106}	1.0 years	β^-	0. 51	0. 21
			0. 62	0. 11
Sb^{124}	60.4 days	β^-	0. 60	0. 98
			1. 69	0. 46
Sb^{125}	2.8 years	β^-	‡0. 44	0. 4
Sc^{46}	84 days	β^-	0. 89	1. 00
			1. 12	1. 00
Sn^{113}–In^{113m}	112 days	ϵ	0. 39	0. 68
Sr^{85}	64 days	ϵ	0. 51	0. 99
U^{235}	7.1×10^8 years	α	0. 185	0. 55
Xe^{133}	5.3 days	β^-	0. 081	0. 35
Zn^{65}	245 days	$\epsilon(\beta^+)$	1. 11	0. 50
			¶0. 51	0. 03
Zr^{95}	65 days	β^-	0. 72	0. 55
			0. 76	0. 43

*In alphabetical order of symbols.
† Photons emitted per disintegration.
‡ Mixture of gammas not resolved by scintillation spectrometry.
¶ Annihilation radiation.
§ ϵ=electron capture.

been employed, but the most useful is the neutron, which is copiously available in nuclear reactors. Charged-particle reactions are not discussed in this section. The radionuclides produced possess characteristic half lives and types and energies of decay. These characteristics make possible identification of radionuclides and lead to identification of the elements present in a sample. Activation thus constitutes a qualitative tool of some versatility.

14–2.1 Quantitative Determinations

Measurements of the quantity of a given element may be done on the basis of the equation

$$W = \frac{AM}{0.60\sigma\phi[1-\exp(-\lambda t)]}$$

where W = weight of target element, g
A = activity of product radionuclide, sec^{-1}
M = atomic weight of target element
σ = atomic activation cross section, barns
ϕ = neutron flux, neutrons/cm^2/sec
λ = decay constant of radionuclide, sec^{-1}
t = time of bombardment, sec

The cross section is the probability of the reaction, which is dependent on the target nuclide and the energy of the neutrons. Tabulations of cross sections for neutron reactions are available.[32] Values are usually given in barns; a barn is 10^{-24} cm^2. Values are normally given for particular nuclides. A useful quantity is the atomic-activation cross section for capture of neutrons, which is the product of the cross section of a given nuclide for the production of a radioactive product multiplied by its natural isotopic abundance. For example, the cross section of Fe^{58} for the production of Fe^{59} is 1 barn; its abundance is 0.3 per cent. The atomic-activation cross section of iron for the production of Fe^{59} is thus 0.003 barn.

The above discussion is the basis for the absolute method of activation analysis, in which a sample is bombarded for a definite time at a known flux, the disintegration rate of the element of interest is measured, and the weight of that element is calculated from the values for the cross section and the half life. This method is often not satisfactory because it is not easy to measure the neutron flux accurately and because cross sections are not known precisely for many elements. A simpler and more accurate approach is the comparative method, in which a standard containing a known amount of the element of interest is bombarded along with the unknown sample. The activity of the desired element is measured in the standard and the unknown; a simple activity ratio gives a resultant value in terms of the weight of the element in the unknown.

In simple cases much of the induced activity in a sample may be due to the element or elements of interest. A nondestructive method such as gamma spectrometry can be used for analysis. In general, however, a chemical separation of the desired element is necessary. In most analyses a carrier is used.

The procedure consists of the following steps: (1) preparation of the sample [grinding, cutting, or other steps (preseparation occasionally is necessary)]; (2) bombardment of the sample and the standard; (3) separation of the activity of the desired element from other activities (if necessary); and (4) measurement of the activity of the element in the sample and the standard.

14–2.2 Advantages and Limitations

The advantages and limitations of activation analysis have been discussed at length.[29, 33, 34] Among the advantages the most important is its spectacular sensitivity for many elements.[29, 35] From the equation given earlier, the weight of a given element required to produce a preassigned activity is readily calculated. If this activity is the smallest quantity that can be readily measured, the weight of the target element becomes the limit of measurement. Note that high flux, a large cross section, and a short half life lead to a low limit, or great sensitivity. Winchester [36] has prepared a table of the limits in nanograms (10^{-9} g) for 73 elements, assuming that the activity of the product radionuclide is 10 dis/sec, the neutron flux is 10^{13} neutrons/cm^2/sec, and the times are 1 and 150 hr. For many elements the limits by activation are lower than by any other method.[35] They range upward from the order of 10^{-12} g for rhodium, indium, europium, and dysprosium. Typical values in nanograms (ng) are: sodium, 0.08, aluminum, 0.2, chlorine, 0.4, vanadium, 0.02, copper, 0.03, and silver, 0.003. On the other hand, the sensitivity for some elements is very poor because of a low cross section or a long half life.

The activation method is quite fast and simple in many instances. It is usually free of interference because the activity of the desired element is unlikely to be introduced after bombardment, and tests for the presence of foreign activities can be made by instrumental techniques. Thus no special precautions are necessary to avoid introducing small amounts of the desired constituent, once bombardment has been completed; and methods of assuring that the desired activity is being measured are easily applied. Limitations, in some cases, include intense radioactivity of certain samples, self-shielding and moderation by the sample matrix material, and nuclear reactions in other elements yielding the desired radionuclide. Matrix effects include an enhancement of several per cent in the specific induced activity of a given element by the moderation of neutrons by low atomic number element

atoms, particularly hydrogen in aqueous samples.[37] More serious errors can result from self-shielding if the matrix of the sample or the standard has a high absorption cross section for neutrons of either thermal or resonance energies;[37] such an error can be as large as 50 per cent or more.

14–2.3 Facilities and Applications

In choosing a source of neutrons for activation analysis, one must consider a number of factors.[31] These include the magnitude of the flux, its stability and spatial gradient, and the spectrum (energy distribution). Further, one must think of the temperature developed in the target, the accessibility of the bombardment position, the ease of handling the materials, and the economics of the operation. The most prolific source of slow neutrons is a reactor, and most activation analysis has involved the use of such a device.[29] Accelerators, particularly of the Cockroft-Walton and Van de Graaff type, are also used as neutron sources (Refs. 29, 33, 38, and 39). So-called "isotope sources" are also used; these consist of an alpha or gamma emitter in contact with beryllium or boron. Examples are antimony-beryllium[40] and americium-beryllium[41] preparations. The accelerator and isotope sources furnish fast neutrons, which are useful for the determination of oxygen,[42] nitrogen, and other light elements. Transportation and laboratory facilities range from very simple[40] to rather complex ones,[29, 43] depending upon the levels of radioactivity. Applications have been numerous.[29] In addition to those uses listed in Sec. 14–5.1(*c*), activation has been used for determining rare earths,[44] for analysis of marine organisms,[45] and for many other purposes.[9, 10]

14–3 NEUTRON ABSORPTION

Neutron absorptiometry[1, 41, 46] depends upon the fact that each nuclide has a characteristic cross section for the capture of neutrons. Nuclides of large cross section can therefore be determined in samples of low cross section. The treatment of Strain[41] is followed in the following paragraphs (see Figs. 14.1, 14.2, and 14.3).

The apparatus in Fig. 14.1 is used for analysis by neutron transmission through foils or cuvettes. From basic principles[1] the equation for such transmission is

$$CR = CR_0 \exp(-N_a \sigma)$$

where CR = count rate with sample present
CR_0 = blank count rate
n_a = atoms per square centimeter of absorber element or elements
σ = total cross section of absorber element or elements, cm^2

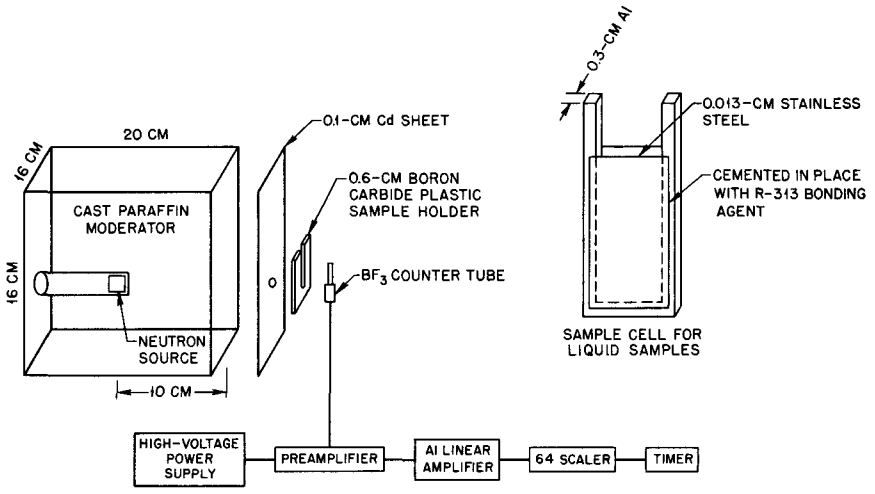


Fig. 14.1—Neutron transmission apparatus.

Rearranging and substituting,

$$\frac{CR_0}{CR} = \exp\ (-n_a\sigma) \cong 1 + Km\sigma'$$

where m = millimoles of absorber per square centimeter

K = empirical constant

σ' = experimentally determined cross section, barns

The type of calibration curve obtained is shown in Fig. 14.2.

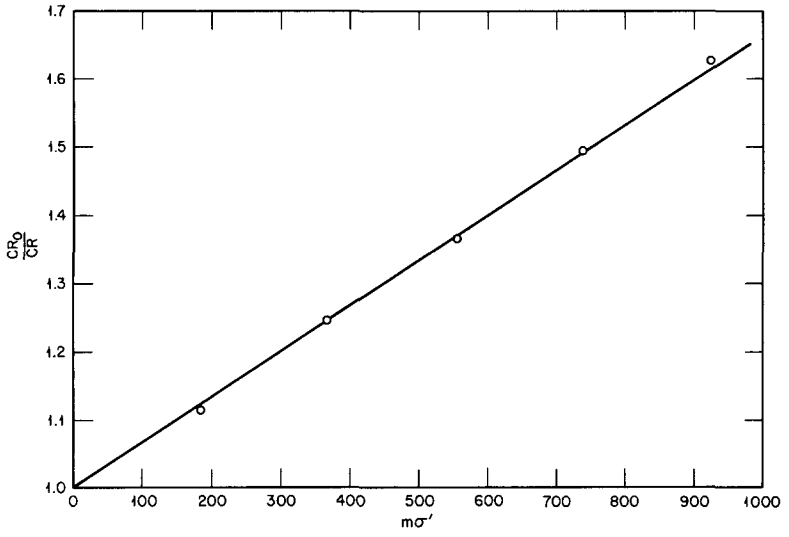


Fig. 14.2—Neutron transmission calibration curve.

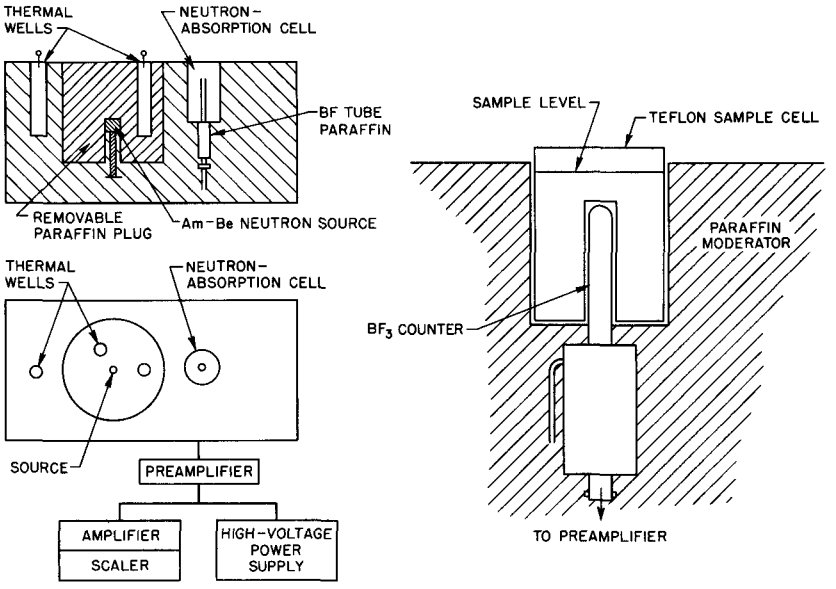


Fig. 14.3—Neutron absorption apparatus.

If the sample surrounds the detector, as shown in Fig. 14.3, an equation of similar form [41] applies:

$$\frac{CR_0}{CR} = 1 + KX\sigma_a$$

where X = molar concentration of absorbing element
σ_a = absorption cross section, barns

The method is of considerable value in determining such elements as cadmium, boron, indium, and certain nuclides of interest [see Sec. 14–5.3(b)].

14–4 ASSAY BY RADIOACTIVITY MEASUREMENTS

14–4.1 Uranium

The naturally occurring isotopes of uranium are alpha active and are parents of radionuclides having alpha, beta, and gamma activities.[1, 47] Each of the types of activity is used, under various conditions, for the measurement of uranium. A review of the radiochemistry of uranium is given in Ref. 48.

(a) *Alpha Measurements.* The specific alpha activity of natural uranium is 1.50 dis/min/μg, and alpha measurements are used on this basis for assays, e.g., in water and urine.[49] The methods require the

separation of uranium by a suitable technique [48] and the preparation of an alpha plate, often by electrodeposition of uranium on platinum or nickel disks.

Care must be taken to employ the proper specific activity in calculations, especially for enriched U^{235} preparations, since most of the alpha activity of these preparations is due to U^{234}. The ratio of U^{234} to U^{235} is somewhat variable. It is necessary to know, or to determine, the specific activity before valid uranium assays can be made. (An activity of approximately 150 dis/min/μg has been observed in some enriched-uranium samples.)

(b) *Beta Measurements.* Several of the daughters of the uranium isotopes are beta emitters, and a limited application of beta-counting

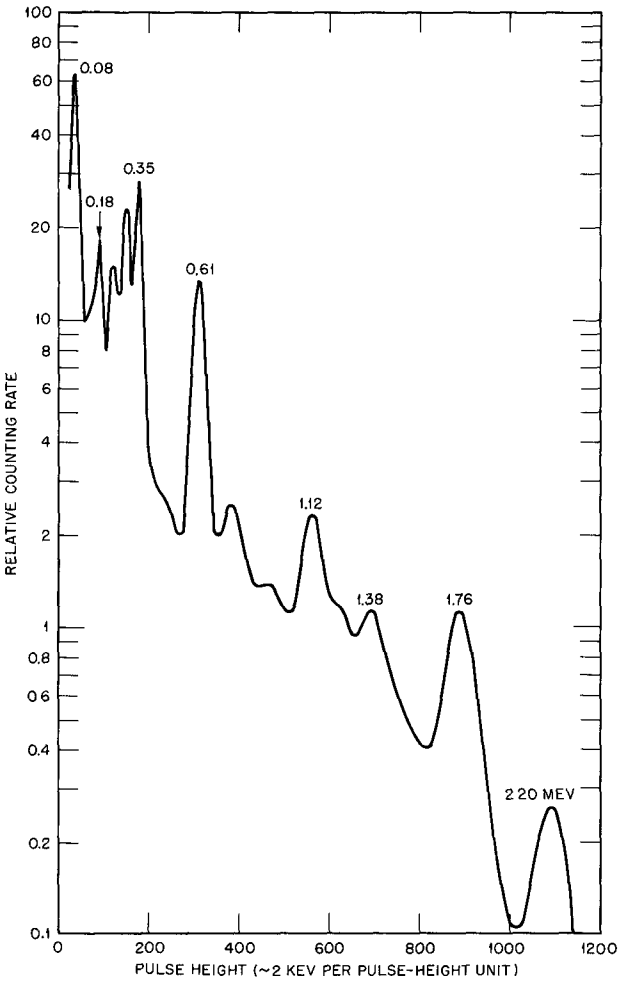


Fig. 14.4—Gamma spectrum of uranium ore.

techniques has been made.[50] Interference from K^{40} and thorium-series beta activities must be guarded against.

(c) *Gamma Measurements.* Most radiometric assays for uranium are made through gamma activity. These are exemplified by prospectors with their Geiger counters and by analysts with scintillation spectrometers.[51] This method is limited to ores in which radioactive equilibrium exists. Most workers measure the 1.76- or 0.61-Mev gamma (both from Bi^{214}). The 0.61-Mev gamma, however, is subject to interference from the 0.58-Mev gamma in the thorium series (see Sec. 14–4.2). The gamma spectrum of uranium ore, measured with a 3- by 3-in. NaI(Tl) crystal, is shown in Fig. 14.4. The chief sources of error in this method lie in radon escape during grinding or other treatment and in geochemical separation of the early members of the series from the later (radium family) members.

The procedure is quite straightforward. It consists in the measurement of the counting rates at 1.76 and 0.18 Mev, with the sample weight used dependent on uranium content. (*Note:* If the sample has been treated in such a way that radon is driven out, it must be sealed after it is weighed and retained 2 weeks or more to permit the regrowth of radon and its daughters.) The peak counting rates of a standard of similar concentration are determined under the same conditions of weight and geometry. (Such standards are available from the AEC's New Brunswick Laboratory.) The ratio of counting rates at the two peaks should be the same in the sample and the standard; if not, another method must be used. The limit of measurement is about 0.1 to 1 ppm.

14–4.2 Thorium

Radiometric measurements of thorium are essentially limited to gamma spectrometry of ores, except in the special cases of Th^{228} (radiothorium) and Th^{230} (ionium). The specific alpha activity of natural thorium (Th^{232} and Th^{228}) recently separated from a uranium-free ore is approximately 0.48 dis/min/μg. The Th^{228} decays with a 1.9-year half life.[47] Alpha measurements are of little use because of low sensitivity and dependence on past history. Similarly, beta-activity measurements are dependent on previous history.[47]

(a) *Gamma Spectrometry.* Most workers measure thorium in ores and rocks through the 2.62-Mev gamma radiation [52] of its daughter, Tl^{208}. The spectrum of a thorium ore sample is shown in Fig. 14.5. No difficulty is likely to arise because of nonequilibrium in natural material, since equilibrium of the whole series requires approximately 67 years.[47] The half life of the gas thoron is 52 seconds, resulting in quick regrowth if loss should occur.

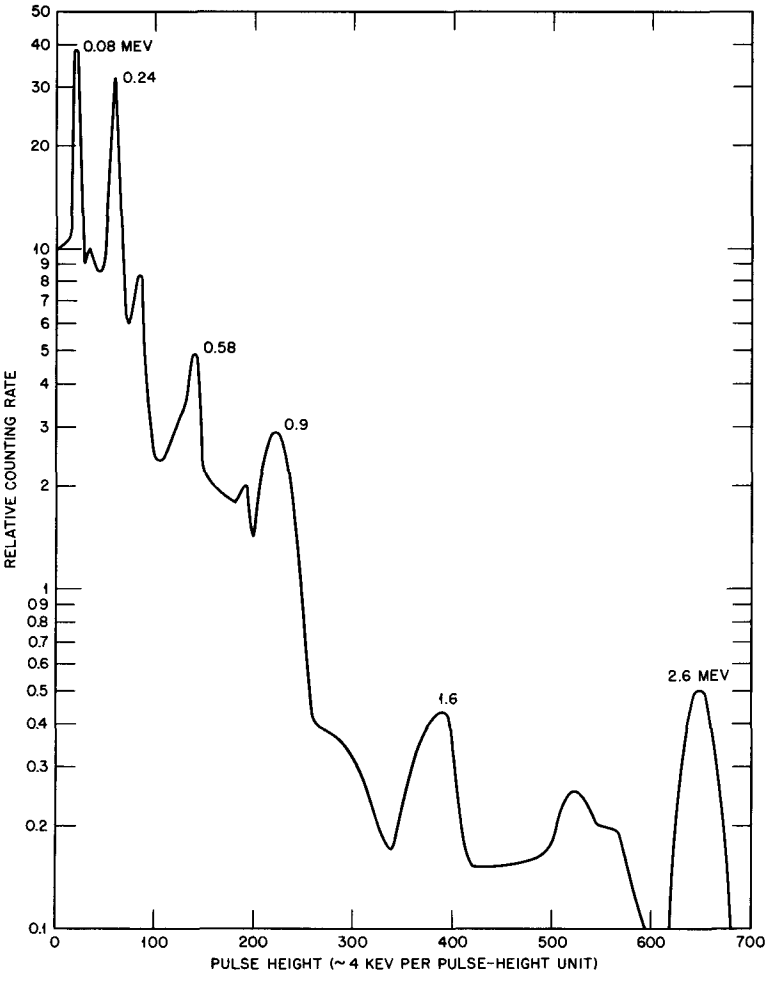


Fig. 14.5—Gamma spectrum of thorium ore.

The procedure is similar to that used for uranium [see Sec. 14–4.1(c)], but it requires measurement of only the 2.62-Mev peak in the sample and the standard. (Thorium standards may be obtained from the AEC's New Brunswick Laboratory.) The practical limit of measurement is approximately 1 ppm.

(b) *Ionium.* For the chemical separation of ionium (Th^{230}), the procedure of Moore [53] is rapid and highly selective. It consists in carrying of thorium from an oxidized solution by lanthanum fluoride, dissolution in aluminum nitrate solution, and extraction into thenoyltrifluoroacetone (TTA)-xylene at pH 1.4 to 1.5. An aliquot of the extract is evaporated on an alpha plate for measurement. Other radiochemical methods [54] are useful in various applications.

14–4.3 Radium

A general review of radium radiochemistry is given in Ref. 55.

(a) *Gamma Methods.* If Ra^{226} is the principal gamma emitter in a sample it can be determined by direct gamma measurement with an ionization chamber or scintillation detector. Such a technique, for amounts above approximately 10^{-8} g, has been reported in detail,[56] with descriptions of the ionization chamber and the sample vials and with corrections for self-absorption and other gamma activities. If it is necessary to distinguish radium-family gammas from others, a scintillation spectrometer can be used. As in uranium measurement [see Sec. 14–4.1(c)], the 0.61- and 1.76-Mev radiations of Bi^{214} are measured. Standard solutions containing 10^{-9} g or more of radium are available from the U. S. National Bureau of Standards.

(b) *Emanation (Radon) Method.* Many workers measure radium by driving out its gaseous daughter radon (Em^{222}) and counting its alphas and those of its short-lived daughters in an ionization chamber,[57] proportional counter, or scintillation counter.[58] In a typical method [57] radon is swept out of the sample solution by nitrogen, the flask is sealed, and radon is allowed to regrow for a definite time. Then radon is swept into an ionization chamber, allowed to stand for 4 hr (to establish equilibrium between radon and its short-lived daughters), and the alpha counting rate determined. It is necessary to calibrate with standards. Good precision (approximately 1.5 per cent) was demonstrated in the determination of 10^{-11} to 10^{-7} g.

(c) *Carrier Methods.* A number of radiochemists employ methods involving the carrying of radium on a suitable precipitate, followed by alpha counting. Typical of such methods are those of Goldin [59] and Petrow.[60, 61] In Goldin's method citric acid is added to the sample, the resulting solution is made alkaline with ammonia, and 2 milliequivalents of lead and 0.1 milliequivalent of barium (as nitrates) are added to it. A sulfate precipitate is formed by the addition of sulfuric acid, and it is washed twice with concentrated nitric acid. The precipitate is then dissolved in alkaline EDTA (disodium salt of ethylenediaminetetraacetic acid). Barium sulfate is reprecipitated by the addition of acetic acid. The barium sulfate is transferred to a tared alpha plate, dried, weighed to determine yield, and counted. Calibration with a standard radium solution is necessary.

The procedure of Petrow involves the carrying of radium on 500 mg of lead sulfate. The lead sulfate is dissolved in ammonium acetate and precipitated by the addition of ammonium carbonate. The carbonate is dissolved in dilute nitric acid, and the nitrate is precipitated by the addition of fuming nitric acid. After centrifugation, excess acid is evaporated, and the precipitate is dissolved in water.

690–457 O—64——72

Lead is partially removed by the addition of concentrated hydrochloric acid; the remainder is extracted into a quaternary amine–benzene solution. The raffinate containing the radium is evaporated, ignited, and taken up in nitric acid. A portion is evaporated on an alpha plate for counting. No yield correction is possible, and calibration with a standard radium solution is required.

14–4.4 Protactinium

A review of the radiochemistry of protactinium is given in Ref. 62, and a rapid and selective radiochemical method has been described by Moore.[63] This method involves the extraction of protactinium from a 6*M* hydrochloric acid–4 per cent oxalic acid solution into diisobutylcarbinol. Both Pa^{231} and Pa^{233} can be measured by gamma spectrometry since they have characteristic radiations at approximately 0.1 and 0.3 Mev.

14.5 ISOTOPIC ANALYSIS

14–5.1 Uranium

(a) *Gamma Spectrometry.* The application of this technique has been in the determination of U^{235} in enriched or depleted material by measurement of its 0.18-Mev gamma. Among reports of the use of this method,[64–66] that of Eldridge [64] is typical. Uranium is separated from other active materials, ignited to U_3O_8, and weighed. The intensity of the 0.18-Mev gamma is measured by a suitable spectrometer. This intensity is directly proportional to the weight of U^{235} in the sample measured. Standards of known U^{235} abundance must be used for calibration.

(b) *Alpha Spectrometry.* The principal alpha energies of the commonly encountered uranium isotopes are listed in Table 14.3 Routine alpha spectrometry permits the measurement of U^{232} in U^{233} preparations, U^{234} in U^{235} preparations, etc. Either a gridded ionization chamber or a diode detector may be used. Sensitivity in some cases is quite good; e.g., U^{232} can be measured easily in samples in which its

Table 14.3—URANIUM ALPHA ENERGIES

Isotope	Energy, Mev
U^{232}	5. 32
U^{233}	4. 82
U^{234}	4. 77
U^{235}	4. 40
U^{236}	4. 50
U^{238}	4. 20

activity is 0.1 per cent of that of U^{233}; this corresponds to an isotopic abundance of 0.5 ppm.

(c) *Neutron Activation.* Uranium isotopes, particularly U^{235}, have been determined by activation analysis involving the production of a particular fission product [67] (usually Ba^{140}) or a fission-product mixture that is subsequently gamma-counted; [68, 69] by a count of the delayed neutrons from fission products; [70] and by a count of U^{239} or Np^{239} for the U^{238} nuclide.[67] The same methods obviously apply to the determination of uranium in various materials [71] if it is assumed that the normal isotopic abundances exist. All these methods are quite sensitive. For example, the delayed-neutron technique can be used for the determination of about 1 ng of U^{235}; it has a precision of about 3 per cent.[70]

14–5.2 Thorium

The alpha-emitting isotopes of thorium can be determined by alpha spectrometry. [Also see Sec. 14–4.2(b).] Th^{232} is determined by neutron activation; [72] by this means readily measurable Pa^{233} is produced. The determination of Th^{232} is, of course, tantamount to the measurement of natural thorium.

14–5.3 Lithium

(a) *Neutron Activation.* Leddicotte [73] has reviewed the determination of Li^6 and Li^7 by three methods: (1) tritium evolution, i.e., $Li^6(n,\alpha)H^3$, followed by measurement of H^3 in an ionization chamber; (2) Li^8 production; and (3) triton activation, in which H^3 is used to produce, for example, F^{18} from O^{16}. All methods were found to be reasonably successful.

(b) *Neutron Absorption.* The cross section of Li^6 for thermal neutrons is 945 barns, whereas that of Li^7 is only 0.04 barns.[32] Obviously, measurement of the cross section, or simple neutron absorption, of lithium samples by methods [41] described in Sec. 14–3 make possible the isotopic analysis.

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CHAPTER 15

ELECTROMETRIC METHODS

By W. N. Carson, Jr.*

In this chapter the electrometric techniques used in the analysis of atomic energy materials are discussed. The wide diversity of the methods involved and of their applications requires that some qualifications be set up to serve as a guide for discussion. This has been done by restricting the methods to be discussed to those in which an electrochemical phenomenon is involved. The restriction thus excludes any methods such as photometry, which involves the measurement of an electrical quantity but which does not involve an electrochemical phenomenon.

The electrometric methods of analysis are divided into two main groups in this chapter. The first group comprises the methods in which measurement of an electrical quantity, such as potential, serves as the primary measurement of the substance being determined. The second group comprises the methods in which the measurement of an electrical quantity serves as a guide to the use of another measurement, such as titration with a standard solution. The second group also includes those methods in which electricity is used as a reagent in the analysis, but the quantity of electricity used does not serve as the measure of the substance being determined.

Material on the theoretical background of the electrochemical phenomena associated with an electrometric method of analysis has been included to show the unifying principles involved, but this chapter is not intended to be a complete guide to the complexities of modern electrochemistry. The emphasis lies on the practical problems involved in applying electrochemical principles.

Similarly, material on the operating principles of the electrical equipment used in the methods of analysis has been included. Since improvements in the electronic and mechanical components used in the equipment are being made constantly, it would be expected that any equipment used today would become obsolete relatively quickly. Hence the emphasis is on principles rather than on details of operation. The present and potential use of electrometric techniques in automatic analyzers in the processing of atomic energy materials is also covered in some detail.

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15–1 APPARATUS AND GENERAL PRINCIPLES

Electrometric methods for routine analysis are not new, but their use was limited until the past 10 years or so because the apparatus for many of the potentially useful methods were inconvenient to use, time-consuming in operation, and unreliable in the hands of the routine analyst. The great promise of electrometric techniques has been partially fulfilled by the development of laboratory apparatus which, if not simple in design, is simple to use and is as reliable as conventional analytical apparatus and which eliminates many of the tedious and time-consuming features through automatic control systems and recording components. The great increase in reliability of the apparatus and the ready adaptation of electrometric techniques to automatic recording have led to the use of these techniques in automatic process analyzers.

The reader may find the general references [1-25] useful as sources of background material on the theoretical and practical aspects of electrometric analysis methods.

15–1.1 Electrodes

Electrodes are the key elements in electrometric methods of analysis. In any electrometric method, two electrodes are required; however, in many methods only the electrochemical phenomena associated with one electrode are useful. This electrode is referred to as the "sensitive," or "working," electrode of the pair; the other electrode is the reference or counter electrode. The sensitive electrodes are discussed in detail in the sections describing the methods employing them; the reference electrodes are described below. A distinction is made between a counter electrode and a reference electrode in that the counter electrode is used in methods involving electrolysis, whereas the reference electrode normally is used only to supply a constant potential reference point for taking measurements. Both a reference and a counter electrode can be used in an electroanalytical procedure.

The passage of electric current through a solution requires that a change from electronic to ionic conduction be made at one electrode and a change in the reverse order at the other. This transfer of charge is always accompanied by chemical reactions of the oxidation–reduction type. In the use of a sensitive electrode, the aim is to emphasize one of the phenomena associated with the oxidation–reduction reaction occurring at the electrode-solution interface and to minimize or eliminate all other phenomena. With reference electrodes, on the other hand, the aim is to design an electrode such that little, if any, change in the electrode behavior occurs during use. With counter electrodes, the aim is to provide the second electrode required for electrolysis. The designer uses the configuration of the electrode, the

materials of construction, and sets the operating conditions he can control to make the electrode produce the desired response.

Since the reference electrodes used in electrometric analysis are common to many of the methods, a listing of the types and their characteristics is given here. Associated with these electrodes is the problem of the junction, or how to connect the reference electrode to the solution in which the sensitive electrode is immersed. The device used is called a "salt bridge," and this bridge is one of the major sources of trouble in electrometric analysis.

(a) *Calomel Electrode.* The calomel electrode is the most used reference electrode in electrometric methods of analysis. The cell reaction

$$Hg_2Cl_{2(solid)} + 2e \rightleftharpoons Hg_{(liquid)} + 2Cl^-$$

is reversible, and the electrode is not easily polarized. Three types of calomel electrode are recognized; these usually have the form

$$Hg_{(liq)}, Hg_2Cl_{2(solid)} \mid KCl(X), Hg_2Cl_{2(saturated)} \mid KCl(Y)$$

where X refers to the concentration of KCl in the electrode solution, and Y refers to the concentration of KCl in the salt bridge used with this form. The differences in types lie in the value of X; thus we have $X = 0.1N$, $1.0N$, and saturated (about $4.8N$) giving the one-tenth normal, normal, and saturated types of calomel electrode. The potentials of each type of electrode are highly reproducible when made from properly purified materials; in use the potentials are stable over long periods of time. The potentials of the calomel and some other electrodes are given in Table 15.1. In the table all potentials are referred to the standard hydrogen electrode.

Although the $0.1N$ and $1.0N$ calomel electrodes have lower temperature coefficients than the saturated electrode and thus have an advantage over the saturated electrode in theoretical electrochemical investigations, these advantages are outweighed in the routine-analysis laboratory by the greater convenience of the saturated electrode. This convenience is a result of the fact that the saturated electrode and the saturated potassium chloride bridge that is used to connect the calomel electrodes to the solution can be made as an integral unit. The other two electrodes require a separate bridge, making them less compact and more subject to breakage. Maintenance of the saturated electrode is simpler since loss of water by evaporation cannot change the composition of the solution and make-up solution for losses due to flow out from the bridge need not be analyzed since the saturated condition can be assured by having an excess of salt present in the storage bottle.

Table 15.1—REFERENCE-ELECTRODE POTENTIALS*

Temperature, ° C	Calomel type†			Potential‡	
	0.1*N*	1.0*N*	Saturated	Ag–AgCl§	$Hg–Hg_2SO_4$¶
0				−0. 2366	0. 6350
5				−0. 2341	0. 6310
10				−0. 2314	0. 6270
12	0. 3362		0. 2528	−0. 2303	0. 6254
15	0. 3360		0. 2508	−0. 2286	0. 6231
20	0. 3358		0. 2476	−0. 2256	0. 6193
25	0. 3356	0. 2801	0. 2444	−0. 2223	0. 6152
30	0. 3354		0. 2417	−0. 2194	0. 6111
35	0. 3353		0. 2391	−0. 2190	0. 6070
38	0. 3352		0. 2375	−0. 2170	0. 6055
40				−0. 2157	0. 6031
45				−0. 2121	0. 5990
50				−0. 2084	0. 5949
55				−0. 2045	0. 5905
60				−0. 2006	0. 5866
70				−0. 1965	
80				−0. 1878	
90				−0. 1787	
95				−0. 1695	
95				−0. 1651	

*Taken from Bates, Ref. 1, unless otherwise noted.
† Includes salt-bridge junction potential; saturated-KCl dual bridge type for unsaturated electrode.
‡ In absolute volts vs. the standard hydrogen electrode.
§ Standard potential.
¶ Taken from Harned and Owen, Ref. 13, standard potential.

The saturated electrode is thus unlikely to have a marked change of potential due to inadvertent change in potassium chloride concentration. The larger temperature coefficient of the saturated electrode is usually not important in its use in electrometric methods of analysis since the error caused by the change in potential is usually not significant compared to the other errors in the analysis. The mechanical and operating advantages of the saturated type make it the choice for use in most methods.

The mechanical construction of a saturated calomel electrode varies for the most part with the nature of the salt bridge incorporated with it; the electrode structure itself varies depending upon the current expected to flow through it. Some common designs are described by Bates; [1] the special designs used in electrometric methods of analysis will be described in the descriptions of the methods. Hills and Ives [26] and Bates [1] have described in detail the various precautions involved

in making and using the calomel electrode as a precise reference electrode; for analysis purposes most of these precautions can be relaxed. Thus, in the preparation of the electrode, unpurified reagent-grade materials can be used in place of specially purified materials, and the electrode can be used in contact with air or oxygen. The potentials of these less carefully made electrodes are not usually the reproducible potentials and may differ by several millivolts or more from the values obtained with the best electrodes. However, the potentials are stable over long periods of time if they are kept uncontaminated with test solutions. For most electrometric methods, a complete calomel electrode assembly suitable for use without modification of the bridge is available commercially; for the remaining methods, the calomel electrode assembly used in the commercial assemblies can be removed and used with the special salt bridge required.

The potassium chloride solutions used in these electrodes tend to creep up the walls of any containers and to evaporate, leaving a coating of salt, which is at best unsightly and at worst interferes with the measurements by shorting out electrode leads. A light coating of high-melting low-volatility stopcock grease on the affected parts is recommended to prevent this creep. Vaseline, Apiezon type greases, and rubber-based greases (e.g., Lubriseal) are satisfactory; silicone-base greases should be avoided unless it is known that they will not creep themselves and cover the glassware with a film of grease in unwanted areas.

(b) *Silver–Silver Chloride Electrode.* The silver–silver chloride electrode is an important reference electrode in electrometric methods in which the solutions contain chloride. In this case the electrode can be used without a salt bridge; the errors caused by changes in the reference voltage with small changes in the chloride content of the solution are negligible compared to the other errors in the methods. The usefulness of the silver–silver chloride electrode in this application is due to the insolubility of silver chloride and the purity of the electrode reaction in the pH range from below zero to over 13:

$$AgCl_{(solid)} + e \rightarrow Ag_{(solid)} + Cl^-$$

Few anions affect the potential, and many that do can serve in place of chloride as the electrode anion, thus sulfide, bromide, and cyanide can be used to give a reference electrode if they are present in solution in the proper concentration ranges.

The silver chloride electrode can be used in reference-electrode assemblies in a manner similar to calomel electrodes; the reproducibility of the electrode potential is very good when properly purified materials are used in making up the electrode.

Three types of silver–silver chloride electrodes, based upon the method of preparation, are recommended for use where precise reference-electrode potentials are needed. These are the electrolytic, thermal-electrolytic, and thermal electrodes. Bates [1] has described the preparation of the electrolytic electrode by electroplating a layer of silver on a platinum substrate, washing the deposit carefully to remove plating-bath impurities, and electrolyzing the electrode in a chloride solution to convert part of the silver to the chloride. He describes in detail the preparation of the thermal-electrolytic electrode in which a paste of specially prepared silver oxide in water is thermally decomposed on a platinum substrate and partially converted to the chloride by electrolysis. The thermal electrode [27] is made by decomposing a paste of silver oxide, silver chlorate (or perchlorate), and water on the substrate. All the electrode types are highly reproducible in potential after an initial soaking period.

Less carefully prepared silver–silver chloride electrodes can usually be used in analysis, particularly for applications where the electrode is used without a salt bridge. Any uncertainty of the electrode potential in this case is due in large part to the uncertainties in the chloride concentration; this uncertainty is many times that introduced by electrode preparation using reagent-grade materials. A particularly useful electrode for titration work is made using pure silver wire annealed by heating to redness before plating with chloride. Pure silver wire is readily available from laboratory supply houses.

(c) *Other Reference Electrodes.* Other electrodes are used occasionally, particularly where the use of chloride salt bridges is not desirable. The mercurous sulfate electrode, which is similar to the calomel electrode in construction, can be used with sulfate systems; the glass electrode is sometimes useful when the acid concentration of the solution is known or held constant and when its high impedance is acceptable. Silver sulfate is too soluble to be useful as a reference-electrode component in most cases where it would otherwise have a number of advantages.

15–1.2 Salt Bridges

The salt bridge is the component used to provide an ionic-conduction path between separated parts of electrometric-analysis apparatus. Salt bridges are used to isolate electrodes from each other when it is necessary to prevent one electrode reaction or its reaction products from interfering with the other electrode reaction. They are also used to preserve the integrity of a standard or reference electrode by preventing contamination of the solution surrounding the electrode; also the use of a bridge enables the reference or standard electrode to be

used at a different temperature and pressure than the rest of the apparatus.

The difficulties encountered with salt bridges are such that most experimenters go to great lengths to avoid their use. Some of these difficulties are:

1. Uncertainties in the elimination or evaluation of junction potentials of the bridges.
2. Relatively high resistance of the bridges.
3. Mechanical and electrical failures.
4. Contamination of solutions.

Junction potentials arise from differences in the composition of the two solutions found at the junction of the salt-bridge solutions and the solution into which the bridge is inserted. The magnitude of this potential is a complex function of the composition of the bridge solution, the nonbridge solution, and the method by which the junction is formed. Theoretical and experimental investigations show that, if concentrated solutions of certain salts such as potassium chloride are used as the bridge solution, the junction potentials are often reduced to a small value that is sufficiently reproducible for most electrometric methods. Ammonium or potassium nitrate (and other salts if necessary) are also useful in reducing junction potentials and are used whenever chloride contamination must be avoided. The theoretical and experimental basis for the use of these salts has been covered in detail by Bates,[1] Charlot,[3] and Glasstone.[12]

The electrical resistance of electrolytic solutions, even of saturated salt solutions, is relatively high. This makes the salt bridge a trouble spot for the designer of electrometric apparatus since the resistance in the over-all circuit must often be kept as small as possible. The salt bridges used with reference electrodes can have up to several hundred thousand ohms impedance, depending upon the measuring equipment used. The salt bridges used with electrolysis electrodes (electrodes through which is passed appreciable current) should have resistance below 100 ohms, preferably less than 10 or so ohms. In electrolysis circuits the junction potential of the bridge is normally of no concern, and bridges that are filled with acid or base solutions that have lower specific resistances than the salt solutions can be employed. The designer uses short bridges of large cross section when the resistance must be kept low; this is completely analogous to the design of low-resistance electronic type conductors.

The mechanical failures of salt bridges are the result of mechanical breakage, the interruption of the solution continuity in the bridge or junction by solids or gases, and the failure of any artifices used to limit solution flow from the bridge. Mechanical breakage can be a serious

routine-analysis laboratory problem; it can be avoided through the use of plastic tubing in the construction of the bridge. Chemically resistant tubing made of materials such as polyethylene, fluorocarbons, and vinyl chloride formulations are as suitable as glass for most applications; the continued use of glass tubing in most bridges must be considered an anachronism.

The interruption of the solution path by solids or gases often occurs at the junction, particularly in cases where the junction is a small hole or a fibrous plug. Changes in the design of the junction and its orientation are the obvious solutions to this problem with both gases and solids; in general, a large-area junction should be used when solids are present. The interruption of the solution path by a bubble of gas in the salt bridge is a common cause of erratic bridge behavior; the salt-bridge design should be such that bubble traps are eliminated, and the source of the gas itself should be removed if possible. This salt-bridge problem is very prevalent in routine analysis if care is not taken to eliminate it in the design of the apparatus.

Electrical failures are usually associated with mechanical failures; the most common is the development of a high internal resistance when the continuity of the solution column is interrupted or partially blocked by gas bubbles or solid materials. Some bridges, particularly those filled with a gelled solution, develop a high resistance when a solid phase develops in the gel. Some bridges, particularly those filled with concentrated salt solutions, develop a high resistance when the solution "freezes" to a more or less solid mass of crystalline salts. Bridges that use a gelled solution of ammonium or potassium nitrate have been known to ignite and char when milliampere currents are passed through them. This is a reaction between the nitrate and the gelling agent initiated by localized heating at some point in the solution. This spot is often the site of a small air bubble or salt crystal imbedded in the gelled solution.

The artifices used to limit the flow of solution from a salt bridge serve to reduce the frequency with which the bridge-solution reservoir must be refilled and to reduce the contamination of the non-bridge solutions with bridge-solution components. For reproducible and low junction potentials, some flow must be permitted to preserve the integrity of the junction. In electrolysis circuits low to zero flow consistent with low resistance is the aim. The common artifices in bridge design to limit flow are: to balance the hydraulic heads involved so that no pressure difference exists between the bridge and other component; to use a gelling agent to immobilize the solution; to use a plug of fibrous material, fritted glass, porous ceramic, or porous plastic materials; to use a small orifice or capillary path through an otherwise sealed end; and to use an ion-permeable mem-

brane. Balancing hydraulic heads is not recommended. The use of plugs of fibrous materials such as asbestos or glass wool is quite satisfactory for reference-electrode bridges; large bridges of this type are hard to make resistant to collapse when subjected to pressure differences. Glass frit and porous materials are useful; however, care must be taken to use materials with a relatively high void space to hold electrolytic solutions or the bridge resistance will be excessive. Gelling agents such as agar-agar and gelatin are used extensively; bridges using this artifice usually have limited life and must be replaced frequently. These gelling agents are not suitable for elevated-temperature applications. The use of small orifices or capillary paths produces a bridge with high resistance and limits application to reference-electrode bridges. Carson [28] has described the use of a silica gel bridge for an electrolysis circuit operated at elevated temperatures. The improved version of this bridge uses a coarse glass frit to hold the gel in place.

Carson, Michelson, and Koyama [29] have described the use of porous glass in salt bridges. The glass used is available commercially; it is the leached, unfired form of Corning Glass Works Vycor glass. The simplest and most useful bridges are made with short lengths of cane (rod) attached to glass bridges by a short length of plastic tubing; porous glass cannot be sealed to other glasses since it is unworkable in a flame.

The plastic tubing should be clamped or wired tightly to the porous glass plug to hold the plug in place, although bridges using a semi-stiff tubing such as Tygon will be mechanically tight without such clamping. Some bridge-solution salts, such as potassium chloride, tend to crystallize out between the plastic tubing and the glass parts unless the plastic tubing is clamped tightly. When such salt solutions are used in the bridge, allowing the bridge to dry out will ruin the glass plug because the expansion of the salt crystals formed upon evaporation of the water will shatter the porous glass structure.

The performance of salt bridges made with these plugs is definitely superior to other salt bridges in terms of low resistance, low rate of solution flow, and mechanical ruggedness at elevated temperatures and in the presence of pressure differentials. The junction potentials observed vary with the bridge solution; with saturated potassium chloride, the bridges have junction potentials of the same order of magnitude as do bridges using plugs of fibrous materials, gelled solutions, capillary leaks, or small orifices. The flow rates are (for ¼-in.-long plugs ¼ in. in diameter) on the order of 1 ml of solution per month or less, even under pressure differentials as high as 15 psi.

Carson et al.[29] also described the use of ion-exchange resin membranes in salt bridges. These bridges show high junction potentials

and are useful chiefly in electrolysis circuits where a bridge of large cross section is desired. They possess few advantages otherwise over the porous glass bridges.

15–1.3 Electrode Reactions

The electrode reaction is the process by which an electric current creates a chemical change during electrolyses. For use in electrometric analysis, the electrode reaction must take place in such a manner that the chemical change and electrical quantities measured are correlated to each other. This normally requires that the electrode process be controlled in some fashion to prevent or greatly reduce any side reactions that would otherwise interfere in the interpretation of the data. The control of electrode processes requires consideration of the various aspects of electrode-reaction mechanisms and kinetics.

The primary electrode reaction can be considered to be the result of three consecutive transfer steps: transfer of the reaction species to the electrode interface, transfer of electrons at the electrode, and transfer of the reaction products from the electrode. Other processes, such as absorption-desorption of a substance on the electrodes and chemical reaction among the various substances (including the electrode) at the electrode solution interface may also play a part in the primary electrode reaction. The over-all rate of the electrode reaction is a function of the kinetics of the various steps; it is usually possible to alter the rate of any step by altering the conditions at the electrode-solution interface. Some of the many known means of varying the rates of various electrode reaction steps are: altering the rate of mass transfer by stirring, changing the concentration, changing the primary reaction by changing electrodes or adding reagents, changing the temperature, and changing the applied voltage.

The two mass-transfer steps are carried out by three principal modes: diffusion, convection, and migration. Depending upon the type of electrometric analysis being performed, the first two are the important modes of mass transfer in electrolysis. The latter is usually inherently insignificant or is made so by the analysis procedure.

Diffusion is observed whenever the chemical potential (i.e., activity) of a substance varies from point to point in a solution. The diffusion rate depends upon the temperature, the chemical potential differences, the nature of the substance diffusing, and, to a great extent, the path over which diffusion takes place.

Migration is the motion of charged particles in an electric field. In solution all charged particles carry the electrolysis current in proportion to their transport number. If the substance being determined has a small transport number, mass transfer by migration becomes negligible. This is desirable in most electrometric analyses;

the addition of a large excess of supporting electrolyte to the solution is often used to accomplish this goal. Salts of the alkali metals, which do not readily enter the electrode reaction, are frequently used as the supporting electrolyte; in process work many samples have sufficient inert electrolyte concentrations to make the addition of a supporting electrolyte unnecessary.

Convection results from stirring of the solution by mechanical means; it can also result from differences in density from point to point in the solution as a result of temperature or concentration gradients.

Convective mass transfer normally occurs when gases are evolved during electrolysis. Mechanical stirring generally is used when convection is the desirable mode of mass transfer. In microanalysis mechanical stirring becomes a major problem since the small volumes involved are easily splattered and lost.

The basic circuit used in electrolysis is shown in Fig. 15.1. The power source is connected through a switch to the electrolytic cell. In the cell one electrode is chosen as the working electrode; the other electrode then becomes the counter electrode. Depending on the nature of the electrolysis, an ammeter, a voltmeter, or a coulometer may be used. For the circuit shown in Fig. 15.1, the ammeter and coulometer readings should be corrected for the current flowing through V; if V were connected between the points designated X, its reading would have to be corrected for the ohmic drop across A and Q. Usually, if the reading of A or Q is the primary measurement, V will be connected between the points X so that a correction to the reading is

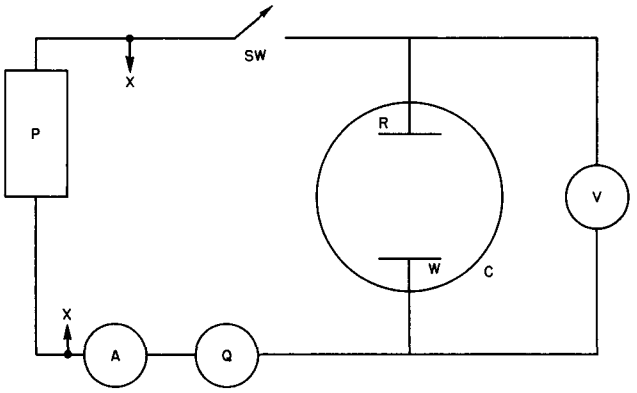


Fig. 15.1—General electrolysis circuit.

P. Power source
C. Electrolysis cell
R. Counter or reference electrode
W. Working electrode
V. Voltmeter
A. Ammeter
Q. Coulometer

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not needed; if the reading of V is the primary measurement, then the connection shown in the figure is better.

The potential of the working electrode when no current is flowing is given by an expression of the type

$$E' = \text{constant} + K \ln \frac{(\text{oxidized})}{(\text{reduced})} \tag{15.1}$$

where K is a constant depending upon temperature and the nature of the redox couple controlling the electrode potential, and oxidized and reduced represent the activities of the oxidized and reduced forms of the redox couple. This equation is a generalized form of the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{(\text{oxidized})}{(\text{reduced})} \tag{15.2}$$

where E° is the standard potential of the couple and R, T, n, and F are the gas constant, absolute temperature, number of electrons involved in the electrode reaction, and Faraday constant, respectively. The numerical values of the potentials E' and E are measured on different electromotive force scales and hence are not necessarily the same. The potential of the electrode with respect to the solution is constant for any given electrode and solution if the electrode reaction is reversible; it may be constant but is not necessarily so if the electrode reaction is not reversible. A knowledge of this potential would be very desirable, but unfortunately it is not obtainable since the measurement of such potential always requires the use of another electrode and only the difference between the two electrode potentials can be measured.

The potential of the working electrode when current is flowing through it assumes a value that is determined by the power-supply characteristics and the rates of the electrode reactions. It is possible, with suitable design of controls for the power supply, to conduct electrolyses in which either the electrode potential (with respect to a constant potential electrode in the same solution) or the current flowing in the electrolysis cell can be held constant. These two cases are the ones most important to electrometric analysis. The third case that in which neither the potential or the current is held constant, is of very limited usefulness in analysis, although it is commonly encountered in electrolytic processes.

(a) *Controlled-potential Electrolyses.* In controlled-potential electrolyses, the potential of the working electrode is held constant by the power supply. The potential is held constant relative to either a

reference electrode or to the counter electrode. In the latter case the counter electrode used must not change in potential during the electrolysis.

The current flowing per unit area (current density) of an electrode during controlled-potential electrolysis is a function of two sets of variables: those associated with the electrical circuit and those associated with the electrode process. The total current in electrolysis is given by the product of the current density and the area; in some cases the power-supply characteristics are such that they limit the total current that can be drawn at the regulated potential, and in others the area of the electrode is too small for the desired current. The circuit variables are largely the impedance of the electrolytic cell, the electrodes, and the power supply and leads. Since, in most cases, the effects of the circuit variables can be held constant, it is possible to compensate for them in the design of the apparatus or to correct for them in the treatment of the data when they affect the analysis of the sample.

The current-density limitation imposed by an electrode process step is often the key part of the electrometric technique of analysis. Thus the limitation of current imposed by the mass-transfer step of diffusion is the basis of polarography. The process steps that may limit current density are the rate of mass transfer to or from the electrode and the rate of electron transfer at the electrode. The former is a function of the stirring, the diffusion characteristics, and the concentration of the reacting species; these mass-transfer steps are normally the current-limiting steps in controlled-potential electrolyses. The rate of electron transfer is a function of the potential of the electrode vs. the potential given for the couple by Eq. 15.1 and the activation-energy requirements. The potential of the couple at the electrode is a function of the concentrations in the electrode-electrolyte interface solution, and, as this potential approaches that imposed on the electrode, the driving force for the electron-transfer step decreases to zero and no further electrolysis can occur. This is the key effect of controlled-potential electrolyses since, by proper selection of the imposed potential, the potential of a couple in a sample can be brought to a desired value. The current in controlled-potential electrolysis is seldom electron-transfer controlled until the final stages of the electrolysis; up to this point the system is usually mass-transfer limited, and all the reacting species reaching the electrode interface react before they move away.

For electrolyses in which the aim is to convert a quantity of reacting species, the control of the electrode potential is used, usually to prevent a side reaction that would occur if the electrode potential

were to exceed the set value. In this case the current limitation imposed by the power supply is not critical since the electrode potential will always be below the set value until the current becomes mass-transfer controlled. The power supply, when it is operating in its current-limited region, is unable to supply electrons (or to remove them if the electrode is an anode) at a high enough rate to maintain the potential. This is analogous to the effect of a constriction in a pipe through which gas or liquid flows when the demand for the liquid or gas is higher at the output end of the line than the possible flow through the constriction. As electrolysis continues, the concentration of the reacting species decreases to a value at which mass transfer becomes limiting, and the electrode potential will then come to the set value.

The current flowing in a constant-potential electrolysis in which the solution is stirred and in which the current is limited by mass transfer is proportional to the concentration of the reacting species. As the electrolysis proceeds, the concentration of the reacting species decreases, and hence the current also decreases. At any time t when the current is mass-transfer limited,

$$\frac{dC}{dt} = -kC$$

where k is a constant for a given set of electrolysis conditions, i.e., stirring rate, electrode area, and applied voltage, and C is the concentration of the relative species. Integrating from $t=0$ and $t=t$ and setting $C=C_o$ when $t=0$,

$$C = C_o e^{-kt} \tag{15.3}$$

The current decreases exponentially throughout the electrolysis.

The concentration of reactive species is defined in Eq. 15.3 as the concentration of reactive species which must be reacted to make the activity ratio, i.e., oxidized/reduced, assume the correct value to meet Eq. 15.1. The value of the initial concentration (C_o) can be made any fraction of the total concentration (C_T) present by suitable choice of the electrode potential since the latter sets the value of oxidized/reduced which will be reached.

The final concentration of the reacting species (C_F) never reaches zero in finite time. Theoretically the concentration will decrease exponentially in accordance with Eq. 15.3; the time t for stopping the electrolysis can be selected such that C_F is negligible compared to C_o. If $C_T - C_o$ is also negligible, than the electrolysis can be said to be complete insofar as any practical significance is concerned. The completeness of the electrolysis is thus a function of the imposed potential and the time of electrolysis; the proper selection of both can

be made using Eqs. 15.1 and 15.3 when the constants for these equations are known for the electrolysis.

Although a complete conversion of the reacting species cannot be achieved in an electrolysis at constant electrode potential, conversions of over 99.9 per cent are readily made in many cases. The limit to the conversion is set by the onset of side reactions that prevent setting the potential at a greater value to increase the fraction converted. The current in a constant-potential electrolysis theoretically never reaches zero in finite time but decreases continuously at a slower and slower rate; practically, the current decreases exponentially to a constant value. This constant final current is known as the residual current and is the consequence of side reactions that are not completely eliminated at the potential imposed on the electrode, the attainment of a limiting rate owing to the electron-transfer step, the hysteresis or lack of instantaneous reversibility in the power-supply control system, and the presence of electrical leaks, such as the charge and discharge of a condenser formed by the electrode and solution when certain electrodes or electrolysis cells are used. The value of this residual current is quite important in electrometric analyses in which the current flowing is measured or the total quantity of electricity used is measured. Of the causes, that due to side reactions is usually, but not always, the largest.

(b) *Constant-current Electrolyses.* In constant-current electrolyses the electrolysis current is held constant by the power source. In the simplest case the electrode reaction is not limiting, i.e., the limit on the electrolysis current is imposed by the power supply. In terms of reaction steps, this means that the mass transport of reacting materials to the electrode is more than sufficient to maintain the over-all rate. The electron-transfer step requires that at least a minimum potential, depending upon the nature of the reacting materials, be maintained at the electrode-solution interface to provide the driving force for the step. The electrode reaction that requires the lower potential will be the one that takes place.

As long as the rate of the reaction with lowest potential is sufficient to sustain the electrolysis current, other reactions with higher potential requirements will not occur. However, if the mass-transport step limits the rate of this lowest potential reaction, the potential of the electrode will increase until additional electrode reactions with higher potential requirements can take place.

Electrolysis at constant current is not as selective as electrolysis at constant potential. However, if the electrode process desired is the one with the lowest potential requirement in the cell and if the current is kept below the limiting mass-transfer rate, then the electroly-

sis will proceed only by this reaction. This type of electrolysis is used extensively in constant-current coulometric titrations.

15–1.4 Direct-measurement Methods

In these methods the measurement of the electrical quantity serves as the primary measurement of the analysis.

(a) *Potentiometry.* In potentiometric methods the potential developed by the substance to be determined in a suitable galvanic cell is utilized to measure the quantity of the substance present. The relation between the potential of a galvanic cell and the concentration of the substance is complex; and only a few systems are known in which a useful relation for analytical purposes is experimentally achieved. Although the substances that can be analyzed by potentiometry are few in number, the need for the determination of one of these, hydrogen ion, makes this method one of the most commonly used methods in routine analysis.

(b) *Voltammetry.* The voltametric methods employ the current-voltage characteristics of an electrode system which is subjected during electrolysis to a limit on current or potential by the kinetics of one step in the electrode reaction. Of the voltametric methods, the ones measuring the limited current are known as "amperometric methods"; no general term has been agreed upon for methods measuring potential.

From a routine-analysis standpoint, direct electrometric methods based upon voltammetry offer the advantages of being useful for measuring a variety of substances, of having high sensitivity, of allowing speed in making the measurements, and of requiring relatively simple, low-cost equipment. The accuracy and precision of the results is usually poorer than for other methods of analysis but is often very satisfactory for control purposes or for development work.

(c) *Coulometry.* Coulometry methods utilize the quantity of electricity required to chemically change the substance as the measure of the substance. In a sense electricity is used as a reagent to effect the chemical change, and the procedures closely resemble those of volumetric analysis. The basis of the methods consists of the laws of electrolysis formulated by Faraday in 1834 which relate the quantity of chemical change associated with passage of electricity through an electrode-electrolyte system and the quantity of electricity.

Coulometry methods have been particularly useful in micro- and ultramicro-analysis since the amount of electricity for as little as 10^{-7} equivalents of chemical change is readily measured with high accuracy using simple electrical equipment.

(d) *Other Methods.* Other methods of analysis in which an electrical quantity serves as the measure of the substance to be determined

are possible. These methods have not been investigated or developed to any great extent. The only method falling into this category in this presentation is the measurement of dielectric constant to analyze a two-component organic system.

15–1.5 Indicator Methods

In these methods electrometric techniques are employed to indicate the status of a chemical reaction involving the substance to be measured. The amount of reagents needed to produce the reaction is measured by some other means when the "indicator" shows that a certain state of reaction has been reached. Although it is possible to convert almost any property of the substance to be analyzed into an electrical signal by appropriate transducer systems and although this would allow definition of the transducer systems as electrometric, only those transducer systems that are based upon electrochemical phenomena are defined as being electrometric. The remaining transducer systems form the basis of a number of physical methods of analysis. Typical of these nonelectrometric methods in which an electrical signal is measured are the photometric methods based upon measuring the radiation transmitted by a sample with an appropriate radiation detector.

15–2 DIRECT TECHNIQUES

15–2.1 *Potentiometry*

The use of the potential developed by an electrode as the measure of the concentration of a substance in solution is theoretically applicable to a large number of substances. Potentiometry is simple in principle and employs relatively simple experimental techniques. However, there are many theoretical and practical limitations to the accuracy and precision obtainable in relating concentrations to measured potentials. At present the application of direct potentiometry is limited largely to the determination of pH; a few methods have been described for the determination of halides in special samples.[30, 31]

This discussion of potentiometry is limited to the determination of pH; no discussion has been included on the determination of substances by potentiometry since it is not used routinely in the analytical work associated with the processing of atomic energy materials. A further limitation is made in that only procedures involving the glass electrode have been included; the use of other pH sensitive electrodes is not often encountered in the analysis of atomic energy materials.

(a) *pH Scale.* The pH scale can be defined in a number of ways, none of which are free of arbitrary assumptions or problems of interpretation. From a process-control standpoint, a pH scale can best be considered as a set of numbers which serves as a practical scale of

acidity and alkalinity. A particular pH scale is framed in terms of a set of operations and calculations. Process-wise, there is little value, if any, in considering the meaning of pH in terms of solution theory.

This practical pH scale is a consequence of how pH is used in process control and other applications. Many properties of solutions which are difficult to measure directly can be correlated with pH; hence pH can be used as the measured variable for process control. Among the properties of solutions in which a pH correlation is often found are: long-term storability of waste solutions in terms of tank corrosion and formation of undesirable precipitates; product yields in organic synthesis, biochemical processes (antibiotics, brewing); rate of reactions in a process; and tendency of a solution to form gels upon cooling.

A common example familiar to most readers is the neutralization of acid waste solutions before storage to prevent them from damaging the storage facilities. The cost of neutralizing materials is not trivial, and it is generally desirable to avoid overneutralization, particularly for cases in which precipitates may form. The stability under storage of neutralized waste can be correlated with pH, and the plant operation can be adjusted to bring the pH of the waste to the correct value. The waste solution can then be placed in the storage tanks with some degree of confidence that the storage characteristics of the solution have been fixed to the desired value in spite of the fact they cannot be readily measured directly.

The operational definition of the practical pH scale is formulated as follows:

$$\mathrm{pH} = \mathrm{pH}_s + f(T)\,(E - E_s) \tag{15.4}$$

where pH_s is the assigned pH of a solution used as a standard reference point, $f(T)$ is the coefficient relating electrode voltage to the pH unit which, as is indicated, is a function of temperature, and E_s and E are the voltages of the pH electrode assembly when it is immersed in the standard solution and in the unknown solution, respectively. Note that pH_s and $f(T)$ need not conform to any solution theory concept to be useful. A set of standards that define a practical pH scale has been developed; use of this scale permits intercomparison of pH values obtained by different groups. This pH scale has been endorsed by standardizing groups in the United States and Great Britain.[32, 33] When these standards are used, the factor $f(T)$ is assigned the theoretical value $n\mathfrak{F}/2.303\ RT$, where $\mathfrak{F}$ is the faraday constant, R is the gas constant, and T is the absolute temperature. Note that if the two measured potentials E and E_s are obtained at different temperatures, there is actually no definition of the pH scale unless the two temperatures are explicitly expressed and the value of T in $f(T)$ is assigned.

For valid comparisons between pH data obtained by two different pH measurement systems, it is necessary that the two systems agree on the assignment of pH_s and $f(T)$. The blind assumption of such agreement can lead to disastrous results since the numerical pH value obtained on a solution in one system may differ by a large amount from the numerical pH value obtained by the other system on the same solution. For example, in a study of the difficulties being encountered in a waste neutralizer that was controlled by a plant pH measurement system, it was found that the numerical plant pH values differed by one to two units from the measured laboratory pH values. The waste solution, neutralized to pH 9.5 to 10.5 according to the plant pH system, had a laboratory pH value of 7.8 to 8.8. Before the situation was resolved, the laboratory results were unfortunately confirmed by the rapid failure of several large circulating pumps due to corrosion by the improperly neutralized solution. The difficulty arose because the plant pH control set point was being taken from the laboratory pH data on the storability of the waste solution. When the plant pH control set point was moved to the numerical value given by the plant pH system for properly neutralized waste, the difficulties due to improper neutralization ceased.

It should be noted that the buffers recommended by the National Bureau of Standards (commercially available) are internally consistent with respect to the value of pH_s and $f(T)$. Also the potential of the hydrogen electrode, and hence of the pH systems correlated to the hydrogen electrode, is defined only for one temperature. The changes in potential with changes in temperature cannot be correlated by resort to nonthermodynamic assumptions.[6] In the operation of conventional electronic pH meters, the temperature compensation supplied applies only to the factor $f(T)=n\mathfrak{F}/2.303RT$ and does not correct for any changes in pH_s with temperature.

Other pH scales offer no advantages in so far as process control is concerned over the practical scale. Difficulties in eliminating the effects of junction potentials, the change in activity with salt content, the change in activity and actual stoichiometric concentration with temperature, and the difference in temperature coefficients of the reference electrode and the sensitive electrode make it unlikely that any absolute method will be simpler or less subject to application errors. In this regard, the determined efforts of manufacturers of pH-measuring equipment and the standardizing groups in making equipment and standards interchangeable insofar as the practical pH scale is concerned are noteworthy and are leading to a universal pH scale, which, if not fundamental, meets all practical needs.

(b) *Electrodes.* The electrodes used in pH-measuring systems are used in a galvanic cell of the type

pH-sensitive electrode||solution X|reference electrode

Note that the junction potential of the salt bridge between the reference electrode and solution X is not eliminated. This bridge is usually a saturated potassium chloride bridge, and the reference electrode is usually a calomel electrode. The operational definition of pH includes the junction potential of the reference electrode in any voltage measurements.

The hydrogen electrode is the standard electrode for determination of pH values, but it is inconvenient for routine use. Other electrodes that are more convenient to use experimentally, such as the quinhydrone electrode, the antimony electrode, and glass electrodes, closely approximate the response of a hydrogen electrode to changes in pH over a part of the pH scale; hence they can be used in place of the hydrogen electrode within the limits of their range. The performance of these electrodes is always measured in terms of the equivalent hydrogen-electrode system. The hydrogen electrode has been studied for many years, and the reader is referred to Bates [1] for a more complete discussion.

The hydrogen electrode, quinhydrone electrode, and antimony electrode are pH-sensitive electrodes that function by virtue of an oxidation-reduction reaction occurring at the electrode-solution interface. This has been described more fully by Bates and others; what is of concern in this discussion is that this electrode reaction is usually sensitive to the presence of other oxidation-reduction reaction systems present in the solution. In such solutions, the error in the pH value determined from the voltage of the electrode can be quite large. The presence of other materials in solution can also affect the pH response; this is given in more detail by Bates.[1]

The glass electrode differs from the other pH-sensitive electrodes in that its response is due to a mechanism other than an oxidation-reduction reaction.[8, 34] This difference in mechanism is due to the fact that the glass electrode is a membrane system; the voltage of the electrode is a composite voltage of a reference electrode and the potential developed across a glass membrane; for example, Hg, $Hg_2Cl_{2\ (solid)}$ $Hg_2Cl_{2\ (saturated)}$ HCl (fixed N)|glass membrane|test solution. The mercury–mercurous chloride internal electrode and the internal solution of the glass electrode are used to make electrical contact with the membrane. The mercury–mercurous chloride electrode is commonly used as the internal electrode, but other electrodes are also used. The potential of the internal electrode and of the glass membrane-internal solution interface is constant; any changes in the potential of the glass

membrane-test solution interface will change the over-all potential of the glass electrode by an equal amount. The value of the internal potential is not critical so long as it is kept constant.

If a solution of the same molar concentration of hydrochloric acid as is used in the internal solution is used as the test solution, the potential difference across the glass membrane would theoretically be zero. This is not often the case; a small potential is usually found. This potential is known as the "asymmetry potential"; its existence is one of the reasons glass-electrode pH systems must be standardized periodically by buffer solutions of known pH. The asymmetry potential of an electrode tends to change with time; the rate of change is dependent upon the history of the electrode. Thus, when a new pH electrode that has been stored dry for some time after its preparation is wetted, the pH response is developed within a few minutes; the asymmetry potential of the electrode, however, may not stabilize to a low rate of drift for days. The drift rate of a stabilized electrode is usually small enough to be neglected in pH work if the electrode-pH meter system is standardized every day or two.

The pH response of a glass electrode is not altered upon exposure to the beta-gamma radiation fluxes as found in atomic energy material process streams. Carson and Michelson [35] found that all the common electrodes used in electrometric methods of analysis were essentially unaffected by the presence of beta, gamma, or alpha radiation although, in the case of glass electrodes, the glass was darkened to the point of opacity.

The pH response of most glass electrodes is imperfect at both ends of the pH scale. The errors in highly acid solutions are not as technically important as the errors caused by a partial sodium-ion response at high pH since the latter type solutions are more often encountered, particularly in waste treatment. Special-purpose glass electrodes, made using a pH-sensitive glass that uses lithium ions to replace most of the sodium ions present in the general purpose pH-sensitive glass, are available for use in such cases. A description of commercially available pH electrodes and their properties has been given in Bates.[1]

(c) *Measurement of pH.* The measurement of pH with a glass electrode varies somewhat with the pH meter–glass electrode system used. The manufacturer's manual should be followed with respect to the time the pH meter must be warmed up for use, the internal zeroing of the pH meter scale or reference circuits, and the specific standardization procedure to be followed. For laboratory instruments, the general standardizing procedure is:

> Allow the pH meter to warm up for the required period, and perform any zero adjustments required. Place the glass and reference electrodes

in the buffer solution used for standardization. Adjust the manual temperature control to correspond to the temperature of the buffer; alternatively, if automatic temperature compensation is used, allow time for the detecting element, which should be immersed in the buffer alongside the glass electrode, to come to equilibrium. Adjust the standardization control until the pH meter reads exactly the known pH of the buffer. Remove the buffer solution, rinse the electrodes carefully, using, if possible, a portion of the unknown solution as the last rinse. Place the electrodes in the unknown solution, and read the pH.

Several points in the procedure should be noted: (1) If the glass electrode has been dry and has not been used for some time, it may show a drift in potential until it gets back into equilibrium with water. A dry electrode can be used after a few minutes soak if the standardization is checked frequently until it is apparent that the electrode is equilibrated. This will be shown during standardization by the lack of the need to adjust the standardization control when the electrodes are placed in the buffer solution. (2) The buffer solution used should be within a few pH units of the unknown for highest accuracy. This technique minimizes the errors that may be present in the pH meter scale. (3) The temperature of the unknown must be the same as the buffer or it must be the same for the series of measurements with a constant buffer temperature used. This technique is required to allow definition of the pH scale and thus to allow reliable correlations of pH values with solution properties. (4) The pH values measured should be corrected for any sodium-ion error as necessary to give the correlation needed. With solutions above 0.1*M* in total ionic content, the pH of the solution cannot be readily correlated in a simple fashion with the hydrogen-ion activity.[11]

Plant pH-measurement systems are standardized in much the same manner as the laboratory instruments, i.e., the electrodes are immersed periodically in a buffer solution and the meter is adjusted. Some precautions are required to prevent process upset: (1) The process controller must be "locked out" before any standardization actions are initiated. In automatic control systems the lockout should be made automatically as part of the initiation of the standardization procedure. (2) The pH cell should be rinsed before standardizing. For installations in which the sampling operation cannot be checked by visual observation (i.e., to see if solution is flowing into the cell), a rinse of markedly different pH should be used to produce a large displacement of the pH meter reading. This will check the rinsing, as well as assure that flow through the cell is taking place. (3) The temperature of the buffer should be within the range allowed by the particularly defined pH scale being used. (4) If the process can be upset or altered by material from the usual standardizing buffer solution getting from the pH cell into the process solution, a procedure that

guards against possible plumbing or operator failures is to use process solutions for the rinse and standard pH solutions. Synthetic process solutions or a batch of actual process solution can be used. The rinses need not be analyzed; the pH of the solution that is to be the standard is carefully measured in the laboratory, with precautions being taken to avoid errors in scale assignment, changes in pH of the solution during the measurements, etc. The stock is then used as the standard solution in the standardization procedure. Care must be taken to avoid unknown changes in this solution during storage by carbon dioxide absorption if the solution is alkaline.

Hahn and Koyama [36] have described a pH cell used in plants processing essential materials which takes into consideration the radiation hazard associated with such processes. Michelson and Carson [37] described an earlier version.

(d) *pH meters.* The pH meter used with glass electrodes was one of the first applications of electronics in the routine-analysis laboratory. Without such meters the glass electrode would still be a laboratory curiosity. The development of the electronic pH meter has been described in detail by Ewing,[9, 10] Bates,[1] and others. Although the electronics circuitry and components vary with different manufacturers, two general types of instrument are distinguishable: the direct-reading type and the deflection, or comparison, type. The direct-reading type allows continuous recording or indication of the pH; the accuracy and precision obtainable are less than that obtainable with a deflection type. For routine analysis and process-control purposes, a direct-reading instrument has ample accuracy and is the most convenient type for use. The deflection type uses the sensitive electronic circuit to indicate a null; the voltage comparison is made with a bridge circuit.

The modern electronic pH meter is one of the most versatile instruments available for use in the analysis laboratory. Müller [38] has reviewed the varied uses to which a pH meter has been put which are of interest to analytical chemists. An additional use not mentioned by him is the use of a pH meter as an amplifier for simple filter photometers. All these uses depend in a large part upon the fact that the input impedance of a pH meter is 10^{13} to 10^{15} ohms; this enables its use with inputs having a large internal impedance of their own.

(e) *Direct Potentiometric Determination of Hydrogen-ion Concentration.* This technique has been developed by Jones, Rider, and Hendrickson [39] for solutions containing uranium, thorium, or aluminum nitrates. The pH of nearly neutral solutions of uranyl, thorium, or aluminum nitrate is a sensitive indicator of the free-acid content of these solutions. Hence a measurement of the pH of a solution

containing one of these ions can form the basis of a free-acid determination if the concentration of this ion is known.

The apparatus described by Jones et al.[39] is a Beckmen model H–2 pH meter with a Beckman number 270 calomel reference electrode and a number 290 glass electrode. Since the composition of the standard buffers is not given in the paper, the calibration curves cannot be used without checking several points to establish the identity of the pH scales used. A more modern pH meter and other models of glass and calomel electrodes can be used; here again the pH-scale identity must be determined. The pH meter–electrode pair was standardized at pH 7, using the asymmetry (standardization) control. The electrodes were then placed in a pH 2 buffer, and the meter reading was adjusted to conform by adjustment of the temperature control. This procedure adjusts the meter scale to conform with the Nernst equation. A third standard buffer solution with a pH value close to the pH value of the samples is used as a check on the setting. For control-analysis purposes, the direct-reading pH meters are less subject to operator error than the potentiometric types, offsetting a possible advantage the latter would otherwise have for this determination.

The calibration curves are made by taking a series of pH measurements on standard solutions containing known amounts of uranium (or thorium or aluminum) and free acid. The preparation of uranyl nitrate, thorium nitrate, or aluminum nitrate free of acid or basic impurities is difficult; the best procedure appears to be to make up several solutions of relatively high acid or base content which can be accurately titrated using large samples and to mix them in the stoichiometric ratios necessary to obtain solutions of the desired final acid concentration. Several standard solutions made up in this manner can be used to check the free-acid content of the salts used to make up other standard solutions.

The procedure is to rinse the electrodes carefully with distilled water; dry them with absorbent paper or cotton, taking care not to scratch the glass-electrode bulb; and immerse them in the sample or diluted sample. If possible, rinsing them with the sample before making the measurement is a good technique. The range of the method is $-0.2M$* to $+0.2M$ free acid. Samples falling outside this range should be diluted with standard base or standard acid to bring them into the correct acid range. The acid value found must be corrected for the dilution and added base or acid. For highly radioactive solutions the small samples permitted can be diluted 10- or 100-

*A negative concentration of acid can exist in these solutions because the so-called "neutral solutions" (free acid $\equiv$ 0) can dissolve appreciable quantities of the metal oxide to form stable solutions.

fold before the pH is measured; this gives a larger volume and permits the use of the standard size pH electrodes. For uranium the fluctuation in pH with uranyl-ion content has been found to be smaller than the other errors in the method when the sample is diluted 100-fold; hence only one calibration curve is necessary. However, the precision of the dilution method is somewhat less than with the more concentrated solutions, since a small error in acid concentration is multiplied by the dilution factor. This is partially offset by the greater change in pH with acid content at the dilute salt concentrations.

The precision of the method lies in the range of $\pm 0.03M$ to $\pm 0.05M$ free acid for uranium samples. The direct method gives the better precision. With proper calibration the method could be used for mixtures of salts, etc., but the necessary calibration work could become very great if a wide range of concentrations were to be encountered.

15–2.2 Coulometry

The techniques used in coulometric analyses are closely akin to those used in classical volumetric analyses. In coulometric titrations the standard solution is replaced by an electric current operating by means of a suitable electrode reaction on the substance to be determined. The buret is replaced by a device or system that gives the number of coulombs passed through the electrode during the titration. The detection of the end point, the sampling, and the preparation of the sample for analysis are the same as for classical volumetric analysis.

Although Faraday elucidated his laws of electrolysis as early as 1834, coulometry as a general analytical technique is relatively new. The work of Szebellédy and Somogyi [40] in 1938 can be considered the start of coulometric analysis; the major effort in coulometry has come since 1948. Evans and Bannister [41] used coulometric principles in their measurements, but their work did not receive the attention of analytical chemists until much later. Lingane,[20, 42-54] Furman,[55-58] and Swift [25] have been the pioneers in the use of coulometry in analysis; they and their students have demonstrated the versatility and practical usefulness of coulometry in modern analysis. Comprehensive reviews of coulometry have been prepared by DeFord [59-62] and Ashley.[63] Tutundzic [64] has proposed the use of the coulomb as the standard for titrants.

Coulometric techniques help give high precisions and accuracies to micro- and ultramicrotitrations, help simplify the design and operation of remotely controlled titration apparatus, and are highly amenable to automation. These advantages are very useful for handling

radioactive samples and have made coulometry important in the analysis of atomic energy materials.

(a) *General Considerations.* Faraday's laws of electrolysis form the basis of coulometry; these laws can be summarized by the equation

$$W = kQw \tag{15.5}$$

which states the quantity of substance W that is transformed by the electrode reaction in an electrolysis in which Q coulombs have been passed. In the equation, k is a proportionality constant and w is the equivalent weight of the substance for the reaction in the same weight units as W. The value of k is $1/f$, where f is the faraday, 96,490 coulombs (chemical scale) per gram equivalent, i.e., 1.0364×10^{-5} gram equivalents per coulomb. The usefulness of coulometry in micro- and ultramicroanalyses lies in the smallness of this proportionality constant; a large amount of electricity is required for titration of small amounts of material. Since values of Q as small as 10^{-4} coulombs can readily be measured with an accuracy and precision greater than ± 0.1 per cent, the accurate analysis of 10^{-9} equivalent of a substance is theoretically feasible. Titrations involving this small an amount of material are not yet made routinely because of end point detection difficulties.

The devices used to measure the amount of electricity used in an electrolysis are known as coulometers. As a class, these devices are current-time integrators:

$$Q = \int_{t_1}^{t_2} I_t \, dt \tag{15.6}$$

where Q is the number of coulombs passed in the time interval $t_2 - t_1$, I_t is the current in amperes, and t is time in seconds. The earliest coulometers, some of which are still used, were chemical coulometers. In these the electric current is used to electrolyze a solution under conditions such that the chemical change resulting from one or both of the electrode reactions can be measured by a gravimetric or volumetric procedure. Thus in the silver coulometer the weight of silver deposited from a silver nitrate solution is determined; in a gas coulometer the volume of hydrogen and oxygen produced in the electrolysis of a dilute acid solution is measured. Chemical coulometers are the standard coulometers to which other coulometers are compared; the silver coulometer is the ultimate reference for electrical quantity and current. However, application of chemical coulometers in analysis is limited because they are relatively inconvenient to use and are not as precise or as accurate in their usual forms for the integration of

the small currents used in micro- and ultramicrocoulometric titrations as are other types of coulometers. Page and Lingane [65] have described a micro gas coulometer suitable for coulometric titrations. The coulometer is based on the electrodecomposition of hydrazine in an acid solution to form nitrogen and hydrogen.

If the current employed in a coulometric titration is held rigorously constant, the integration of Eq. 15.6 leads to:

$$Q = kI\ (t_2 - t_1) = kI\ \Delta t \qquad (15.7)$$

i.e., the measurement required is the time lapse Δt. This method of measuring the coulombs used in a titration has proven very useful, and a large number of analytical procedures have been developed using this form of a coulometer. The precisions and accuracies of this form of a coulometer can be very high without elaborate or expensive equipment, particularly for small currents. Relatively simple electronically controlled current sources can hold currents constant to within ± 0.1 to ± 0.01 per cent; time measurements can be made readily to within plus or minus a few hundredths of a second. Since the starting or stopping of the addition of current in a titration is controlled by a switch or relay, the use of electric stop watches wired to start and stop in synchronization with the switching of the titration current has proven convenient.

Electronic coulometers suitable for the integration of small currents have been developed and applied to coulometric titrations with controlled electrode potentials. A wide variety of basic methods for integrating a current (or more often, a voltage derived from the current by passing it through a resistor) are employed. Among these are the velocity type integrators. In these the outputs are shaft rotations, or a series of pulses whose rates are proportional to the input current. A totalizing counter is used to indicate the number of pulses or revolutions and thus give a digital output proportional to the number of coulombs. Meites [66] has described a velocity servo system in which the revolutions of a servomotor shaft are counted. The input is amplified, and the output is used to drive the motor. A small tachometer generator on the motor shaft supplies the necessary feedback to maintain the linearity of the system.

Meites [67] has also described a coulometer based on the use of a Weston model 806 integrating relay. This relay consists of a small d-c motor constrained to oscillatory motion between two contacts and a counting circuit that registers the number of complete cycles of the motor armature. The net counting rate is proportional to the potential drop across an input resistor. The value of this resistor affects the counting rate above several thousand ohms; a blank counting rate at

zero current is also found. With proper calibration the unit gives reasonably good integration of 5 μa to 80 ma currents, but only if the currents integrated are reasonably constant.

The use of a special low-inertia integrating motor, such as that manufactured by Electro Methods, Ltd., Stevenage, England, as a coulometer has been described by Bett, Noch, and Morris,[68] Parsons, Seaman, and Amich,[69] Lingane,[52] and Furman and Fenton.[70] These are permanent-magnet d-c motors with low iron losses, low brush contact resistances, and negligible shaft friction; hence their speed is proportional to the driving voltage. Their low inertia gives them a small time constant of less than 10 msec; they give negligible errors in starting or stopping. The model 913, used by Parsons, has a nominal 24-volt input; its linear range of operation within ± 0.5 per cent is from 5 volts up. The current drain is well below 0.5 ma. The accuracy and precision of these units appears adequate for routine analysis applications where titrations with reasonably constant but not controlled currents can be used.

There are electronic circuits that enable the conversion of d-c inputs into a train of pulses having a frequency proportional to the level of th d-c input. One such circuit is shown schematically in Fig. 15.2. The d-c current flowing in the electrolysis cell charges the condenser up to a voltage V_t known as the triggering voltage for the gating circuit G, shown in the figure as a block. The trigger of the gating circuit initiates discharge of the condenser through the gate and sends a pulse to the output which can be used to drive a counter to count the number of times the condenser is charged and discharged in an interval of time. When the condenser is discharged, the gating circuit resets itself for the next cycle. The principle of the circuit is straightforward; the quantity Q of electricity (coulombs) held in a

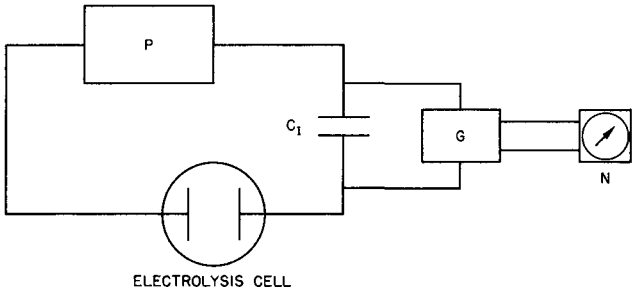


Fig. 15.2–Schematic diagram of a pulse-generating coulometer.

P. Power supply
C1. Integrating condenser
G. Gate
N. Counter

condenser of capacitance C (farads) is proportional to the voltage E (volts) impressed across the condenser:

$$Q=CE \tag{15.8}$$

For a fixed value of C and E, the quantity Q is also constant; in the circuit the total number of coulombs passed in the electrolysis is found by multiplying the number of pulses by the number of coulombs per pulse.

The principal difficulty in using a circuit of this type is devising a gating circuit that has stable triggering characteristics so that V_t is the same for all pulses and that discharges the condenser to a constant voltage level (this may be zero, but not necessarily). A desirable feature is that the range of the converting circuit be extendable to zero inputs without loss of linear characteristics in the integration. Until recently no reported circuit was able to integrate widely varying values of the d-c input with precisions better than several per cent; now, however, at least two instruments are available (Vidar Corporation and Geotechnical Corporation) that give precisions of 0.1 per cent or better in d-c frequency conversion and give linear conversions from zero to the maximum voltage input allowed. The instruments give a large number of pulses per volt input in the lowest ranges; hence, a count represents a very small quantity of electricity. Currents are easily converted to voltage inputs by passing them through a suitable resistor. The two instruments, plus others that may appear, offer the possibility of a flexible, precise current or voltage integrator for the electroanalysis laboratory. As of June 1960 no reports on their use in analysis had been received by the author, probably because of the newness of the instruments.

Another large class of electronic integrators is based on the proportionality between the charge stored on a condenser and the voltage of the condenser (Eq. 15.8). In these integrators the voltage developed across a condenser is the output measured. For the integrations the output voltage e_0 is related to the input current (or with appropriate circuit changes input voltage) by

$$e_0=\frac{1}{C}\int_{t_1}^{t_2} I(t)\,dt \tag{15.9}$$

where $I(t)$ is the current flowing as a function of time (in amperes if C is in farads). For low-level coulometric titrations, the simple circuit (a) of Fig. 15.3 would theoretically be feasible for integrating the current. All the current is stored in the condenser; the condenser must have a low leakage rate, the power-supply voltage (E) must be larger than the final read-out voltage (e_0) obtained for the

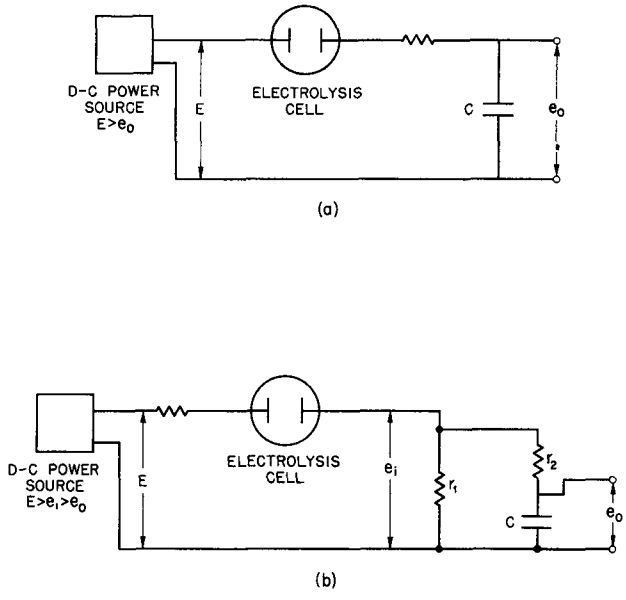


Fig. 15.3—Condenser-based coulometer circuits. (a) Basic circuit. (b) Resistance-capacitance integrator.

quantity of electricity used in the titration, and the read-out voltmeter must draw only a very small current. These requirements can all be met without much difficulty; the drawback lies in the size and cost of the high-quality condensers needed to integrate more than a few microcoulombs. Low-leakage condensers of 1 μf capacitance are relatively large units and are expensive; if the read-out voltage for 1 coulomb is to be 100 volts, then a condenser bank of 10,000 μf capacitance would be needed. Yet 1 coulomb represents only 10^{-5} equivalents. Obviously, this simple direct-integration circuit is not very practical, even though feasible.

The second circuit (b) in Fig. 15.3 shows a modification of the basic circuit in which only a fraction of the current to be integrated is used to charge the condenser. The current is split by the resistors, and the fraction r_1/r_2 is used for charging the condenser. This fraction can be made very small, and the capacitance values needed for integration of moderate amounts of electricity are kept in the few microfarad range. A problem arises in that the charging current is equal to

$$i_c = \frac{e_i - e_0}{r_2} \tag{15.10}$$

where e_i is the potential drop across r_1 rather than

$$i_c' = \frac{e_i}{r_2} \tag{15.11}$$

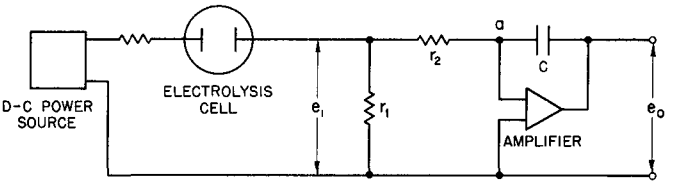


Fig. 15.4—Analog computer integrator.

which is the condition for linear integration of the electrolysis current. Assuming the simplest case, where e_i = a constant, and performing the integration indicated in Eq. 15.9, substituting i_c (from Eq. 15.10) for $I(t)$ yields

$$e_o = e_i(1 - e^{-t/r_2C}) \tag{15.12}$$

and, using the value of i'_c from Eq. 15.11 for $I(t)$ in Eq. 15.9,

$$e'_o = \frac{e_i t}{r_i c} \tag{15.13}$$

The difference between these two outputs represents the error of the integration and is

$$\delta = \frac{e_i t}{r_2 c}\left[1 - \frac{r_2 C}{t}(1 - e^{-t/r_2C})\right] \tag{15.14}$$

which increases rapidly with increase of t/r_2C. Thus the second circuit (b) of Fig. 15.3 can be used only if t is small compared to r_2C. The circuit shown in Fig. 15.4 overcomes the nonlinearity in the charging rate introduced by the buildup of potential across the condenser through the use of an operational amplifier. These amplifiers are d-c amplifiers with an amplification factor of 10^7 or more and are widely used in analog computers. With appropriate input and feed-back elements, they can be used to perform a variety of arithmetical operations, including integration. Soroka [70] and Philbrick [71] have discussed their use in analog computers. The amplifier is shown in Fig. 15.4 connected for integration using a condenser as the feed-back element. The potential at point a is

$$e' = \frac{e_0}{A} \approx 0 \tag{15.15}$$

where $-A$ is the amplification factor of the amplifier, which, as noted above, is very large. The voltage e_0 is the voltage appearing across the condenser as before; the condenser is charged at a rate equal to e_i/r_2 by the amplifier. Since no significant back emf is developed at a, the charging rate remains proportional to e_i/r_2, and the integration

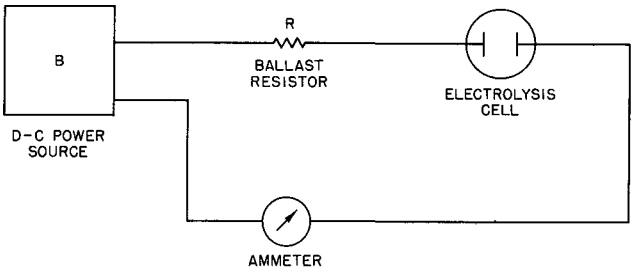


Fig. 15.5—Basic constant-current source.

is linear over the range of the amplifier output. Booman *et al.*[72] and Kelly *et al.*[73] have described the use of this type coulometer in controlled-potential electrolysis. Precisions of ±0.01 per cent in integration are reported.

Constant-current power supplies for coulometric titrations have been described by a number of investigators.[47, 74-87] The current needed in a titration can be estimated from the sample size and desired length of titration:

$$i=\frac{f\times S\times N}{1000t} \tag{15.16}$$

where i is the titration current in milliamperes, f is the faraday (96,490 coulombs per equivalent), S is the sample volume in microliters, N is the normality of the substance to be determined, and t is the titration time in seconds. Titration times between 5 and 10 min are desirable; hence, for sample sizes below 100 μl and 1N concentration, the current will be less than 20 ma. For the highly radioactive solutions often encountered in atomic reactor material analyses, the currents range from a fraction of a milliampere to 20 ma.

Figure 15.5 shows the basic circuit of a constant-current supply. A source of d-c potential (B), such as a battery, is connected in series with a ballast resistor (R), the titration cell, and the ammeter. In the analysis that follows, R includes the internal resistance of B and the ammeter. The voltage drop across the cell is composed of the back emf, e, and the potential drop across the cell resistance ($i\times r$), where i is the titration current and r is the cell resistance. The condition for absolutely constant current is that changes in B, R, e, and r cause zero change in i. The purpose of the ballast resistor is to make the internal impedance of the power supply vary large so that changes in $(e+ir)/i$ are small compared to R. Let us designate by r' the value of $(e+ir)/i$; r' is the effective cell resistance. The value of B and R can be calculated if r, the change in effective cell resistance ($\triangle r'$) that is to be guarded against, i, and the change in current ($\triangle i$) that is allowable are assigned. A typical electrolysis cell used in coulometric

titrations will have an effective resistance in the 500-ohm region, plus or minus 500 ohms. Hence $\triangle r'$ is 1000 ohms. Assigning i the nominal value of 1 ma and $\triangle i$ the value of ± 0.1 per cent, we have from Ohm's law:

$$i' = \frac{B}{R+1000} = 0.000999 \text{ amp (low limit)} \tag{15.17}$$

$$i'' = \frac{B}{R} = 0.001001 \text{ amp (high limit)} \tag{15.18}$$

Solving for B and R, we have

$B = 500$ volts

$R = 499{,}500$ ohms

These high values show why constant-current power supplies seldom use a pure resistance R for the ballast; for microampere currents, however, a simple circuit composed of a battery for B and good-quality carbon resistors for R is very suitable. Highly precise current regulation can be obtained without an excessively large battery. A close approximation of the value of B and R can be computed directly:

$$R = \frac{i \triangle r}{2 \triangle i} \tag{15.19}$$

$$B = \frac{i^2 \triangle r}{2 \triangle i} \tag{15.20}$$

where i is in amperes, B in volts, and r and R are in ohms; r is taken as the maximum cell resistance expected.

For small currents the basic constant-current source can be used with R a pure resistance; for larger currents, other means for compensating the effective cell resistance changes are used. Two general schemes are used: one is to use as the ballast a dynamic device with an impedance that can be changed by an input signal, and the other is to pass most of the current around the control section in a shunt circuit and to use the dynamic device to control only a part of the total current. This latter is the most widely used scheme for constant-current power supplies rated at more than a few milliamperes.

A generalized constant-current power supply is shown in Fig. 15.6. The d-c voltage supply usually consists of a transformer-rectifier-filter system operating from the 110- or 220-volt a-c line. The output voltage is in the range of 200 to 500 volts and can be stabilized against line transients and drift by appropriate control circuits. The output current (i) passes in part through the shunt, which is usually a power resistor, and in part through the control element(s). The latter may be purely electronic, such as vacuum tubes and transistors, or they may be mechanical, such as servo-driven rheostats. In

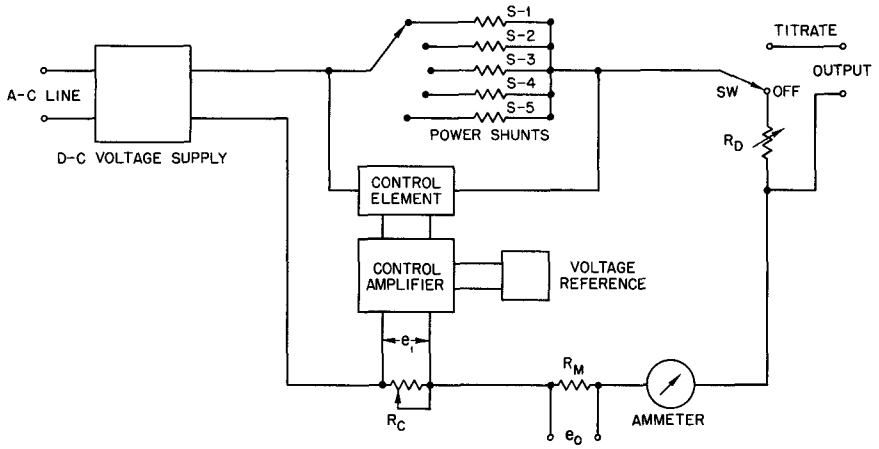


Fig. 15.6—Electronically controlled constant-current power supply.

R_c. Input resistor
R_m. Precision resistor for current measurement
R_o. Dummy load
S_w. Switch can be ganged to switch an electric timer

a few cases the control regulates the output voltage of the voltage supply, rather than the current.

In Fig. 15.6 the current is shown passing through a dummy load; this is required in some units to prevent upset of the control system. The value of this dummy load in most cases is zero ohms; however, in some cases, particularly with mechanical control elements, the load is adjusted to approximately the value of the external circuit. It is important to open the output circuit with the switch as indicated and not merely to shunt the output circuit, even if R_d is zero. The switch preferably has shorting contacts; it is usually ganged with the timing control so that the power to the electric stop watch and the titration current are switched simultaneously. The ammeter shown is usually supplemented with a precision series resistor R_M; a precise measurement of the current can then be made using a potentiometer to measure $e_0 = iR_M$.

The current passes through the input resistor R_c', which is usually a variable resistor that can be adjusted to give a continuous adjustment of i over the current range for a single shunt. This resistor must have good thermal stability and, preferably, a low temperature coefficient. A drift in the output current is often caused by a drift in this resistor. The input signal e is amplified as required and applied to the control element such that changes in i are nullified. The control amplifier usually operates by comparison of the input voltage to a reference voltage; the latter may be a standard cell, a voltage-regulator tube, a Zener diode, a mercury cell, or another constant-

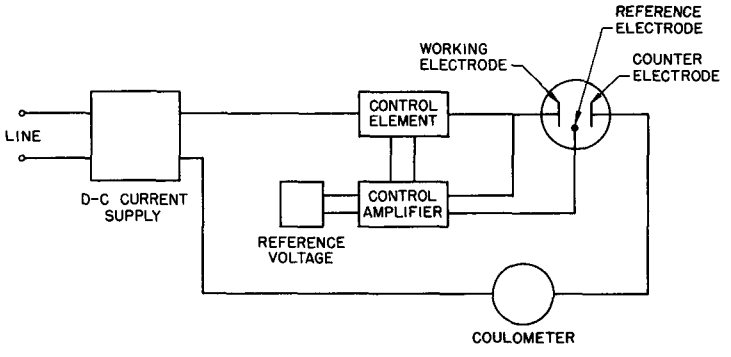


Fig. 15.7—Controlled-electrode-potential power supply.

voltage element. A possible method of adjusting the value of i is to change the reference potential, holding R_c' constant.

When a constant-current supply is used, it should be remembered that the voltage at any break in the current loop will rise to the value of the output from the voltage supply, which is at least several hundred volts. The best technique in the use and selection of switching methods is to maintain a continuous circuit at all times. Note that shorting a constant-current source normally does no harm to the supply. In power supplies with a slow-acting control element, the unit will be upset momentarily.

Power sources for coulometric titrations using a controlled electrode potential have been described by a number of investigators (Refs. 47, 72, 73, and 88 to 95). The power sources are essentially constant-voltage regulators in which the input is the potential between the working electrode at which the electrode reaction of interest is taking place and a reference electrode. A generalized circuit is given in Fig. 15.7. The control circuits are similar to those used in constant-current sources, except that all the current normally passes through the control element. Since the potential drop between the reference electrode and the working electrode is included in the input to the control, it is desirable that the control amplifier input have a high impedance to minimize the current flowing between the reference and working electrodes, thus keeping the potential drop at a minimum. The d-c current source should have a well-filtered output since any ripple in the electrolysis circuit will affect the precision of the potential control at the electrode. The reference voltage is used to set the potential applied. Because of the large size and expense of low-voltage high-current control elements, the control system may take the form in which the line input to the current source is controlled. This may be done by using a saturable reactor to regulate the input current to the rectifier circuits, or it may be done by using phase-

shifted thyratrons or controlled silicon rectifiers in the rectifier circuits.

(b) *Constant-current Coulometry.* The need to add a suitable reacting species to the electrolytes used in constant-current electrolyses to ensure 100 per cent current efficiencies with respect to a desired reaction has led to the use of electrolytically generated reagents as

Table 15.2—ELECTROLYTICALLY GENERATED REAGENTS USED IN COULOMETRY

Reagent	References	
	General	Atomic energy material
Acid—Base type:		
Acid, H^+	40, 76, 77, 96	
Base, OH^-	44, 76, 77, 97, 98	99–102
Oxidizing type:		
Chlorine, Cl_2	77, 84, 103	
Bromine, Br_2	40, 49, 75, 77, 84, 93, 104–109	28, 99, 110
Iodine, I_2	50, 84, 85, 98, 111	
Ceric, Ce(IV)	55, 112	57, 113
Argentic, Ag(II)	114	
Manganic, Mn(III)	115, 116	
Hypobromite, BrO^-	117	
Dichromate, $Cr_2O_7^{-2}$	118	
Reducing type:		
Ferrous, Fe(II)	55, 77, 90, 91, 119, 120	99, 121, 122
Uranic, U(IV)	65	
Uranium, U(V)	123	
Titanoyl, Ti(III)	124–126	48, 127
Cuprous, Cu(I)	49, 54, 77, 82, 102, 128	
Vanadyl, VO^{+2}	129	
Copper, Cu	130	
Stannous, Sn^{+2}	54, 105, 131	
Precipitation and complexing:		
Ferrocyanide, $Fe(CN)_6^{+4}$	50	
Ferricyanide, $Fe(CN)_6^{+3}$	132	
Versene*	133, 134	
Mercuric, Hg^{+2}	135–138	
Mercurous, Hg_2^{+2}	136, 138, 139	
Silver, Ag^+	46, 80, 140–142	122
Miscellaneous:		
Hydrogen gas, H_2	132, 143	
Karl Fischer Reagent, (I_2)	83, 144	
Ferrous versenate	145	

*Ethylenediaminetetraacetate $(HOOC)_2N—CH_2—CH_2—N(COOH)_2$.

the basis of constant-current coulometry. In addition to solving the problem of electrode efficiency, electrolytic generation of reagents makes possible the use of titrants not used in conventional titrations because they are unstable in solution or are hard to prepare and keep as a standard solution. It also makes possible the coulometric titration of substances such as 8-hydroxyquinoline and aniline, for which there is no known direct electrode reaction suitable for use in a coulometric titration.

The use of electrolytically generated reagents in the titration of materials that can react at an electrode is also common. In these the titration will proceed, in part, by a direct electrode reaction of the substance to be determined and, in part, by reaction of the substance with the generated reagent; this latter is known as the indirect reaction. An example is the constant-current coulometric titration of ferrous ion described by Furman et al.[55] The sample is added to a saturated solution of cerous sulfate in dilute sulfuric acid and electrolyzed at a smooth platinum anode. The cathode is isolated from the titration compartment by a salt bridge. During the electrolysis ferrous ion is oxidized at the anode, but, as the concentration of ferrous ion decreases, the potential of the anode rises until cerous ion is oxidized. Any ceric ion generated reacts with ferrous ion in the solution, and the concentration of ceric ion remains low until the end point is reached. The titration is equivalent to a titration in which a standard ceric solution is used to oxidize the ferrous ion.

Although normally cerous ion cannot be oxidized to ceric ion at 100 per cent current efficiencies to achieve solutions with appreciable ceric-ion concentration, the oxidation of the first few parts of the cerous ion present occurs at 100 per cent efficiency. Since the concentration of ceric ion is kept small during most of the titration by reaction with the substance to be determined, the current efficiencies found in practice are very close to 100 per cent.

The key to the electrolytic generation of ceric ion is the high overvoltage required for oxygen evolution from smooth platinum. This enables oxidation of cerous ion to ceric ion rather than the oxidation of water, which should, but does not, occur at the potential used. A number of reagent systems used in coulometry show behavior similar to the generation of ceric ion. Table 15.2 lists the reagents that have been electrolytically regenerated in coulometric titrations. The references have been selected to give a representative, but not comprehensive, listing. The wide variety of reagents that have been shown to be generated for use in titrations is noteworthy; the span of reagents covers most of the range required for conventional titrations. The principal reagent not as yet generated which is in widespread use is thiosulfate. The electrolytic generation of arsenite could prob-

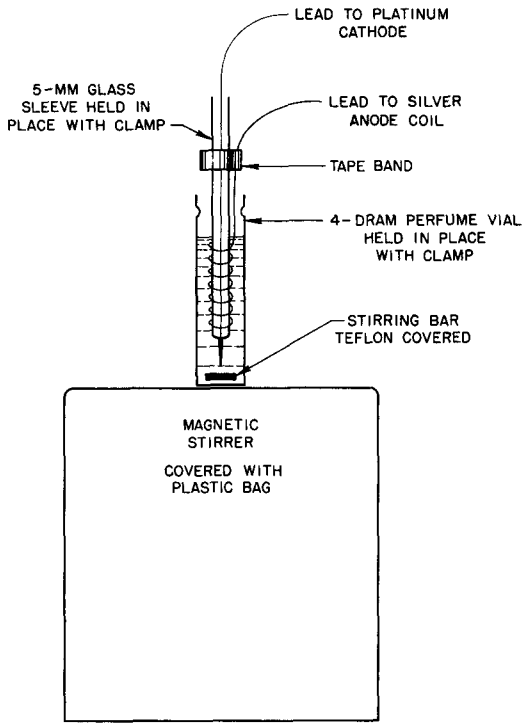


Fig. 15.8—Coulometric (color end point) acid cell.

ably be used as a substitute for thiosulfate in iodometry, but this has not been reported to date. In Table 15.2, titrations used in the analysis of essential reactor materials are indicated; they are described in the following paragraphs.

(c) *Determinations by Constant-current Coulometry.* Constant-current coulometric methods for the analysis of essential reactor materials have been reported for the determination of acid, uranium, and plutonium in process streams. Coulometric methods have not supplanted conventional volumetric techniques in the analysis of nonradioactive solutions or in the analysis of process raw materials such as nitric acid, although coulometric methods can readily be adapted to such analyses.

(1) *Determination of Acid.* On a routine basis, the coulometric titration of acid in radioactive samples is used extensively. The procedures use the cell and electrode system shown in Fig. 15.8. The electrode reactions are:

Cathode (platinum)---------- $H^+ + e^- \rightarrow \frac{1}{2} H_2$

$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$

Anode (silver)---------- $Ag + Br^- \rightarrow AgBr + e^-$

The electrolyte may contain chloride in place of bromide. The use of this electrode pair eliminates the salt bridge that is necessary if both electrodes are inert since, in this case, the anode reaction is

$$2OH^- \rightarrow \tfrac{1}{2}O_2 + H_2O + 2e^-$$
$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$

in effect reversing the cathode reaction. This platinum-silver electrode pair can be used in solutions containing nitric acid but not in solutions containing readily reduced ions, such as dichromate or ferric ion. Anions that react with silver ion to form insoluble precipitates do not interfere; reducing ions may interfere if they can reduce the silver salt formed.

The titration vessel shown in Fig. 15.8 is a 4-dram perfume vial; other small glass or plastic vessels can be used. The use of the perfume vial is recommended for routine analyses of radioactive samples since it is inexpensive enough to be discarded after use, a much less costly procedure than cleaning a more permanent vessel. A Teflon or other fluorocarbon vessel is recommended if a permanent vessel is required. Adsorbed radioactivity can be removed readily from Teflon by a rinse in dilute nitric acid; whereas a prolonged treatment with hot dichromic acid would be required to remove the same activity from glassware. Magnetic stirring is the most convenient stirring method since it does not require a shaft running through the top of the vessel. Teflon, or another fluorocarbon plastic, covered stirring bars are the most economical in the long run since they can be readily decontaminated. Covering the stirring motor assembly with a polyethylene bag such as is used in food preservation will minimize the damage resulting from a spill of solution or radioactive sample; the control can be operated through the bag. Note that no ventilation of the motor or control rheostat is possible if the bag is used; the stirrer should not be left running when not in use, nor should the bag be used if ventilation is required to keep the motor or rheostat cool.

The determination of acid in the presence of hydrolyzable ions such as uranyl, plutonium, aluminum, iron, etc., requires the use of complexing agents to hold the ion in solution. Fluoride and oxalate have been the best agents found. In the absence of hydrolyzable ions and oxidizing agents such as dichromate and permanganate, the determination of acid is straightforward. Either colorimetric or potentiometric end points can be used.

Colorimetric end points are recommended because of their inherent simplicity and ease of use. The most precise determinations are obtained by having the operator pretitrate the supporting electrolyte to an end point he can duplicate, adding the sample and titrating back to the end point. A comparison sample made by titrating a separate

sample of the electrolyte to an end point can also be used to aid in matching end points. With a little practice, most operators can make replicate determinations to within a few tenths of a per cent. The choice of indicator should be made to fit the pH of the end points; it has been found that even color-blind operators can distinguish the end point of an indicator that goes from a light color (pink or yellow) to a dark color (blue) at the end point. Thus thymol blue and bromothymol blue are good choices when they can be used.

Acid titrations with potentiometric end points are also feasible; a titration assembly using a glass electrode is shown in Fig. 15.9. The electrolysis-current field can affect the pH indication of the glass electrode to a large degree, unless precautions are taken to minimize the field about the glass electrode. A suitable artifice is to use a coil of silver wire as the generator anode, and place the platinum wire cathode within this coil. It is also necessary to us a highly salted stock electrolyte to minimize the solution resistance. The glass electrode and reference electrode are thus kept out of the generator field set up by the electrolysis current. An additional problem arises if the pH meter used cannot be used with grounded electrodes. In this case the generator power-supply output must be isolated from ground, and care must be taken to avoid grounding the titration vessel. The use of a pH meter that allows a grounded input is recommended. Generally speaking, potentiometric end points give slower titrations than colorimetric end points since the end point must be approached more slowly.

The silver bromide deposit on the silver electrode must be removed periodically. A convenient reagent for this is hydriodic acid (sp. gr.,

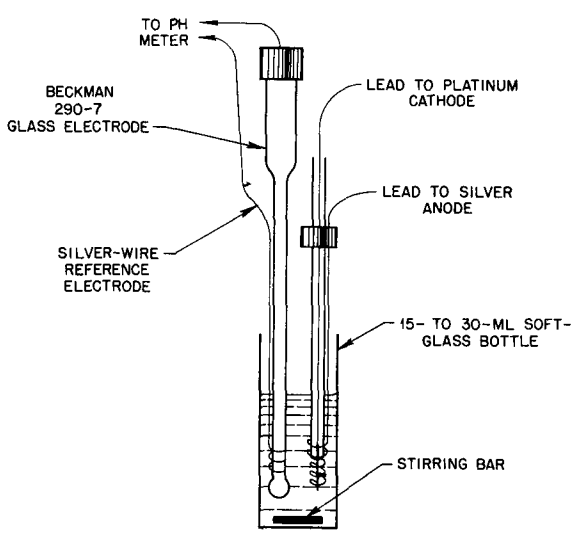


Fig. 15.9—Potentiometric acid titration cell.

1.5 to 1.9). Rinse the electrodes with water to remove any titration solution and then with acetone to dry them; then immerse them in 1 to 2 ml of hydriodic acid for a few seconds. The acid can be used a number of times. Rinse the electrodes free of hydriodic acid with acetone first, then with water. The hydriodic acid converts silver halide deposits to iodide complexes; these are soluble in hydriodic acid and a number of organic solvents. Dilution with water precipitates silver iodide.

Procedure (in Absence of Hydrolyzable Ions). Add 1 to 2 ml of stock reagent solution to the titration vessel, and titrate to an end point. Add the sample and pipet rinses, and titrate back to the end point. Several samples, if the volume and radioactivity level are not too large, can be run in succession. Clean the electrode after each set of determinations. This method can be used for 0.01 microequivalent of acid up to several milliequivalents per sample.

The stock electrolyte is 5 per cent sodium or potassium bromide plus 10 per cent sodium sulfate for potentiometric titrations. If pretitration to an end point is used, the stock solution should be made slightly acid to allow a 20- to 30-sec pretitration time. The pretitration procedure eliminates any blanks in the acid determination due to the presence of traces of acid or alkali in the water or reagents. Standard deviations on a single sample of ± 0.01 to ± 0.2 per cent are obtained routinely, using both potentiometric and colorimetric end points on 10- to 200-μl samples.

Procedure (in Presence of Hydrolyzable Ions. Oxalate Complexing Method). This procedure and its modifications have been developed by Carson[102] and can be used for solutions containing 0.0*M* and up of uranium and 0.2*M* and up of free acid. Phosphate, permanganate, dichromate, and aluminum interfere. Lower acid concentrations can be determined if a known spike of acid is added to the sample; this technique extends the acid range to negative values up to 0.2*M*.* For solutions containing at least 0.5*M* acid, add the sample and the pipet rinsings to the titration vessel. Add a volume of 25 per cent potassium oxalate solution equal to five times the product of the uranium molarity and the sample size in microliters. Stir vigorously until a precipitate forms; seed with uranyl oxalate crystals if necessary. Add 500 μl of 5 per cent sodium or potassium bromide solution (to which is added bromothymol blue indicator if a colorimetric end point is used). Mix and then add 100 per cent isopropyl alcohol until the solution is 70 to 80 per cent alcohol by volume. Titrate at 3 to 5 ma to the end point.

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*Uranium nitrate solutions at low acidities contain chain polymers of uranyl ion linked through oxygen, i.e., —O—UO_2—O—UO_2—. These are formed by the hydrolysis of uranyl salts with the formation of free acid:

$$2UO_2(NO_3)_2 + H_2O \rightarrow U_2O_5(NO_3)_2 + 2HNO_3$$
$$UO_2(NO_3)_2 + H_2O + U_2O_5(NO_3)_2 \rightarrow U_3O_8(NO_3)_2 + 2HNO_3$$

and so on. This permits the existence of the so-called "acid-deficient" solutions in which the stoichiometric ratio of nitrate ion to uranyl ion is less than 2; these solutions can be made by dissolving uranium trioxide in uranyl nitrate solutions. The designation 0.2*M* acid deficient thus means that 0.2*M* nitric acid must be added to give a stoichiometric ratio of two nitrate ions per uranyl ion.

For solutions containing less than 0.5*M* acid, use an acid spike to bring into the range of 0.2*M* to 0.5*M* acid if necessary. Add the sample, the spike, and the pipet rinses to the titration vessel. Add a volume of 2.5 per cent sodium citrate and 1*M* potassium thiocyanate equal to twice the product of the uranium molarity and the sample volume in microliters. Stir vigorously for 1 min; then proceed as above.

The citrate and thiocyanate break up the basic uranium complexes to simple uranyl compounds; oxalate tends to precipitate the basic complexes, giving high results. The alcohol is used to precipitate neutral oxalates and lessen the pH buffering effect of oxalate ion, thus making the titration end point sharper. In essence, the procedure converts the free acid to oxalic acid, which is titrated.

Single-sample standard deviations of ±0.1 to 2 per cent are obtained on 10-μl samples without spike additions. With spike additions single-sample deviations of up to ±7 per cent are obtained, based on the original acid content, i.e., total acid less the spike.

Procedure (*in Presence of Hydrolyzable Ions. Phosphate Precipitation Method*). This procedure has been developed by Carson [102] and is useful for microsamples containing 1*M* acid and up, phosphate, and less than 0.5*M* uranium. Aluminum and oxidizing agents interfere. The sample is added to 1 to 2 ml of a pretitrated stock electrolyte composed of 0.001*M* disodium phosphate, 5 per cent sodium bromide, and 0.025 per cent thymol blue. The uranium precipitates as sodium uranyl phosphate, releasing 1 mole of acid:

$$Na_2HPO_4 + UO_2(NO_3)_2 \rightarrow NaUO_2PO_4 + NaNO_3 + HNO_3$$

The titration is carried out at 3 to 10 ma to the blue-green end point. A correction for the acid released by the uranium must be made; since the

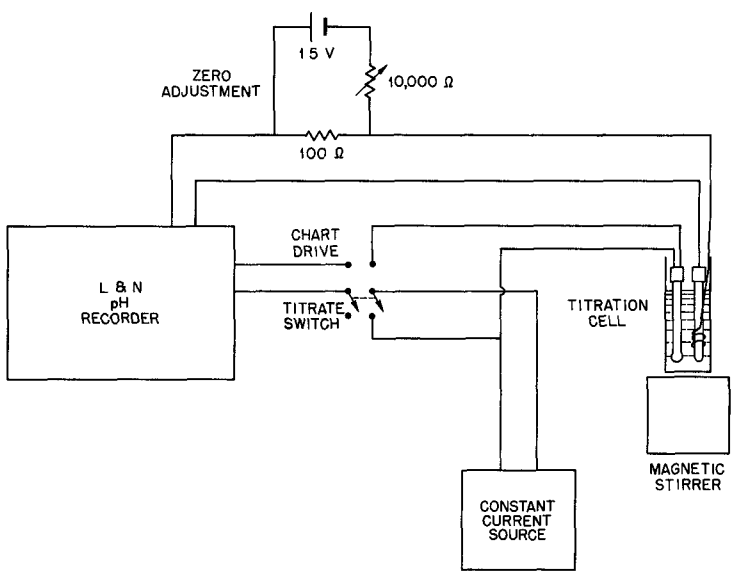


Fig. 15.10—Acid–uranium titration apparatus.

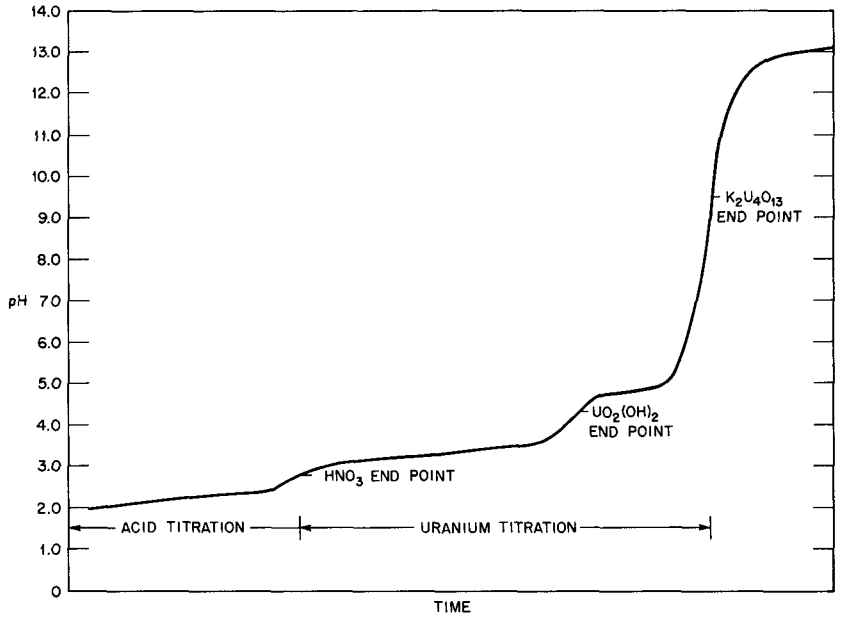


Fig. 15.11—Coulometric titration of acid and uranium by base generation.

uranium is normally determined anyway, this does not necessarily make an additional determination necessary. Large samples, in excess of 3 to 5 microequivalents of uranium, should be avoided since the precipitate tends to interfere with the titration. Standard deviations of a single sample of ±0.5 to ±1.5 per cent are obtained on 10-μl samples; these would be subject to an additional precision factor by whatever error is made in correcting for the uranium content.

Procedure (in Presence of Hydrolyzable Ions. Differential Titration of Acid and Uranium). This procedure has been developed by Carson[102] and is useful for samples containing 1.5*M* and up of acid and 1.0*M* and up of uranium. The titration determines both the acid and uranium in a 10-μl sample added to 2 ml of 5 per cent potassium bromide. Figure 15.10 shows the apparatus used. The titration is conducted at 5 to 6 ma and uses potentiometric end points determined from a plot of pH vs. time (titrant added). The titration vessel and electrodes of Fig. 15.9 are used. A typical titration curve is shown in Fig. 15.11. The first inflection is the pH change as the acid is neutralized. The second inflection does not always appear; it corresponds to the formation of $UO_2(OH)_2$ (2 moles base to 1 mole uranium). The last inflection occurs for moles of base to moles of uranium ratio of 2.5 to 1; a yellow precipitate forms at this point. This corresponds to the formation of potassium tetrauranate, i.e., $K_2U_4O_{13}$. The formation of diuranate or uranate is not observed; such formations require moles of base to moles of uranium ratios of 3 to 1 and 4 to 1, respectively. The addition of complexing agents, such as fluoride or thiocyanate, and other salts (except phosphate), such as sulfate or chloride, does not affect the stoichiometry. The first uranium inflection is suppressed in solutions containing

690-457 O—64——75

fluoride, thiocyanate, acetate, and other complexing agents. Phosphate gives a different stoichiometry, as explained above. If the phosphate molarity is greater than the uranium molarity, all the uranium precipitates as the alkali uranyl phosphate; if it is less, all the phosphate precipitates, and the excess uranium precipitates as the tetrauranate.

A similar titration involving aluminum can be made. In this case the final inflection corresponds to $Al_2(OH)_5^+$; a number of inflections are found between the free-acid one and this.

For 10-μl samples the single-sample standard deviation is ± 2 to 3 per cent for uranium and ± 2 to 5 per cent for free acid. Most of the error is in the determination of the time of titration.

Procedure (*Acidmetric Titration of Phosphate*). Carson and Gile[10] determined phosphate in samples containing uranium by a modification of the method of Helrich and Rieman.[146] In this procedure the sample is passed through a short cation ion-exchange resin column (Dowex 50 or equivalent) in the acid form to remove uranium and other metals. The eluate of mixed acids is preneutralized to a methyl red end point, which corresponds to the neutralization of all the strong acids plus the first hydrogen of phosphoric acid. The titration is now made at 5 to 8 ma to a thymol blue end point, which corresponds to the neutralization of the second phosphoric acid hydrogen. For 25-μl samples of 0.15 to 0.40*M* phosphate containing 0.2*M* to 0.3*M* uranium, the standard deviation of a single sample was ± 3 to ± 5 per cent.

(2) *Determination of Uranium.* The coulometric determinations of uranium are redox type titrations in which the uranium is titrated from the U(IV) valence state to the U(VI) valence state or from the U(VI) valence state to the U(IV) valence state. Nitrates, chromium compounds, tungstates, and molybdates are interferences in the methods, in addition to other substances, depending upon the method employed.

Procedure (*Electrolytically Generated Ceric Ion Titration*). Furman, Bricker, and Dilts[57] developed a procedure in which U(IV) is titrated with electrolytically generated ceric ion. The titration and the reduction of the uranium are carried out under a blanket of nitrogen or carbon dioxide; a sulfate medium is used. The reagent-generation system employs a two-compartment cell, with the cathode separated from the bulk of the solution in a glass tube sealed at the bottom with a glass frit, which serves as the connecting salt bridge. The anode is a 2- by 2-cm piece of platinum-iridium foil. The catholyte is 12*N* sulfuric acid, and the anolyte is the titration medium. The anolyte consists of 5 ml of 5 per cent ferric sulfate, 20 ml of saturated cerous sulfate in 3*N* sulfuric acid, and 5 to 10 ml of the sample and the column rinses. The medium is pretitrated to the end point before the sample or rinses are added.

The indicator system is an amperometric system described by Cooke, Reilley, and Furman[147] and consists of a saturated lead amalgam-lead sulfate reference electrode and a platinum-wire operating electrode for the larger uranium samples or a 1-cm square platinum-iridium foil electrode for the smaller uranium samples. The end point is set such that the indicator current is zero when the potential of the solution is 1.300 volts vs. the reference electrode.

The uranium sample in 3*N* sulfuric acid is degassed to free it of oxygen and is then reduced by passing it through a column of finely divided 26 per cent cadium amalgam. The reduction is quantitative to the (IV) valence state. Iron and other reducible ions, halides, and nitrates must be absent. The eluate is caught in the pretitrated titration medium. In this, the U(IV) reacts with the ferric ions present to give U(VI) and ferrous ion.

$$U^{+4}+2H_2O+2Fe^{+3}\rightarrow UO_2^{++}+4H^{+}+2Fe^{++}$$

Theferrous ion is then titrated with the generated ceric ion. Although the oxidation of U(IV) by ferric ion is slow, the large excess of ferric ion present makes the rate high enough to permit titration at room temperature. The direct oxidation of the uranium with ceric ion is too slow to be useful in titration. The reported precision, expressed as the deviation from the accepted value, for 5-mg samples was less than ±0.5 per cent and for 25 μg samples, ±9 per cent. A 1- to 2-μg blank was found.

Procedure (Electrolytically Generated Bromine Titration). This procedure was developed by Carson [28] and later modified by Carson and Blouin [110] for the titration of uranium in nitrate solutions. The titration vessel is a special all-glass system with ports for the various electrode assemblies, a thermocouple well, and gas and solution inlets. The generating system is a two-compartment system. The cathode is a short heavy-gauge platinum wire immersed in dilute sulfuric acid contained in an 8-mm tube sealed at the bottom with a silica gel plug that serves as the electrolysis circuit salt bridge. The anode is a 4- to 6-in. length of platinum wire wound in a tight spiral about the cathode compartment. The indicator system is the derivative polarographic system described by Reilley, Cooke, and Furman; [148] the electrodes are short lengths of platinum wire sealed into a lead-glass tube. These electrodes are polarized with a constant current of 1 μa obtained from a battery and resistor current supply. The potential across the electrodes is read using a line-operated pH meter.

The uranium sample, which may contain phosphate, sulfate, fluoride, perchlorate, iron, oxidizing agents, or reducing agents, is pretreated by heating it several minutes with an excess of hydrobromic acid (48 per cent) to remove oxidizing interferences or with a mixture of acid and free bromine to remove reducing interferences. The sample is transferred to the titration vessel and swept free of air by a continuous flow of oxygen-free carbon dioxide or nitrogen; then 5 to 7 ml of electrolyte are added (3*M* HBr plus 0.02*M* Fe). The sample is heated to 90°C and is reduced by the addition of a small excess of chromous chloride solution. The excess reductant is titrated at 90°C with electrolytically generated bromine. The end point is a sharp increase in indicator potential from below 100 mv to 300 mv or more. The uranium is titrated to the second end point; the potential rises to 600 to 700 mv during the titration, then falls rapidly at the end point to below 100 mv.

The direct oxidation of uranium by bromine is slow, even at the elevated temperature, and the addition of iron is required to prevent loss of the volatile reagent. The sluggishness of the ferric-U(IV) reaction gives a number of false end points during the titration. In automatic titrator terminology this type of behavior is known as an anticipation of end point. It is desirable since it prevents gross overtitration of the

sample by cutting off titrant addition until the previous additions of titrant are reacted. The indicator behavior is as expected for the reversible chromous-chromic and ferrous-ferric couples and the irreversible U(IV)–U(VI) couple.

The original procedure used a lead column described by Cooke, Hazel, and McNabb [149] for the preliminary reduction of the uranium. Hydrobromic acid with iron was used in place of the hydrochloric acid called for in the reference. The titration results using the column were satisfactory. The change to chromous-ion reduction was made because the lead column always produced some chromous ion when solutions containing chromium were analyzed, which required a change in the automatic titrator to make this preliminary titration. It proved convenient to use chromous chloride for the reduction and pretitration of all samples analyzed.

The precision, expressed as the standard deviation of a single result, was ±0.3 per cent for 7 mg of uranium and ±6 per cent for 30 μg. A blank correction was required for samples below 1 mg.

(3) *Determination of Plutonium.* The determination of plutonium by a redox type titration is based either on the oxidation of plutonium from the Pu(III) to the Pu(IV) valence state or by the reduction of the Pu(VI) to the Pu(IV) valence state. The oxidation from the Pu(IV) to the Pu(VI) valence state is difficult to accomplish quantitatively unless an excess of the oxidizing reagent is employed; hence this redox reaction is not used as the basis for a titration method. Dreeben [113] has described a coulometric titration of plutonium from the (III) to the (IV) valence state with electrolytically generated ceric ion as the oxidizing agent. Since the potential of the Pu(III)–Pu(IV) couple is close to the Fe(II)–Fe(III) couple (about 0.70 volts), iron impurities in the sample and reagents constitute a serious interference in methods using oxidation of Pu(III) to Pu(IV). The reduction of Pu(VI) to Pu(IV) is not subject to an iron interference, although under some conditions chromium and ceric ion interfere.

Procedure (Hanford Constant-current Method). This procedure was developed by Carson, Vanderwater, and Gile [121] for the direct determination of plutonium nitrate samples that might contain iron, chromium, uranium, fluoride, rare earths, and organic acids. Sulfate interferes if chromium or cerium is present, although the direct determination is possible with sulfate present and chromium absent if the pretreatment step is modified. The method has been tested for 2 μg to 10 mg of plutonium.

The pretreatment of the sample to remove interferences and to oxidize the plutonium to Pu(VI) is carried out in a reaction vessel attached to the titration vessel by a length of capillary glass tubing. This tubing extends as a center tube in the vessel; it is used to introduce gas for stirring during the pretreatment and to transfer the sample to the titration vessel. The pretreatment vessel is fitted with one side tube to permit addition of sample and reagents and a second tube connected to the gas exhaust scrubber. During pretreatment a gas stream is used

to stir the sample and reagents added to the pretreatment vessel. This gas is vented thru the exhaust side arm along with a stream of air drawn into the vessel through the other side arm. This air sweep is necessary to prevent difficulties in adjusting the stirring gas stream. The titration vessel is all glass, with ports for the addition of electrolyte, generator electrodes, and indicator electrodes. Magnetic stirring is used.

The reagent-generation system uses a divided cell in which the anode is isolated from the titration by a silica gel salt bridge. The anolyte is 2*N* sulfuric acid and the anode is a short heavy platinum-10 per cent iridium wire. The generator cathode is a 6- to 8-in. length of platinum-10% iridium wire wound in a coil about the anode compartment. The two indicating electrodes are platinum-10% iridium wires sealed in a lead-glass tube; about ⅛ in. of the length is exposed. These electrodes are used in a derivative polarographic type end point system and are polarized with a 0.1-μa current.

The titration medium is 0.6*M* ferric ammonium sulfate in 25 per cent sulfuric-10 per cent orthophosphoric acid. To this stock solution just before use is added 6.5 g of urea per 100 ml. This solution is pretitrated to the end point before the sample is added. Potassium dichromate is added if necessary to give a 50- to 100-sec blank titration. Ferrous sulfate is used to adjust the solution if larger blanks are found. The urea is added to permit generation of ferrous ion in the presence of nitrate. It acts by breaking the reaction chain found in nitric acid oxidations at the nitrite stage:

$$(NH_2)_2CO + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O$$

In the absence of nitric oxide, nitrogen dioxide, and nitrite, cold dilute nitric acid does not oxidize ferrous ion.

The plutonium sample is placed in the pretreatment reaction vessel, diluted to 1 to 2 ml with perchloric acid (1+1), and oxidized with 0.1*M* potassium permanganate at 70 to 80°C. If the sample volume is below 100 μl or below 1*M* in nitrate, 100 μl of 5 to 6*M* nitric acid is added with the sample. The excess permanganate and any manganese dioxide or dichromate formed are removed by adding an excess of 57 per cent formaldehyde solution and heating to 90°C. Further heating initiates the reaction between nitric acid and the excess formaldehyde. The sample is cooled and pulled into the pretitrated electrolyte solution through the connecting capillary. A portion of the pretitrated electrolyte solution is withdrawn in a clean dry pipet first; this is used to rinse the reaction vessel.

The excess permanganate and manganese dioxide are destroyed with hydrochloric acid if the sample contains sulfate, and no nitric acid is added. This procedure does not reduce Pu(VI) or dichromate; if formaldehyde is used in the presence of sulfate, Pu(VI) is reduced along with dichromate. The reason for this behavior is that Pu(IV) forms a sulfate complex that increases the Pu(VI) to Pu(IV) oxidation potential to about the same value as the dichromate-chromic couple of 1.3 volts. In the absence of sulfate, the potential of the Pu(VI) to Pu(IV) couple is about 1 volt.

The indicator potential during titration rises from about 300 mv to over 700 mv and falls sharply to below 100 mv at the end point. The

break is very sharp; a rounding of the break point is found only for low-current generation. The polarization current is critical; above 0.1 μa the sensitivity falls drastically. Samples containing 300 μg or more of uranium and less than 10 μg of plutonium require a partial separation of the uranium, which otherwise interferes in the pretreatment by blocking the reaction of nitric acid with formaldehyde. A convenient procedure is a coprecipitation of plutonium fluoride on lanthanum fluoride.

The precision of a variety of sample types, expressed as the standard deviation of a single result, was ± 3 per cent for 2-μg samples.

(d) *Controlled Electrode Potential Coulometry.* The attainment of 100 per cent current efficiency in an electrolysis can be obtained in many titrations by using controlled electrode potential electrolyses. This technique requires the use of a current-time integration system that will integrate a variable input. The basic power source and coulometer systems have been described above. Meites [150] has described a procedure for determining Q, the number of coulombs needed to complete a controlled-potential electrolysis, from data obtained in the early part of the electrolysis. The determination of Q by this method gives good precision and accuracy and cuts down the required electrolysis time by a factor of 2 to 3. Controlled-potential coulometric procedures have been gaining in acceptance compared to constant-current techniques as the precision and accuracy of the coulometers and electrode controls have increased. The inherent accuracies and precisions of the most recent apparatus are as good as the better constant-current systems, and the applications of controlled-potential coulometry should increase.

(e) *Determinations of Controlled Electrode Potential Coulometry.*

(1) *Determination of Uranium.*

Procedure (Simultaneous Determination of Uranium and Copper). The original procedure of Farrar, Thomason, and Kelley [15] has been revised by Shults and Thomason [152] to allow for varying ratios of uranium and copper in the sample. The power supply used is the one described by Kelley, Jones, and Fisher.[73] The cell is a cup that is sealed on top of a two-way glass stopcock through which a mercury-pool cathode is supplied from a reservoir or is sent to waste. The electrolysis anode is a coil of platinum wire immersed in a tube sealed with a fine glass frit; the anolyte is 1*N* sulfuric acid. The reference electrode is a silver-silver chloride-potassium chloride electrode separated by a glass-frit bridge from the solution. The solution is stirred by a mechanical stirrer that has a 4-cm-diameter glass disk positioned horizontally at the mercury-electrolyte interface. A Teflon cap covers the vessel; a nitrogen inlet, a sample port, and holes for the counter electrode (anode) and reference electrode assemblies are provided.

Approximately 6 ml of clean mercury, 5 ml of 1*N* sulfuric acid, and the sample are placed in the cell. The solution is deaerated for 5 min in a stream of nitrogen gas that has been passed through two chromous sulfate scrubbing towers. The apparatus is adjusted so that reduction

at −0.3 volt vs. the reference electrode will be made. This step reduces both copper and uranium. The titration is stopped when the current falls below 50 μa. The coulometer read-out voltage is then read, and the coulometer is set to zero by shorting the capacitor. Adjustments are made to give an oxidation at +0.175 volt to oxidize the copper and the titration is continued until the current falls to 50 μa. The difference in the number of coulombs between the first and second titrations represents the uranium.

The precisions, expressed as the deviation from the standard value, are in the range of ±0.007 mg for 5-mg samples of uranium to ±0.012 mg for 1.4-mg samples; the copper values are ±0.003 mg for 1-mg samples to ±0.004 mg for 0.1-mg samples.

Procedure (Uranium in Nitrate Solution). This method was developed by Booman, Holbrook, and Rein.[153] The titration is carried out with the apparatus described by Booman,[72] which employs a controlled cathode potential electrolysis using a mercury cathode and an electronic coulometer. Two alternative procedures are described; one uses an electrolyte of 1*M* sulfuric acid and the other, an electrolyte of 1*M* citric acid and 0.1*M* aluminum sulfate neutralized to pH 4.5 by potassium hydroxide. The sample is added to 5 ml of electrolyte and deaerated with a stream of oxygen-free nitrogen. The sulfuric acid procedure calls for reduction at −0.25 volts vs. the reference electrode (a silver-silver chloride electrode immersed in saturated potassium chloride). The citrate procedure calls for a prereduction at −0.10 volts vs. the reference for 20 min, followed by reduction at −0.60 volts for the uranium analysis.

The sulfuric acid electrolyte is used for solutions free of interferences that contain more than 2 mg of uranium. Other samples require the use of the citrate buffer electrolyte. Chloride, nitrate, and aluminum do not interfere with the titration unless present in very large molar ratios to uranium. Mercuric ion, cupric ion, ferric ion, and ceric ion can be tolerated in small amounts. The most serious interference is from ferric ion.

The precision, as expressed by the standard deviation of a single result, for 75-mg samples of uranium in the sulfuric acid electrolyte is ±0.01 to 0.03 per cent; for 7.5-mg samples, it is ±0.03 per cent. In the citrate medium, for 0.750-mg uranium samples, the precision is ±0.06 per cent; for 0.0750-mg samples, it is ±0.4 per cent, and for 0.00750-mg samples it is ±0.2 per cent. A background correction for the residual current found in the citrate electrolyses is applied to the citrate titrations.

Procedure (Prior Extraction of Uranium). The controlled-potential coulometric method of Booman et al.[153] for uranium has been extended by Booman and Holbrook[154,155] to solutions containing large amounts of interferences by first extracting the uranium. The extractant is methyl-isobutyl ketone, which extracts uranium in a single contacting from a solution containing aluminum sulfate, ammonium hydroxide, and tetrapropylammonium hydroxide. The extraction is at least 99.8 per cent complete. Uranium is effectively separated from all metal ions except ruthenium and technetium. The organic extractant and the two remaining metals are removed from the uranium by fusion with sodium bisulfate-perchloric acid at 600°C.

For highly radioactive samples, a 0.750-ml sample is pipetted in a shielded facility into a 15- by 150-mm test tube containing 60 ml of 2.8*M* aluminum nitrate, 1.0*M* ammonium hydroxide, and 0.005*M* tetrapropylammonium hydroxide. The mixture is vigorously contacted with 3.0 ml of methylisobutyl ketone for 2 min and allowed to separate. Then 2.5 ml of the organic phase is taken from the shielded facility, and an exact 2.0-ml aliquot is placed in the coulometric cell and evaporated to dryness with hot air. Fifty-five hundredths of a gram of sodium sulfate and 0.20 ml of 72 per cent perchloric acid are added. The electrolysis cell is placed in a muffle furnace at less than 200°C and heated rapidly to 600°C; it is held there for 20 to 30 min. The fusion mix is cooled and dissolved in 2 ml of water with gentle heating. After the mix has cooled to room temperature, 0.50 ml of 0.25*M* aluminum sulfate in 0.25*M* sulfuric acid plus 4.0 ml of 1.2*M* potassium citrate that has been adjusted to pH 4.6 are added. The proper quantity of fresh mercury is added to the cell. Exactly 4.0 min are allowed for making the preliminary adjustments of the cell electrodes, stirring rate, etc. The cell is deaerated for 15 min, the sample is prereduced at −0.25 volts vs. S.C.E. for 20 min, and then the U(VI) is reduced at −0.65 volts vs. S.C.E. for 14 min. One minute is allowed to determine the background correction. No bias has been observed in the results from impurities in the sample.

(2) *Determination of Plutonium.* This procedure was developed by Scott [156] and is based on the titration of Pu(III) to Pu(IV). The electronic apparatus is patterned closely to that of Booman et al.; [72] modified slightly to allow oxidation and reduction at the working electrode. Two different titration-cell designs are used. Both designs employ isolated counter-electrode and reference-electrode compartments. The compartments are connected with the titration compartment by silica gel bridges and are filled with 1.0*N* sulfuric acid. The counter electrode is a platinum-wire coil; the reference electrode is a commercial calomel electrode. Both cells employ magnetic stirring and have appropriate connections to allow introduction of the sample, degassing by helium, and the use of an exhaust-gas spray trap of glass wool to prevent plutonium-containing droplets from being exhausted during degassing. The mercury cell employs a mercury electrode pool; the other cell employs a platinum gauge cylinder. In both cells the ratio of area of electrode to volume of electrolyte is kept large to allow speedy titrations.

The titration medium used in the mercury cell is the citrate buffer (1*M* citric acid plus 0.1*M* aluminum sulfate, neutralized with potassium hydroxide to pH 4.5) used by Booman, Holbrook, and Rein [153] for the titration of uranium. The titration medium in the platinum cell is 1*N* nitric acid or 1*N* hydrochloric acid. When the nitric acid medium is used, or when considerable nitrate is present, a trace of sulfamic acid is added to prevent interference from nitrate ion.

Procedure (Samples Containing Primarily Plutonium). For samples containing primarily plutonium, the titrating medium and sample are added to the cell and deaerated for 5 min with helium. An electrode potential approximately 180 mv below $E^{0\prime}$, the characteristic potential of the Pu(III)–Pu(IV) couple in the electrolyte vs. the calomel reference electrode, is applied, and the prereduction electrolysis is carried out until the current falls to the residual current level. The potential of the working electrode is now changed to a value 180 mv above $E^{0\prime}$, and the oxidation of Pu(III) to Pu(IV) is carried out. Ten minutes is usually sufficient for the reaction. Additional reductions and oxidations can be carried out on the sample if desired. It has been found that the oxidation data for the mercury cell are more precise and accurate than the reduction data; the converse is true for the platinum cell. A blank is found for the titration which is significant for low-level samples and the most accurate work.

The characteristic potential of the plutonium couple is found by making the prereduction and carrying out the oxidation stepwise by increasing the electrode potential by a small increment and noting the number of coulombs required to bring the solution to the set potential. The plot of potential vs. coulombs gives a characteristic sigmoid curve from which the characteristic potential is determined graphically for the point where the concentration of Pu(III) is equal to the concentration of Pu(IV). The potential can also be determined from the modified Nernst equation:

$$E' = E^{0\prime} - \frac{RT}{n\mathfrak{F}} \ln \frac{C_{\mathrm{Pu(III)}}}{C_{\mathrm{Pu(IV)}}} \qquad (15.21)$$

where E' is the observed potential, $C_{\mathrm{Pu(III)}}$ and $C_{\mathrm{Pu(IV)}}$ are the plutonium concentrations, and R, T, n, and $\mathfrak{F}$ are the gas constant, absolute temperature, number of electrons, and the faraday, respectively. In this case the concentration of Pu(IV) is proportional to the number of coulombs passed, and the concentration of Pu(III) is proportional to the total number of coulombs less the number passed at the point in question. Thus $E^{0\prime}$ is the potential of the midpoint of the potential-coulomb curve. The determination of the characteristic potential is required only once for a series of similar samples using the same titration media; also, since the sample can be repeatedly analyzed, no sample is lost because of the need to use it to determine the electrolysis conditions for a precise, accurate determination.

Procedure (Irradiated Uranium Fuel Element Samples). For these samples only the platinum cell can be used since the uranium titrates in the citrate buffer used in the mercury cell. Five milliliters of 0.1*M* hydrochloric acid plus 500 μl of the sample containing 100 to 200 μg per milliliter of plutonium are placed in the cell, and the solution is deaerated 5 min with helium. The solution is prereduced at 580 mv vs. the reference, at which potential the plutonium is reduced to Pu(III) but Fe(III) is not reduced to Fe(II). The solution is now oxidized back to Pu(IV) at 130 mv above $E^{0\prime}$ and reduced at 130 mv below $E^{0\prime}$. The narrower range of potentials used prevents interferences from iron and other materials in the sample. Even so, only a limited amount of iron can be present.

A blank is found. This is due in part to the residual current and is related to the titration medium and, in part, to the slow disproportionation of Pu(IV) to Pu(III) and Pu(VI). The blank is thus partly a

function of plutonium concentration, although in the 1*N* acid solutions the disproportionation rate is very slow. The standard deviation of a single result for titrations of about 10 mg of plutonium is ±0.05 per cent for the mercury cell on a standard plutonium solution made by dissolving pure plutonium metal in hydrochloric acid. For the uranium solutions at 50- to 100-μg level, the standard deviation is ±0.3 per cent.

The plutonium values must be corrected for a small loss of 0.1 per cent caused by migration into the separated compartment and for a loss in the deaeration by spray carrying some of the samples away. A further correction based on the Nernst equation for incompleteness of oxidation or reduction owing to the voltage span is used. This is about 0.2 per cent if an electrical calibration of the instrument is used; it is zero for a chemical calibration.

(3) *Other Determinations.* Stromatt [94, 95] has described the controlled-potential titration of neptunium, which is similar to the titration described above for plutonium. Shults [157] has described the controlled-potential titration of europium which takes advantage of the fact the europium has a valence of (II), in addition to the more customary rare-earth valence of (III). Shults [158] has also described a method for plutonium.

(f) *Automatic Coulometric Titration Techniques.* An advantage of coulometric methods over conventional titration methods lies in the fact that the control of the addition of the reagent in the titration and the measurement of the amount of reagent added are essentially the control and measurement of an electric current. Since precise control and measurement of electric currents are quite advanced compared to the precise control of the addition of small volumes of solution and the measurement of such volumes, automation of coulometric titrations can be accomplished relatively easily. Highly developed and reliable control circuitry and components are available to the designer of automatic coulometric titration equipment.

However, it must be remembered that the addition of the titrant is only one of a number of important operations required during a titration. Fully automatic titration equipment would require provision for automatic sampling, automatic pretreatment of the sample (if needed), automatic control of addition of the titrant, automatic measurement of the amount of titrant added, and probably automatic data reduction (computation) to give a direct read-out of the results of the analysis for recordkeeping or for feedback into the process-control system. With few exceptions, most "automatic titrators" perform only a part of the titration automatically; the control of the titrant addition is often the only automatic feature.

The few fully automatic titration systems based on coulometric techniques are continuous analyzers that continuously sample the material being analyzed. Their output is current, but the principles

involved are those of coulometric techniques rather than amperometric techniques since the total amount, rather than a relatively small portion, of the sample components being analyzed are reacted. Because of the high sensitivities possible with coulometric techniques, the analysis of minor constituents of the sample is a principal application of these analyzers.

Although many direct coulometric titrations require controlled-potential electrolysis procedures, the direct determination of water can be made without resort to special power supplies. Keidell [159, 160] and others [83, 89] have found it feasible to determine small amounts of water in gases and liquids. For gases, a sample of the gas stream is passed over an adsorber composed of P_2O_5 spread in a thin film on a suitable electrical grid. The water is electrolyzed to hydrogen and oxygen; the current flow is proportional to the water content of the film, which, in turn, is generally a direct function of the sample flow rate and the water content of the gas. For liquids the water is stripped from the sample by passing a suitable stream of dry gas through the sample; the gas is then analyzed. Presumably, water contents of solids could be determined by appropriate gas drying of the solid. The integrated current is an accurate measure of the water content if the gas is allowed to stay in contact with the absorbing film until it has been dried to a level below the detection limit. Continuous sampling offers difficulties in maintaining linear adsorption over the entire concentration range.

A commercially available water analyzer, the Beckman Instruments electrolytic hygrometer, has a full-scale range of 0 to 1000 ppm of water vapor, with narrower ranges available down to 0 to 10 ppm.

The Consolidated Instrument Company, Inc., Titrilog is a somewhat more sophisticated analyzer that employs an electrolytically generated reagent, bromine, to titrate sulfur-bearing gases present as contaminants in air or other gases. A metered gas stream is passed through a titration cell in which the contaminants react with free bromine. The bromine is replaced by electrolytic generation as it is used; the current required is thus proportional to the amount of contaminants in the gas stream. Since a number of the contaminants found in air samples will be titrated, the instrument is not highly specific for the determination of a single impurity unless the gas stream is pretreated by passage through scrubbers that selectively remove the interfering contaminants. With proper scrubbing, the analyzer can analyze for single contaminants as well as for total impurities. The control system is designed to maintain a small zero-point concentration of free bromine in the titration-cell electrolyte. As the concentration of bromine is decreased by reaction with the

sample, the control system increases the electrolysis current to restore the zero-point concentration of bromine. This type of control action is called "inverse feedback" since the controlled output increases with decrease in signal and vice versa. Through the use of a high-gain power amplifier, the decrease in bromine concentration from the zero-point value is kept very small over a wide range of electrolysis current. The commercial instrument has been described by Austin, Turner, and Percy;[104] the original instrument has been described by Shaffer, Briglio, and Brockman.[93] The original work was done to develop an analyzer for mustard gas, a war gas that contains a titratable functional group (mercaptan).

An analyzer to determine the free chlorine in water samples has been described by Eckfeldt, Proctor, and Perley.[90] The water sample is metered into a cell containing electrolytically generated ferrous ion. The control system maintains a constant ferrous-ion content by regulating the generation current. The use of water samples requires the continuous addition of iron solutions to maintain the electrolyte concentration in the titration cell; the excess electrolyte is removed continuously. Eckfeldt[91] has also described work on a continuous analyzer in which the electrode potential is maintained constant.

None of the above systems has been reported as being in use for atomic energy material analysis or in atomic energy material processes. However, instruments of this type, either developed separately or modifications of the commercial units, would appear to have useful applications in process control and automatic analysis in the processing of atomic energy materials.

The controlled-potential titrators described by Booman[72] and by Kelley, Jones, and Fisher[73] are essentially automatic titrators as the term is commonly taken. The control of the current is a function of the state of completion of the electrolysis, which is the basic condition for automatic control of the addition of titrant. Hence controlled-potential methods are inherently automatic in so far as the titration step is concerned if the power supply is controlled automatically. This latter condition applies for all the latest methods reported.

The use of constant current in automatic titrators (limited to the automatic addition of reagent) is well established. The key to this type titration is the trigger circuit that shuts off the titration at the end point.

Automatic coulometric titrators using constant current have been described by Bett, Nock, and Morris,[68] Carson,[119, 121, 161, 162] Gerhardt, Lawrence, and Parsons,[79] Kelley, Stelzner, Laing, and Fisher,[144] Leisey,[80] Lingane and coworkers,[44-46] Malmstadt and Roberts,[125] Parsons et al.,[69] Stelzner,[163] and Wise, Gillis, and Reynolds.[98]

15–2.3 Voltammetry

(a) *General Considerations.* Voltammetric methods of analysis are based on the use of electrode reaction rates as measured by the current-voltage relations shown by the electrode during the electrolysis. The controlling reaction rates are the rates of mass transfer of the reacting species by diffusion and convection. Voltammetry includes polarography, in which the electrolysis current at constant applied electrode potential is the measure of the substance being determined, and chronometry, in which the time required for the electrode potential to change by a characteristic amount during an electrolysis at constant current is the measure of the substance. Closely related to voltammetric methods is amperometry, in which the current at constant electrode potential is used as an indicator in titration procedures. Polarographic and amperometric methods are differentiated from conductivity methods by the type of current control used. In polarographic and amperometric methods, the current is limited by the rates of diffusion and convection. In conductometric methods, the current is limited by the rate of electromigration. Voltammetric methods eliminate, or at least minimize, the effect of electromigration of ions.

To date no reactor-material analyses employing chronometry, a relatively recently developed analytical technique, have been reported. A basic understanding of the techniques involved can be obtained from Delahay [7, 164] and Gierst.[165]

Amperometry is discussed with indicator methods. The measurement of the potential of a pair of electrodes through which is passing a constant current is also used as an indicator method and is classified as a potentiometric system by most authors, although it could be classified logically as a voltammetric system.

(b) *Polarography.* (1) *General Discussion.* If a well-stirred solution containing material that can react at an electrode, say ferric ion, is electrolyzed between two large inert electrodes, the current-voltage curve will have the form shown in Fig. 15.12. If the potential applied to the cell is less than the decomposition voltage (V_D), then the current remains small. At higher potentials the current is given by Ohm's law:

$$i = \frac{V - V_D}{r}$$

where r is the resistance of the cell. When rapid stirring and a large-area electrode are used, the current is limited only by the resistance of the solution. The concentration of ferric ions at the surface of the electrode remains equal to that in the body of the solution, and the electrode is not concentration polarized.

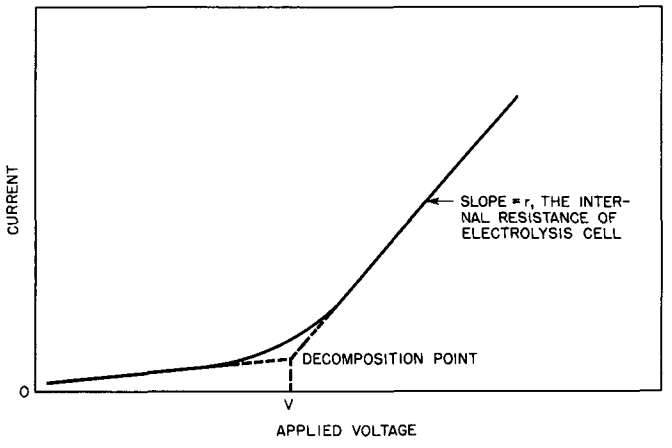


Fig. 15.12—General electrolysis current–voltage curve.

If the working electrode is very small and if the solution is unstirred, the voltage-current curve will have the form shown in Fig. 15.13. Increasing the applied potential decreases the concentration of ferric ion at the working electrode until this becomes zero, i.e., all the ferric ion reaching the electrode reacts. A further increase in applied potential can no longer increase the current, which is now limited by the rate at which ferric ions from the body of the solution reach the electrode surface. The current remains constant with increasing applied potential until a potential is reached which allows another electrode reaction to take place. The current in the constant-current region is known as the limiting current, and the electrode is said to be concentration polarized for the electrode reaction taking place.

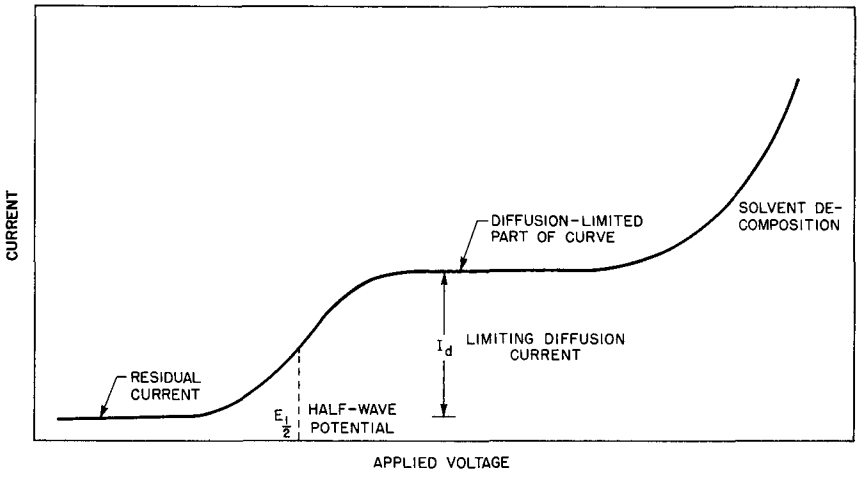


Fig. 15.13—Microelectrode current–voltage electrolysis curve.

If other substances that can react at the electrode are present, a continued increase in applied potential will result in additional electrode reactions. These may also give a limiting current; however, the continued increase in applied potential will eventually reach a value where the solvent will react or one of the electrodes will undergo dissolution. The solvent reactions and electrode-dissolution reactions are not subject to limiting current conditions; their onset limits the potential range that can be used in analysis.

In aqueous solutions the applied potential can seldom exceed about ± 3 volts with respect to the hydrogen electrode before oxygen or hydrogen evolution occurs or the electrode itself undergoes reaction. The pH of the electrolyte, the electrode material, and the condition of the surface of the electrode all affect the potential at which water decomposition will occur.

The limiting current is made up of three components: the migration current, the residual current, and the diffusion current. The migration current is made negligible by adding a large excess of a supporting electrolyte containing ions that do not readily undergo reaction at the electrode. Since the number of these ions is many times larger than the number of ions that can undergo reaction, they carry almost 100 per cent of the migration current, making the migration current due to the reacting ions negligible. The use of a supporting electrolyte is necessary in voltammetric analysis since the migration-current contribution is very sensitive to changes in total ionic concentration unless this is large.

The residual current is the current flowing at the applied potential in the absence of the desired electrode reaction. It is due in part to reactions occurring at lower potentials, which are due to other materials present in the electrolyte. The residual current also can include a component due to the charging of a condenser; this condenser is formed at the electrode-solution interface and gives a charging current when the dropping-mercury electrode is used.

The diffusion current is the portion of the limiting current of greatest interest since it is, for most substances, proportional to the concentration of the substance in solution. This current includes any contribution made by convective mass transfer. This contribution must be held to a constant fraction of the total if the relation between diffusion current and concentration is to remain linear. The widespread use of the dropping-mercury electrode is, in part, due to the ease with which the convection contribution can be kept relatively constant by operating in an unstirred solution compared with operating in a solution that requires stirring.

The diffusion current is dependent upon a number of factors, such as the area of the electrode, the concentration of the reacting material,

the diffusion coefficient of the reacting material, and the number of electrons involved in the cell reaction. For analysis purposes polarographic methods usually hold all but the concentration factor constant.

A datum of interest in polarography is the half-wave potential, which is the applied potential, corrected for solution-resistance drop, for which the electrolysis current, corrected for the residual current, is one-half the limiting diffusion current. For a given material and supporting electrolyte, this potential usually is a constant and can be used to identify the material. If the electrode reaction is thermodynamically reversible, this potential can easily be related to the standard potential of the reaction, and considerable thermodynamic information on materials can be deduced from data on the effects of variations of the composition of the solution on the half-wave potential.

The science and art of polarography have been described in detail by Kolthoff and Lingane [17] and by Meites.[21] A recent review by Heyrovsky [15] is also of general interest. These references give details of the techniques used in polarography, and the first gives the details of a number of applications. The place of polarography is well established in both analytical and physical chemistry, and a large amount of work each year is reported.

(2) *Apparatus.* A number of laboratory supply houses carry complete lines of polarographic equipment and accessories, which can meet most of the needs of routine analysis and many of the needs of the research worker. The equipment needed for many applications is simple and inexpensive; the investigator should not feel that the more elaborate types of equipment described in the current literature are needed to produce useful results.

Descriptions of a number of commercially available instruments and a number of instruments developed by workers in the field have been given in the literature.[15, 17, 21] A few critical points regarding the techniques and apparatus require some comment here, but the details will not be discussed.

The basic polarographic cell consists of a polarizable microelectrode, a vessel to hold the electrolyte, and a nonpolarizable counter electrode. To this basic design are added, depending in large part upon the individual investigator's tastes and preferences, extra features intended to make the manipulations easier or to aid in obtaining more precise results. The cell is usually thermostatted to eliminate the changes in diffusion currents caused by temperature fluctuations. A third electrode, usually a reference type such as a calomel, is used to make accurate determinations of the potential of the electrolysis electrodes. Provision for removing dissolved oxygen is usually required. This is conveniently done by sparging the electrolyte with a

stream of an oxygen-free inert gas such as hydrogen or nitrogen. The effectiveness of the sparge gas is increased by using gas-dispersing devices such as porous disks or cylinders of glass or ceramic. The tank gases usually have sufficiently low oxygen content to permit their use without further purifications, although most workers use purification trains to assure the sparge-gas quality. The vanadous sulfate scrubbing train of Meites and Meites [166] is convenient and effective. In this train, which can also be used with chromous ion in place of vanadous ion, the spent reductant solution is continually regenerated by contacting with amalgamated zinc and acid. Traces of hydrogen will be added to the gas stream when this type of train is used. The classic method using a tube filled with copper turnings heated to 450 to 500°C is highly effective although somewhat inconvenient to use intermittently. Possibly the most convenient devices for removing oxygen are units (Englehard Mfg. Co.) which catalyze the reaction between oxygen and hydrogen at room temperature. For gases other than hydrogen, hydrogen in small amounts is added to the gas before it is passed through the unit.

A number of types of microelectrodes can be used in polarography, but only two, the dropping-mercury electrode and the rotating microelectrode (usually platinum), are used extensively in analysis. The stationary microelectrode is not used extensively because it is very sensitive to vibration, which causes changes in the convection contribution, and because the current flow depends upon the length of time the electrolysis has been carried out as well as on the concentration of the reacting substance. The rotating microelectrode is not as reproducible as the dropping-mercury electrode and is used chiefly in indicator systems rather than in direct-measurement systems.

The dropping-mercury electrode uses a glass capillary tube of very fine bore. A length of 2 to 3 in. of this tube is connected to the end of a tube containing a column of mercury, and the free end is dipped into the electrolyte solution. The mercury flows through the capillary at a rate dependent upon the diameter of the bore, the pressure of mercury, and the interfacial tension between the mercury and the electrolyte solution. This rate is adjusted by proper selection of pressure and bore size so that the mercury forms a series of small drops of highly reproducible size. The reproducibility of the size is important, but even more important is the reproducibility of the electrode surface, which is new for each drop and hence is not changed by previous deposition of material from solution.

The advantages of the dropping-mercury electrode are:

1. Because of the high overvoltage for hydrogen-ion reduction on clean mercury surfaces, it is possible to reduce many substances that would theoretically be reduced only at applied potentials greater than

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those required for hydrogen ion or water. As a result, the determination of substances more difficult to reduce than hydrogen ion and water can be carried out.

2. Since mercury can serve as a solvent for many metals, it is possible to determine substances such as the alkali metals compounds in which the free metal formed upon reduction reacts with the solvent unless it is removed from contact with the solvent.

3. This solvent action of mercury also aids in maintaining the high overvoltage for reduction of hydrogen ion and water which would be lost if active metals such as zinc or nickel were deposited on the electrode surface and remained there.

4. The reproducibility of the surface characteristics of each drop is very high compared to the reproducibility of the surface of solid electrodes.

5. The absence of stirring minimizes the effects of changes in convection rates.

These advantages explain why the dropping-mercury electrode is the usual preference in polarographic methods.

The disadvantages of this electrode are:

1. Mercury undergoes dissolution at relatively low oxidation potentials in the presence of many common anions such as the halides.

2. The overvoltage for oxidation of hydroxyl ion on mercury surfaces is not as high as it is on smooth platinum.

3. The periodic fluctuation in current from the dropping-mercury electrode introduces a component in the residual current, the condenser or charging current, which arises from the charging of the condenser formed by the electrode double layer. This charge, which is lost when the drop falls, can be a significant fraction of the total limiting current.

4. The periodic fluctuation of the current is not at a constant frequency over the applied potential ranges or from electrode to electrode. This, plus the low frequency, makes the use of simple a-c measurement equipment unsuitable. The use of more complex a-c equipment or filtering circuits to allow use of d-c measuring equipment is subject to the change in apparent value of the current with the particular equipment used.

A recommended electrode arrangement is shown in Fig. 15.14. The length and bore size of the electrode capillary is selected such that a moderate pressure (about 10 psi, or 50 cm Hg) gives a drop weighing 6 to 10 mg every 3 to 6 sec. Tubing of the proper characteristics is commercially available as "marine barometer tubing" from the Corning Glass Works and from a number of laboratory supply houses that furnish polarographic equipment. Two to three inches of the tubing is customarily used; the bore should be uniform over most of this

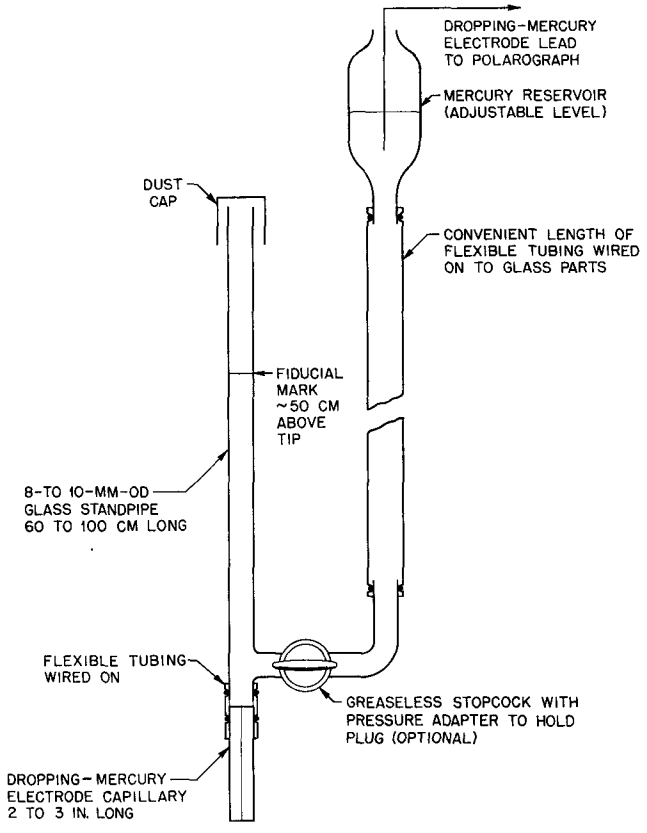


Fig. 15.14—Dropping-mercury electrode arrangement.

length, and the end dipping into the solution should be cut square to the tube. Every precaution should be taken to keep the bore of the capillary clean and free of foreign liquid and solid matter. The tip should be kept free of greasy deposits such as are deposited from fingerprints. All tubing, etc., which comes into contact with the mercury should be thoroughly cleaned of dirt and any materials such as sulfur that can react with mercury. Tygon tubing and pure gum rubber steamed for several hours with oil-free steam are quite suitable for the tubing portions of the arrangement. Polyethylene and other hard, difficultly flexible tubings, although satisfactory from the chemical-resistance standpoint, are difficult to fasten securely to glassware. If the optional stopcock is used, a greaseless type should be employed. The storage of the electrode can be in air if the tip is protected against fumes and dusts; alternatively, clean distilled water is satisfactory. Mercury can be saved if the stopcock shown is closed during storage periods; the mercury in the standpipe will flow until the pressure head

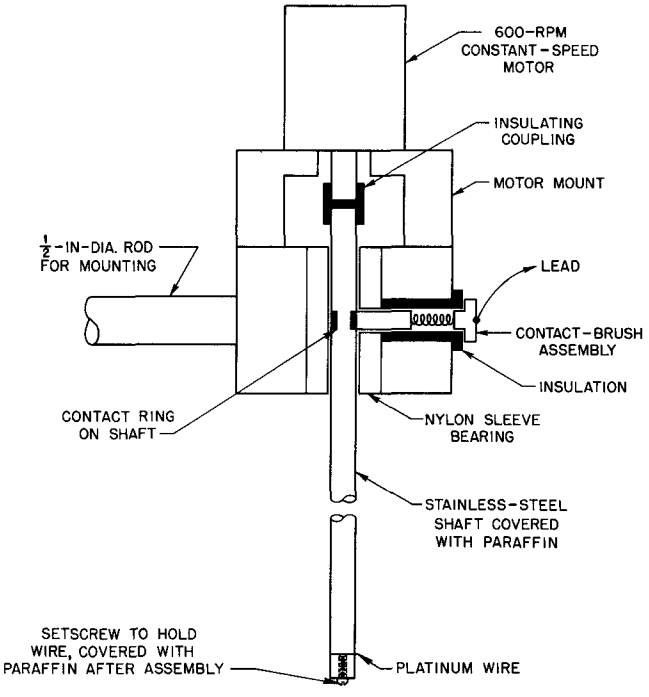


Fig. 15.15—Rotating microelectrode assembly.

no longer can overcome the interfacial tension of the mercury drop and water. This procedure keeps the capillary filled with mercury at all times and prevents the entry of water into the capillary.

A simple rotating electrode is shown in Fig. 15.15. The platinum or other metal electrode is a piece of wire secured in place by the setscrew at the bottom of the shaft. The lower part of the assembly is coated with paraffin wax or another low-melting, relatively hard wax to provide insulation. The tip of the electrode is carefully scraped clean. Connection to the shaft is via a drop of mercury at the top of the shaft with a wire dipping into it from the power source. Rotation is by small air or electric motors; some means of determining the speed is needed since the observed diffusion current is quite sensitive to the speed; alternatively, a synchronous motor can be used. The lack of surface renewal during electrolysis makes the rotating electrode difficult to reproduce from run to run; the electrode behavior is critically dependent upon the previous treatment of the electrode.

A number of counter electrodes have been proposed for use in polarographic cells. The major requirements are that the electrode have a constant potential with respect to the solution during electrolysis and that the electrode material not materially affect the composition

of the electrolyte by reacting with the ions present except as planned. An electrode area of the order of 1 sq. in. is required to prevent polarization effects; if a salt bridge is used to isolate the counter electrode, the bridge must have low electrical resistance to prevent a large IR drop in the electrolysis circuit. The use of a salt bridge is not required when an internal pool of mercury or a large-area silver electrode is used as the counter electrode since either of these electrodes will operate at constant potential if the supporting electrolyte contains the proper concentration of some anion that forms slightly soluble salts. This formation of a saturated solution of the salt stabilizes the electrode potential by maintaining a constant concentration of the mercury or silver ion in solution; the quantity of salt required at the start of an electrolysis can usually be formed from the metal and the dissolved oxygen in the electrolyte. The use of these internal mercury or silver electrodes is limited to solutions in which a stable potential for the electrode is obtained. These are generally solutions that do not contain components that readily attack mercury or silver or that do not form soluble complexes of silver or mercury with small instability constants. Complexes with large instability complexes (e.g., cyanide) are permissible since the potential of the electrode is stabilized over a large fluctuation in the concentration of silver or mercury ions.

Electrode materials other than silver or mercury find only limited use in polarographic analysis; however, in special cases one of these electrodes might be very convenient for routine analysis.

The electrical circuits used in polarography serve two basic functions: to supply the voltage that is impressed on the polarized electrode and counter-electrode pair and to measure the current flowing in the electrolysis cell which results from the impressed voltage. Conventional circuits employ a source of direct current, such as a battery, to supply a bridge-type voltage divider from which a selected potential can be taken to serve as the polarizing voltage. The current is measured either by meters using D'Arsonval movements in the microampere and submicrosampere ranges or by electronic amplifiers in recorders. In recent years interest has been shown in the development of more elaborate circuits that provide for the taking of the derivative of the current-voltage curve normally obtained by conventional circuit arrangements for the use of alternating currents of various wave shapes impressed upon the d-c polarization voltage, for the use of controlled potentials at the polarized electrodes, for the use of controlled currents in the electrolysis, for the use of oscilloscopes for displaying the current-voltage curves, and for the provision of automatic compensation of the residual and condenser currents. A number of these new circuits are employed in the instru-

ments developed by Kelly and coworkers [156-170] which have been used for the analysis of uranium solutions.

Alkire et al.[171] have described an automatic polarographic analyzer for uranium in solvent-extraction process waste streams; Bertram et al.[172] have described an automatic polarographic analyzer for process streams containing large concentrations of uranium. Michelson and Koyama [173] have discussed the requirements of automatic analyzers for uranium in process waste streams.

(3) *Determinations.* Polarographic techniques are suitable for the determination of most oxidizable or reducible ions in the general range of 10^{-3} to 10^{-5} M concentrations. In many cases only a few other ions will interfere in the polarographic determination of any particular ion because of the inherent selectivity of the electrode process, and in many cases interferences from an ion can be eliminated by use of the proper supporting electrolyte and pretreatment procedure without resort to difficult separation procedures. For example, traces of nitrite ion interfere with the polarographic determination of uranyl ion; this interference can be removed readily by sparging the solution with a stream of oxygen-free gas containing methyl alcohol vapor, which reacts to form methyl nitrite, which then evaporates from the solution. The methyl alcohol left in solution does not interfere with the determination of uranium. Since the solution must be sparged to remove oxygen, this offers a simple and convenient way to remove the nitrite interference. Ferric ion interferes with the polarographic determination of uranyl ion. The interference can be removed in acid electrolytes by the addition of hydrazine or other reagents that reduce the ferric ion but not uranyl ion; the excess hydrazine or ferrous ion does not interfere with the subsequent analysis. In another example, the half-wave potential of the U(VI) to U(V) reduction can be shifted away from the half-wave potential of the Fe(III) to Fe(II) reduction through the use of an aluminum sulfate-citrate buffer solution. The choice of the proper supporting electrolyte and pretreatment comprises a large part of the work required to develop a polarographic analysis of an ion.

Precisions of the analyses vary from 30 to 50 per cent (uncommon) down through 3 to 6 per cent (common) to 0.1 per cent or less (uncommon). The precision depends largely on the care taken in sampling and pretreatment and on the nature of the sample itself. Although the precisions obtained are generally better with solutions that are free of interfering ions, many samples of surprising complexity can be analyzed without difficulty with precisions in the few per cent range.

Uranium. A great number of procedures for determining uranium by polarographic techniques have been described. Uranium gives a

well-defined wave for the reduction of uranyl ion to U(V) in acid solutions (see Refs. 171, 172, and 174 to 187). The limiting diffusion currents are usually proportional to the uranium concentration in the range 10^{-3} to 10^{-5} *M*; the half-wave potentials remain constant in most media over the concentration range. The range of half-wave potential varies between 0.0 to −0.5 volt vs. the saturated calomel electrode for solutions in which strong complexing of the uranium is absent. Special techniques have been used to extend the range of useful concentrations; thus the use of a square-wave a-c polarograph [188] permits determination of uranium at the 10^{-8} *M* level; the catalysis of the reduction of nitrate ion [189] has been used to extend the useful range with more conventional equipment to 10^{-7} *M*. Only a limited amount of work has been done in alkaline systems.[179, 190]

Polarographic techniques are widely used for the analysis of ores and natural waters for uranium (see Refs. 88, 188, 189, and 191 to 201). Generally, if precise results are to be obtained from these samples, some separation of the uranium from impurities is required, as well as concentration of the uranium of the sample to a small volume. The use of complexing reagents in the determination of uranium polarographically has been studied with varying degrees of success (see Refs. 188, 190, 200, and 202 to 208).

In summary, the polarographic methods for the determination of uranium are useful for a wide variety of samples. Many materials can be analyzed quickly and easily with polarographic techniques with adequate precisions and accuracies to fit most needs. These methods should be the first considered for samples in which uranium in trace to relatively large amounts is to be determined. The original papers should be consulted for the details of the procedures and results obtained.

Plutonium. The polarographic determination of plutonium has not been extensively studied since radiochemical methods of great sensitivity and simplicity are available for the determination of plutonium in small concentrations and titration procedures have been developed to cover the higher concentration ranges for which the radiochemical methods are not suited. Fomin [209] has described the polarographic determination of plutonium by the reduction of Pu(IV) to Pu(III) in oxalate media. Since the electrode behavior of the Pu(IV)–Pu(III) couple is known to be reversible, there is every reason to feel that practical polarographic methods of analysis can be developed if a need arises.

Other Elements. The usefulness of polarographic techniques in the analysis of low concentrations has led to many applications in the analysis of trace constituents in a sample. Norton and co-

workers [210-212] have described polarographic methods for determining iron (III), nickel, manganese, copper, and chromium in uranyl sulfate solutions. Bane [213] has described the use of polarographic techniques for the determination of lead, cadmium, and zinc in beryllium metal. In addition to the above determinations, the voluminous literature on polarography describes many other trace analyses, some of which may be applicable to problems arising from the analysis of reactor materials. Although not directly concerned with reactor materials, the analysis of cooling and boiler water used in reactors calls for the determination of trace amounts of various substances; a common deleterious impurity is oxygen, for which Carritt and Kaniwisher [214] have described a polarographic procedure.

15–2.4 Direct Conductometric Methods

The usefulness of direct conductometric methods is limited to a large degree by the inherent lack of selectivity of conductance measurements. This lack of selectivity arises from the nature of electrolytic conductivity; all the ions in a solution help carry the current in proportion to their transport number in the solution. It follows that the direct methods are limited largely to the determination of concentrations of ionic solutes in solutions containing only one solute or to the determination of the ionic solutes present as impurities in samples in which such ionic impurities are significant. An example of the latter is the very common use of conductivity measurements to determine the purity of water following distillation or deionization. This is the only use of direct conductivity methods employed to any extent in reactor-material processing.

Strictly speaking, it is desirable that no net electrode reaction occur during the measurements, hence the use of alternating currents in making conductivity measurements is widespread, in spite of the very real difficulties associated with a-c measurements.

15–2.5 Dielectric-constant Measurement Methods

The dielectric-constant type of electrometric method is useful for the determination of the composition of binary mixtures of two materials that have widely separated dielectric constants. The measurement of the dielectric constant is usually based on the change in the capacity of an air type condenser, i.e., a condenser whose normal dielectric is air. Tuned tank circuits of high Q are used; these are circuits in which capacitative (or inductive) reactance is many times larger than ohmic resistance, a condition that makes the tuning of the circuit very sharp. The circuit goes into and out of resonance at a given frequency with a small change in the capacity of the test or tuning condensers. A calibrated tuning condenser is used to compensate for the change in the test condenser; the change can be correlated with

the composition of the sample through the use of an appropriate calibration curve.

A typical method is the one described by Kelley et al.[215] for the analysis of tributyl phosphate (TBP) in a kerosene solvent. These solutions are widely used in reactor-material processes for the separation of uranium and plutonium from acid solutions. The instrument used was one developed at the Oak Ridge National Laboratory for this determination; the circuitry consists of a crystal-controlled oscillator operating at 1000 kc loosely coupled with the high-Q tank circuit, which is tunable with a pair of condensers. The measuring cell is a copper box surrounding a 50-mmf air condenser; this measuring cell condenser is connected to the instrument by a coaxial cable. One tuning condenser, of 200 mmf, is used to zero the instrument against the standard or reference material (usually the solvent), the other condenser, of 100 mmf, is used to measure the change of capacitance caused by the sample. A vacuum-tube voltmeter is used to detect the resonance condition.

In use the reference material is placed in the cell, and the 100-mmf measuring condenser set to its "zero" position. The instrument is now tuned to resonance by the 200-mmf condenser; resonance is indicated by a maximum deflection of the voltmeter. The sample is now placed in the cell, and the instrument is returned to resonance by the 100-mmf measuring condenser. The difference in dial readings of this condenser serves as the measure of the change of capacity in the cell; the operator enters this difference into the calibration curve and reads off the composition of the sample. The dial units are arbitrary.

For the TBP determination, the kerosene solvent used in making the sample solutions is used as the reference. Since different grades of kerosene with varying dielectric constants are on the market, it is necessary to use the same kerosene in calibrating and zeroing the instrument as is used in the sample. Each kerosene must be calibrated separately. Calibration is performed by mixing known amounts of the materials together and determining the dial settings to establish the calibration curve. If no interaction between solvent and solute occurs, the calibration curve is essentially a straight line, provided the measuring condenser is linear.

Because of its high dielectric constant, water present as an impurity in the sample can give large errors. The water content of organic samples must be stabilized before accurate results can be obtained. Usually, it is difficult to remove the water; hence the procedure is to saturate the sample with water under prescribed conditions. For the TBP-kerosene samples, this is done by contacting the sample with an equal volume of water three times. This procedure

removes any traces of acid or salts that may be in the sample. The solutions are clarified by passing them through filter paper to remove suspended water droplets before the measurements are made. Obviously, the samples used in the calibration must be treated in the same manner.

The agreement of the analysis of TBP-kerosene mixtures was within ± 0.2 per cent of the value obtained by an alternate method based on the determination of phosphate after destruction of the organic matter; this latter method is considered the reference method for the determination of TBP in organic solvents.

Some additional notes on procedure can be given. For TBP mixtures the temperature effect is small, but this may not always be the case. Other polar materials, such as other phosphorus esters or amines, can be determined through the use of the correct calibration curve. Amines may give trouble in the water-washing step if care is not taken to prevent the removal of amine salts by the water. In amine samples the washing could be made with dilute caustic, followed by filtration of the sample through anhydrous sodium sulfate to remove the water and traces of caustic. Filtration through sodium sulfate is recommended for those systems that show marked water solubility since the sensitivity of the method for the solute is enhanced by removal of the water from the solvent system.

15–3 INDIRECT METHODS

Indirect methods of electroanalysis can be divided into two classes: (1) those methods in which the electrode phenomena are used in such a manner that the electric current serves as the equivalent of a chemical reagent in the analysis and (2) those methods in which the electrode phenomena are used to detect changes caused by the addition of reagents to the sample solution. Methods in the first class are called reagent methods in this discussion; methods in the second class are called indicator methods. A well-known example of a reagent method is the precipitation of copper metal by electrodeposition on a platinum electrode in the analysis of copper alloys. Although the electrodeposition of copper was described [216] as early as 1801, the use of the procedure in analysis [217] was not made until after 1864. An equally well-known indicator method, the determination of the oxidation-reduction potential of a solution using a platinum electrode, was apparently first described by Bancroft [218] in 1892. The platinum electrode is still in common use for the same purpose.

15–3.1 Reagent Methods

Ashley [63, 219] and DeFord [59–62] have reviewed the literature on electroanalytical methods including those in which electricity is used

as a reagent. A large part of the modern work is being done on controlled-potential electrolysis. The pioneer work using controlled electrode electrolysis as a reagent was done by Haber [220] in 1898; he described methods for the preparation of various organic materials. Sand [221] and Fischer [222] were the early pioneers in the application of controlled-potential electrolysis to analysis problems. These early methods were highly inconvenient since the operator had to control the potential manually during the electrolysis. Interest in this type of electrolysis lagged until the development of the modern electronically controlled equipment. A large number of equipment designs are recorded in the literature; in addition, a number of commercial devices are available for routine and research work.

A typical application of controlled-potential electrolysis in analysis is given in the work of Alfonsi [223] on his system for the analysis of copper alloys. The application of controlled-potential electrolysis as a reagent method to reactor-material analyses is limited; most such electrolyses are used in coulometric determinations. Since uranium can be reduced to U(IV) or oxidized to U(VI) in acid solutions without difficulty, controlled-potential systems are not needed for making valence adjustments. Rulfs, De, and Elving [224] and Sutton [225] have reported the use of electrolysis for the adjustment of the valence of uranium prior to its determination by titration. In other methods [226-228] electrolysis of uranium solutions prior to determination of the uranium is used to remove impurities which are deposited on a mercury cathode, such as iron, copper, and nickel, and which otherwise would interfere in the determination.

Ko [229, 230] has described an electroyltic precipitation of heavy metals as the hydrous oxides on counting planchets. The precipitates are ignited to stable oxides prior to use in an alpha-particle energy analysis. The energy analysis requires a relatively large sample to produce good counting statistics for short counting times; the sample must be deposited in a thin, uniform film so that the alpha-energy spectrum of the material is not degraded by self-absorption of the alpha particles by the sample. Ko's procedure can be used for thorium, uranium, plutonium, neptunium, americium, and curium; it was developed by an extension of the earlier work of Miller and Brouns.[231] Plutonium solutions are preoxidized by an electrolytic pretreatment.[232] The hydrous oxides are deposited by the reaction of the heavy-metal ions with electrolytically generated hydroxl ions; the planchet is used as an anode, and hydroxyl ion formed in the electrode reaction.

$$2H_2O + 2e \rightarrow 2OH^- + H_2$$

precipitates the heavy metal as an adherent film. The localized concentration of hydroxyl ion serves to direct the precipitation to the

electrode rather than throughout the bulk of the solution. The anode is depolarized during the electrolysis by oxidation of formate ion

$$HCOO^- \rightarrow CO_2 + H^+ + 2e$$

Note that one equivalent of hydrogen ion is generated for every two equivalents of hydroxyl ion, leaving a net gain of one equivalent of hydroxyl ion for the passage of 2 faradays of electricity through the solution. The slow gain in hydroxyl ion aids in making the deposit adherent and uniform. Quantitative deposition of the heavy metal is readily obtained.

15–3.2 Indicator Methods

The use of electrometric indicator methods in analysis is well established. The methods can be divided into three general classes: potentiometric systems, in which the potential of the indicator electrodes is measured; amperometric systems, in which the current flowing through the electrode is measured; and conductometric systems, in which the conductance of the titration solution is measured. Each of the systems has particular merits; however, the potentiometric systems find the largest number of applications in routine analysis. Historically, these are also the oldest systems; dating from Bancroft's work.[233]

The major advantages cited for electrometric indicator systems compared to colorimetric indicator systems are: potentially greater precision and sensitivity of many electrometric indicators, particularly in dilute solutions; availability of electrometric indicator systems for a number of titrations for which no suitable colorimetric indicator has been found; and adaptability to automation techniques. On the other hand, it should be noted that colorimetric indicator systems have as

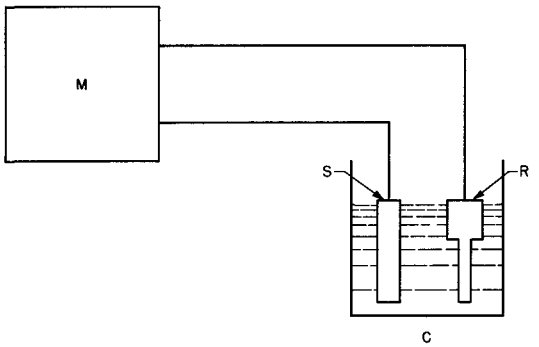


Fig. 15.16—Zero-current potentiometric indicator circuit.

M. pH meter
S. Sensitive electrode
R. Reference electrode
C. Titration vessel

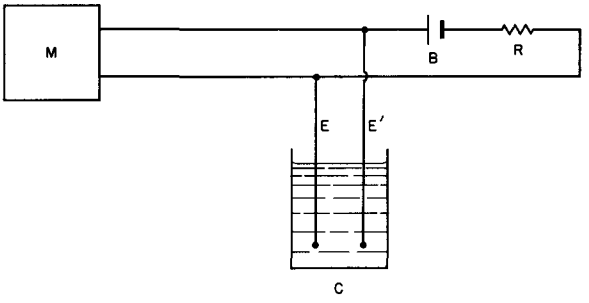


Fig. 15.17—Constant-current potentiometric indicator system.

C. Titration cell
E, E′. Micro platinum electrodes
M. pH meter
B. Battery } Constant-current
R. Ballast resistor } source

good precision and sensitivity as electrometric indicators for many titrations and that the colorimetric titrations are, in general, performed faster with less operator fatigue when such indicators can be used. Also, most of the most commonly used titrants have suitable colorimetric indicators systems, and several do not have satisfactory electrometric counterparts. The investigator should include studies on both types of indicator systems when developing a method for the analysis of a sample.

The popularity of potentiometric indicator systems stems largely from the availability of the modern electronic pH meter. Commercial instruments of good quality and moderate costs are available. These meters have removed a large part of the drudgery associated with the original methods of making the measurements. Although the pH meter has been designed primarily for potentiometric systems, it is equally useful in the other two classes of indicator systems. Figures 15.16 to 15.19 give examples of circuits that can be used to incorporate a pH meter in potentiometric, conductometric, and amperometric indicator systems. All these circuits take advantage of the fact that a pH meter is simply a voltmeter with a very high input impedance; in use negligible current is drawn from the input-circuit element by the meter. Müller [38] has reviewed in part a number of these unconventional uses of the pH meter, including a unique polarographic application by Adams, Reilly, and Furman.[234]

A large number of automatic titrators have been made available commercially. Several of these employ burets that are filled, zeroed, and read after the titration by the operator; the automatic equipment merely performs the titration to an end point. Other units employ syringe type delivery units, which are filled and zeroed automatically, the volume of titrant delivered being read from a counter or other indicator attached to the syringe delivery drive. Both

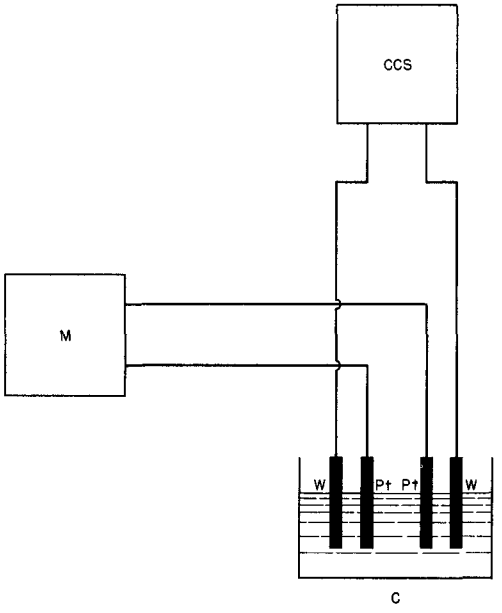


Fig. 15.18—D-c conductometric indicator system.

C. Titration cell
CCS. Constant-current source
M. pH meter
Pt. Platinum probe electrodes
W. Tungsten working electrodes

electrometric and colorimetric units are available. It should be noted that it is possible, with suitable auxiliary equipment, to convert any automatic titrator that uses a pH meter or its equivalent as the input to the control section for use with other electrometric types of end points and for use with colorimetric indicator systems.

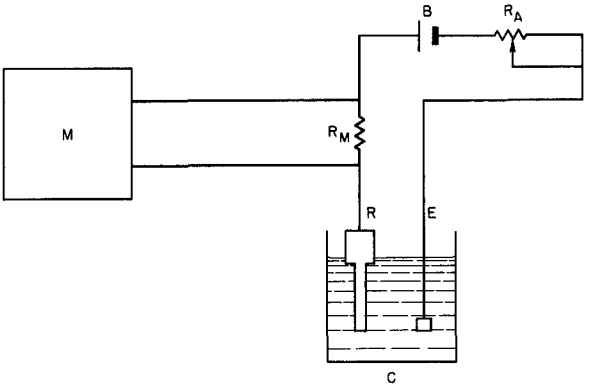


Fig. 15.19—pH meter amperometric indicator system.

M. pH meter
C. Titration cell
R_A. Adjustable resistor
R_M. Measuring resistor
R. Counter electrode
E. Polarized electrode

In addition to the automatic coulometric titrators, the work of Malmstadt,[235, 236] Decker and Susano,[237] Waterbury,[238, 239] and Wise [240] in the development and the use of automatic titrators for reactor-material analyses should be mentioned.

(a) *Potentiometric Systems.* Potentiometric systems have been discussed in detail by Bates,[1] Charlot,[3] Cooke,[5] Ewing,[9] Kolthoff and Laitenin [16] and Kolthoff and Furman; [18] the recent literature has been reviewed by Furman,[58, 241] and Reilley.[242-244] Table 15.3 is a limited list of reactor-material and related analyses employing the various potentiometric indicator systems.

The two types of potentiometric indicator systems are the classical zero-current type and the newer constant-current type. The zero-current types employ a sensitive electrode and a reference electrode. The sensitive electrodes used include pH-sensitive electrodes, such as the glass electrode, which are used in acid-base titrations; redox potential-sensitive electrodes, such as gold or platinum, which are used in redox titrations; and single-ion-sensitive electrodes, such as the silver electrode, which are used in the precipitation or complex-ion formation type titration.

The change in potential of the sensitive electrode with the addition of titrant is highly nonlinear and ideally follows an equation of the form:

$$E = E^0 + \frac{RT}{n\mathfrak{F}} \ln f(C, C_T, \text{Keq}) \qquad (15.22)$$

where C = the measure of the titrant added at any stage of the titration

C_T = the measure of the titrant for which the equivalents of titrant added are the same as the equivalents of titrated materials in the sample; i.e., this is the amount of titrant required to react stoichiometrically with the sample taken

Keq = the equilibrium constant for the titration reaction

E = the potential of the indicator electrodes at any stage of the titration; it is the potential corresponding to the addition of C measures of titrant

E^0 = the potential of the indicator system for which $f(C, C_T, \text{Keq})$ is unity

n, $\mathfrak{F}$, R, and T = constants

The function $f(C, C_T, \text{Keq})$ is obtained by setting up the product quotient, Q, in terms of the three variables. The quantity Q is the product of the concentrations of the products formed in the titration reaction divided by the product of the concentrations of the reactants and is similar in form to the equilibrium constant for the reaction. For any stage of the titration, the actual concentrations must be com-

Table 15.3—POTENTIOMETRIC INDICATOR SYSTEMS IN REACTOR-MATERIAL ANALYSES

Material	Titration reaction	Titrant	Indicator type	Indicator electrodes	References
Uranium	U(IV) to U(VI)	$K_2Cr_2O_7$	Zero current	Pt vs. calomel	245–247
	U(IV) to V(VI)	Ce(IV)	Zero current	Pt vs. calomel	248–250
	U(IV) to U(VI)	Fe(III)	Zero current	Pt vs. calomel	251, 252
	U(IV) to U(VI)	$Fe(CN)_6^{+3}$	Zero current	Pt vs. calomel	253
	U(IV) to U(VI)	$K_2Cr_2O_7$	Zero current	Pt vs. W	254
	U(IV) to U(VI)	Ce(IV)	Zero current	Au vs. Pt[Ce(IV)]	255
	U(VI) to U_4O_{13}	NaOH	Zero current	Glass vs. calomel	102, 156
	U(VI) to U(IV)	$CrCl_2$	Zero current	Pt vs. calomel	257–259
	U(IV) to U(VI)	Br_2	Constant current	Pt–Pt	28, 110
Plutonium	Pu(III) to Pu(IV)	Ce(IV)	Zero current	Pt vs. calomel	79, 113, 239, 240, 260
	Pu(III) to Pu(IV)	$K_2Cr_2O_7$	Constant current	Au–Au	261
	Pu(VI) to Pu(IV)	Fe(II)	Zero current	Pt vs. calomel	238
			Constant current	Pt vs. Pt	121
	Pu(VI) to $PuO_2(IO_3)_2$	IO_3^-	Zero current	Glass vs. calomel	262
Thorium	Th(IV) to $Th(MoO_4)_2$	MoO_4^{-2}	Zero current	Mo vs. calomel	263

puted or estimated using the equilibrium constant and sample size; a general expression is not useful for illustration here.

The plot of C vs. E gives a sigmoid curve. The datum of interest from the analysis standpoint is the value of C_T; this is obtained from the experimental data in a number of ways. The potential for which C is equal to C_T is known as the end-point potential; hence a determination of this potential is used to determine C_T. The end-point potential occurs at the inflection point of the C vs. E curve if the system is behaving properly (if it does not, then the titration cannot be performed). This inflection point can be found by inspection of the C vs. E plot; it is taken as the center of the steepest part of the curve. For well-defined titration curves with a very steep slope at the end point, this procedure is satisfactory since a relatively large error in determining the end-point potential will give only a small error in the determination for C_T. For less favorable cases in which the curve is not symmetrical or does not have a steep slope at the end point, plotting the derivative curve of the titration gives a less subjective and perhaps a more precise determination of the end point. The derivative curve is obtained by plotting the quotient $\Delta E/\Delta C$ vs. C; where ΔE is the change in potential of the indicator electrode system which occurs with the addition of the increment of titrant ΔC. The derivative curve has a cusp form; the apex of the cusp occurs at C_T. Experimentally, the precision of this method of obtaining the end point is dependent upon the size of ΔC at the end point; the smaller the increment, the more precisely the cusp apex can be located.

A derivative titration procedure can be used. In this type titration, two similar sensitive electrodes are used, and the potential difference between them is measured. The titration equipment is arranged such that one electrode is immersed in solution containing the last increment of titrant added and the other electrode is immersed in a small volume of solution that does not have the last increment of titrant mixed with it. A plot of the potentials vs. the total titrant added gives a derivative curve; often, however, plotting is not needed since the increment giving the largest change in potential contains the end point. For small increments, the volume of titrant up to and including this increment is taken as C_T without serious error. During the titration the solutions are mixed after the potentials have been read and prior to the addition of the next increment of titrant.

Plotting the titration or derivative curves need only be done in the vicinity of the end point. In some very favorable cases in which the titration curves have very steep slopes at the end point with considerable change in potential, plotting the titration curve is not necessary since the increment giving the largest change in potential can be

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taken as the end point, provided that a truly small increment ($\Delta C/C_T \approx 0$) is used.

The second derivative of the titration curve shows a discontinuity at the end point; the sign abruptly changes from + to − or vice versa. Malmstadt [235, 236] has devised an automatic titration control circuit based on this behavior. With this circuit no knowledge of the potential of the end point is needed.

Plotting the titration or derivative curve in less favorable cases can be avoided by titrating in small, equal increments across the end point. The end point can be then located analytically through the use of the following interpolation equation:

$$C_T = C_B + \frac{A - B}{2A - (B + C)} D \tag{15.23}$$

where C_T = the titrant measure at the end point
A = the maximum change in potential per increment of titrant
B = the change in potential for the increment added just before A
C = the change in potential for the increment added just after A
D = the measure of titrant per increment
C_B = the total measure of titrant up to the end of increment B

This equation can be used with derivative type indicator systems.

The mechanism by which gold and platinum electrodes develop their response to redox potentials appears to involve the formation of oxides [264] on the surface of the electrode, although the mechanism is far from being settled. Platinum electrodes often show poor response to strong reducing agents such as chromous ion since platinum catalyzes the reduction of water or hydrogen ion by the reducing agent:

$$Cr^{+2} + H^+ \rightarrow Cr^{+3} + \tfrac{1}{2}H_2$$

When this occurs, the platinum electrode potential will be partly due to the redox potential of the solution and partly due to the hydrogen-evolution reaction. In practice, the observed potentials will be too positive (oxidizing). This trouble can be avoided through the use of a mercury pool as the sensitive electrode since the evolution of hydrogen on this metal has a high overvoltage.

The use of single-ion-sensitive electrodes in analysis is limited to titrants for which an ion-electrode material pair exists. Silver is probably the most used electrode metal of this type since silver ion is extensively used as a titrant for substances that form insoluble silver compounds. The precipitation titration of thorium with

molybdate [263] has been followed using a potentiometric indicator system composed of a molybdenum-metal-sensitive electrode and calomel reference electrode.

The calomel electrode is the most commonly used reference electrode in potentiometric indicator systems. The use of a silver wire as a reference electrode is convenient if the solution contains a moderate amount of an anion such as chloride that forms an insoluble silver salt and if neither the titrant nor the titrated material reacts appreciably with free silver or silver ion. For these cases no salt bridge is required; this is a distinct advantage in routine titration methods.

So-called "bimetallic systems" can be devised for potentiometric indicator systems. The most common is the tungsten electrode vs. a platinum electrode. The tungsten electrode shows only a limited redox response and serves as the reference electrode. Voss and Greene [254] describe a precise potentiometric titration of uranium using this bimetallic system.

Another type of bimetallic system employs two sensitive electrodes, one of which is kept immersed in the titrant during the titration; this is connected electrically via the titrant solution in the buret tip to the titration solution. Since the composition of the titrant does not change, the potential of the electrode is constant, and the electrode serves in all respects as a reference electrode. The advantage of this technique lies in the decrease in the number of components that must be placed in contact with the titration solution; specifically it eliminates the the reference-electrode salt bridge. The automatic titration of uranium described by Cooper [255] employs the platinum plunger of the titrant syringe as the reference electrode.

The use of polarized electrodes in potentiometric indicator systems was first described by Willard and Fenwick.[265] Figure 15.17 shows the basic circuit used in this type of electrometric indicator. A pair of small electrodes, usually of platinum or gold, is used in most cases, although a reference electrode can be used in place of one of the metal electrodes. Reilly, Cooke, and Furman [148] have described a system in which the electrodes were polarized with a small constant current; they called the system the "derivative polarographic system." Considerable work has been done since on this method, which, however, has been renamed "constant-current potentiometric indicator system" in a more systematic classification of electrometric indicator systems. The constant current used usually is derived from a B battery–resistor combination as show in Fig. 15.17.

Figures 15.20 to 15.23 show the titration curves obtained in typical titrations employing the constant-current potentiometric indicator system. Figure 15.20 shows the titration curve obtained for the ti-

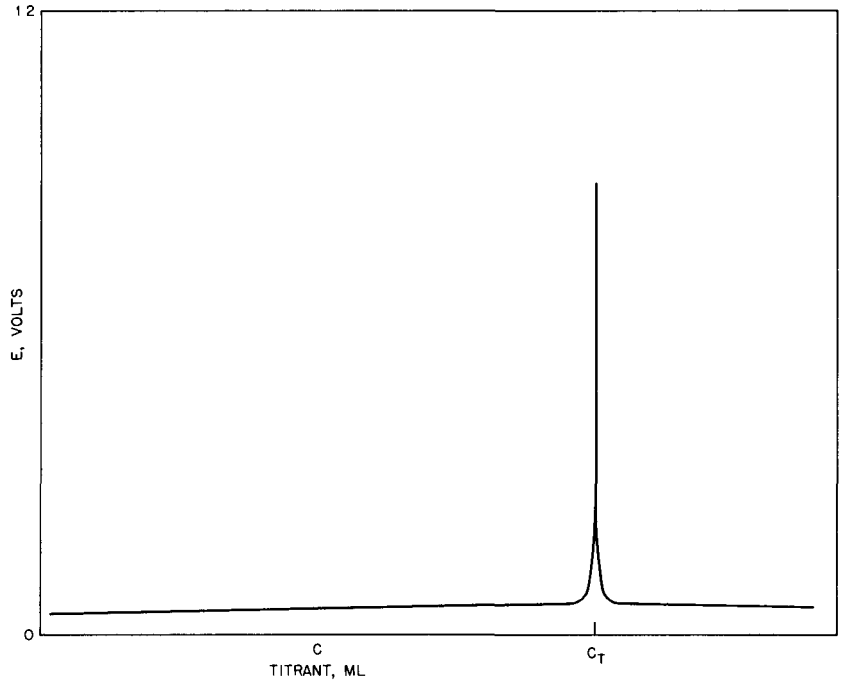


Fig. 15.20—Titration curve (constant-current potentiometric indicator system) for titration of Fe(III) with Cr(II). Titrant and sample couple are both reversible.

tration of Fe(III) with Cr(II). These ions are parts of the reversible redox couples Fe(II)–Fe(III) and Cr(II)–Cr(III), and the curve is typical of titrations in which both the titrant and the titrated couples are reversible. As can be seen, the curve has a form that resembles closely the derivative of the titration curve using a zero-current potentiometric indicator; it was this form that led to the name "derivative polarographic system." The peak of the curve is usually very sharp requiring only a small increase in total titrant added to go from the beginning of the peak to the end of the peak. This indicator system is somewhat inconvenient to use in routine manual titrations where titrant and the titrated substance give this type of response since it is very easy to overrun the end point and miss the peak completely.

Figure 15.21 gives the titration curve obtained in the titration of U(IV) to UO_2^{++} with Ce(IV). The uranium couple is nonreversible, but the Ce(IV)–Ce(III) couple is reversible. Again the end point is very sharp; the knuckle of the curve where the potential drops is not observed except in dilute solutions with small increments of dilute titrant. Figure 15.22 shows the titration curve obtained in titrating

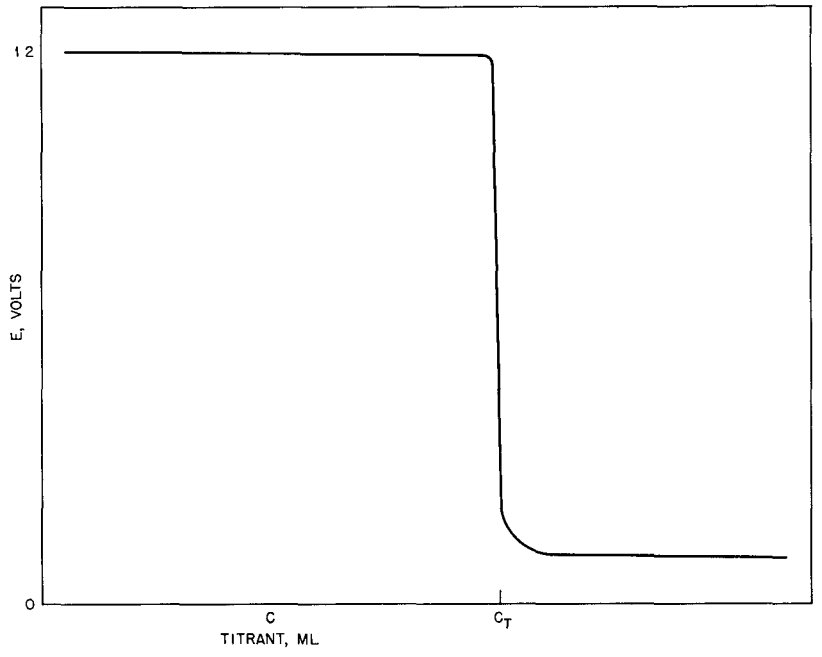


Fig. 15.21—Titration curve (constant-current potentiometric indicator system) for titration of U(IV) to UO_2^{+2} with Ce(IV). Titrant couple is reversible; sample couple is nonreversible.

Fe(II) with $KMnO_4$; here the manganese couple is not reversible. The curve in Fig. 15.23 is one that is obtained in the titration of PuO_2^{+2} to Pu(IV) with Fe(II); the plutonium couple is partially reversible, and a marked rise in indicator potential just before the end point is reached is observed. Dichromate behaves in a similar manner.

Bertin,[266] Bishop,[267] Duyckaerts,[268] and Gaugin[269, 270] have reported additional theoretical studies and practical applications of the indicator system. The very high sensitivity and compactness of the electrode system has made this system very useful in microtitrations, particularly for titrations in which the sample must be diluted extensively before titration.

(b) *Amperometric Systems.* These systems have been discussed in detail by Kolthoff and Lingane[17] and Delahay.[7] Laitinen,[271-273] Reilley,[24] and Stock[274] have reviewed the recent work employing these systems.

Amperometric systems employ electrodes that operate in the diffusion-limited region of the current-voltage curve in much the same manner as polarographic systems. Since the sensitivity of these electrodes with respect to concentration is very high (10^{-3} to $10^{-5}M$),

amperometric systems are widely used in the titration of dilute solutions and in the titration of small amounts of materials. Also they are widely used in precipitation or complexing type titrations since the conventional potentiometric systems often do not have as high a sensitivity as that obtainable from amperometric systems. The primary requisite for an amperometric indicator system is the presence of a material in the titrating solution that reacts at the electrode at some impressed voltage. The titrated material or the titrant can furnish the electrode-active material; in some cases a pilot ion can be added which will give a well-defined current during the titration until an excess of reagent is added, whereupon it is titrated.

The dropping-mercury electrode can be used in amperometric titrations, but it is not as useful as the rotating electrodes or stationary electrodes in stirred solutions. Since the solution must be stirred for each addition of titrant, the use of stationary electrodes is common; some care must be taken to regulate the rate of stirring to obtain reliable indicator behavior. Stationary-electrode systems are widely used in coulometry (see Refs. 49, 50, 75, 85, 103, 106, 108, 109, and 111), particularly in titration with electrolytically generated halogens for which amperometric systems have high sensitivity.

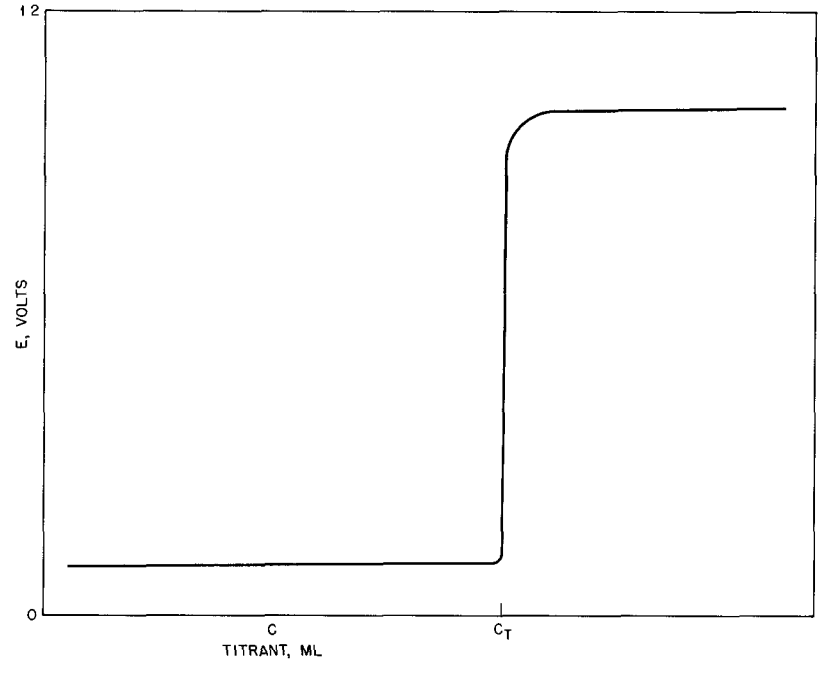


Fig. 15.22—Titration curve (constant-current potentiometric indicator system) for titration of Fe(III) with $KMnO_4$. Titrant couple is nonreversible; sample couple is reversible.

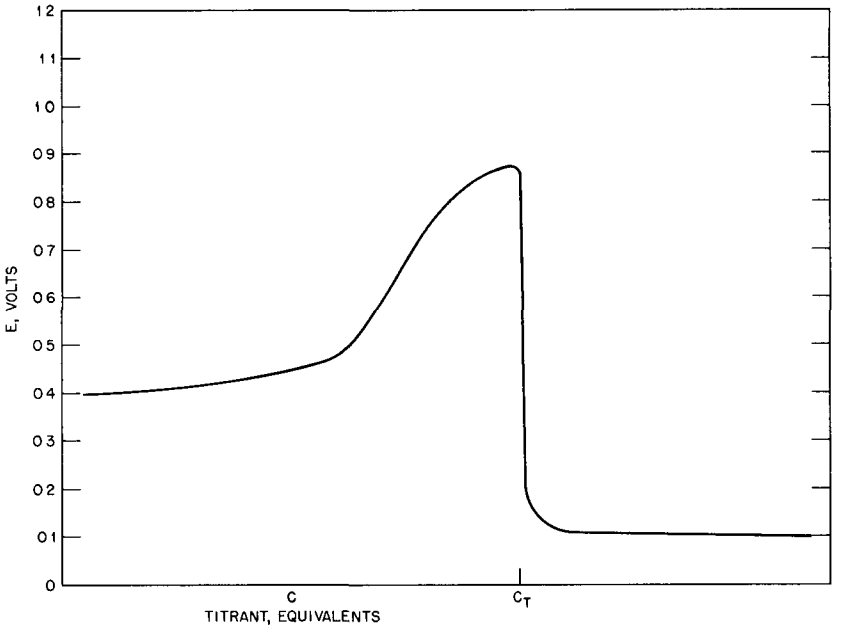


Fig. 15.23—Titration curve (constant-current potentiometric indicator system) for titration of PuO_2^{+2} to Pu(IV) with Fe(II).

Cooke, Reilley, and Furman [147] have described a very sensitive technique for obtaining an end point in low-level coulometric titrations of 0.01 to 0.001 μg of Fe(II) per milliliter. The platinum indicator electrodes are polarized at a potential corresponding to the zero-current potentiometric end point observed for the system in more concentrated systems. The solution is pretitrated by electrolytic generation of reagent until the indicator current is zero. The sample is added, and the electrolysis is continued until the indicator current is again zero. As long as the potential at which zero current is obtained is not changed going from the pretitration end point to the titration end point, considerable variation in the potential setting can be tolerated. This indicator system was used by Furman, Reilley, and Cooke [56] in the coulometric titration of uranium.

A uranium titration that utilizes amperometric end point has been described by Kolthoff and Johnson,[275] who employed *m*-nitrophenylarsonic acid as the titrant. This reagent is reduced to the hydroxylamino and amino derivatives at the polarized electrode. Uranium, thorium, and zirconium can be determined. Morachevskii and Tserkovnitskaya [276] and Smit and Klinkhamer [277] have also described the amperometric titration of uranium.

The determination of thorium by titration with ethylenediaminetetraacetate (EDTA) has been reported by Flaschka and Barakat.[278]

With this system a lead–EDTA complex is added to the sample and the lead ion released is titrated with a standard EDTA solution. The polarographic wave of the lead is followed for the indicator. Thorium was also titrated amperometrically with molybdate by Gordon and Stine.[279]

Kolthoff and Sambucetti [280] have described a rotating aluminum electrode that offers promise in the amperometric titration of fluoride or aluminum. Olsen and Elving [281] have described an amperometric titration of zirconium in the presence of fluoride ion.

The so-called "dead-stop indicator system" widely used in the titration of iodine with thiosulfate or in Karl Fischer titrations has been renamed the "biamperometric indicator system." [282] It will be interesting to see whether or not this name supplants the original name.

(c) *Conductometric Systems.* Conductometric indicator systems are employed in titrations for which a large change in ionic conductance of the solution will occur. The general form of the titration curves are well known and require no comment here.

Several types of conductivity equipment can be used. The most commonly used is the a-c bridge with either an audio or an electronic null indicator. A number of commercial instruments of various degrees of complexity are available; precise bridges are not necessary for titrations.

Taylor and Furman [283] have described a d-c conductivity circuit that deserves more attention in analysis. This circuit employs a pH meter for the detection element; it is shown in Fig. 15.18. A constant current is passed through the working electrodes (tungsten in the reference), and the IR drop between two platinum probe electrodes is measured. Since essentially no current is drawn from the probes by the pH meter, the electric field between the working electrodes remains unaltered when the measurement is made. Also, since a constant current is used, any changes in the IR drop across the probe electrodes is caused by a change only in R. A wide variation in initial conductivity can be compensated for when the measurements are made by changing I. The reading of IR can be plotted just as well as R since I is constant. A titration curve can be obtained in much less time than it would take to manually balance a bridge. Carson [102] has determined the free nitric acid concentration of uranyl nitrate solutions automatically using this type of indicator system. Ten to 25 μl of sample was added to 100 ml of water; and a slight excess of fluoride ion over the amount needed to complex the uranyl ion was added. The conductometric indicator current was adjusted to give a small initial deflection on a recording pH meter, and the titration was made by adding standard 0.1N sodium hydroxide solution

from a Gilmont microburet operated by a small synchronous motor. The recorder-chart-drive and buret-drive motors were switched simultaneously; the amount of reagent added was thus proportional to the length of chart. A smooth peak rounded at the apex but with straight sides was obtained, and the extrapolation to determine the end point could be carried out without difficulty. The large volume of solution in the titration vessel makes correction of the volume for the addition of the titrant unnecessary. Precisions of ±2 to 3 per cent for 10 μl samples containing 2*M* uranyl nitrate and 0.2*M* free acid were obtained. However, the amount of fluoride ion added in excess is highly critical, and a knowledge of the uranium content of the sample is required.

Recently, high-frequency systems have been developed for conductometric systems. These have been discussed by Reilley in Delahay's book.[7] A particular advantage of these systems is that they do not have electrodes immersed in the electrolytic solution and thus obviate a number of difficulties involved in the use of immersed electrodes. The over-all response of these electrodeless systems is similar to conventional conductometric systems in that the phenomena of interest occur in regard to the solution as a whole rather than at an electrode interface. Both the conductance of the solution and the dielectric constant of the solution contribute to the response; it is possible to measure the contributions separately and thus emphasize the one response over the other. For general titration work the mixed response is usually satisfactory, and a simple instrument can be used. Commercial instruments are available. Indicator applications are similar to the more conventional conductometric systems. Uranium has been determined with a high-frequency conductometric indicator system by Hara and West [284] using trisodium ethylenediaminetetraacetate.

Trisodium citrate has been used by Bobtelsky and Simchen [285] for titration of uranium and other metals using a conventional conductometric indicator system. Kubota and Surak [286] have determined fluoride conductometrically following distillation of the fluoride from interferences. Lanthanum ion is used as the titrant.

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CHAPTER 16

X–RAY SPECTROSCOPY

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Over the past decade the use of X rays for analytical purposes has grown tremendously. In the field of nuclear materials, X-ray methods are being used to determine the major constituents in ores, feeds, concentrates, scrap materials, and fuel-element alloys and to determine trace elements in pure materials. These methods have the advantages of speed and ease of sample preparation, frequently with no separations needed. For some samples the methods can be considered nondestructive. Solid, powder, or liquid samples can be handled.

X-ray methods, like those of optical emission spectroscopy, depend on standards from which calibration calculations can be made. Since the methods are susceptible to interelement and matrix effects, the standards must be made to conform to the approximate composition of the material to be analyzed. The availablity of standards may be a limiting factor in the use of X-ray methods in those cases in which only a small number of samples of a given type are to be analyzed.

The theory of the production of X rays and the instrumentation required for their use in analysis is well covered in recent literature and will not be considered in detail here.[1-3] Practical aspects have been discussed to aid the analyst in the choice of instrumental components and sample preparation.[4-8] Continued improvements are being made in commercially available instruments in the aspects of tube excitation voltages, voltage stability, target materials, analyzing crystals, detection equipment, and vacuum spectrometers.

The applications of X rays to the analysis of nuclear materials to be discussed in this chapter are limited to absorption and emission methods, and these have not been covered exhaustively. Only a brief mention is made of the use of radioisotopes as sources. Quantitative applications of X-ray diffraction techniques are relatively unimportant, and the current applications of microprobe analysis belong more in the category of metallurgy.

16–1 ABSORPTION ANALYSIS

16–1.1 Absorption of Polychromatic X Rays

Chemical analysis by absorption of polychromatic X rays is limited to samples in which the composition remains fairly constant except for the element being determined and in which a significant amount

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of the total absorption is caused by the element in question. These limitations have not prevented its routine use in the analysis of solutions of uranium and plutonium.[9, 10]

The absorption of X rays is governed by the exponential equation

$$I_x = I_0 e^{-(\mu/\rho)(\rho x)} \tag{16.1}$$

where I_0 = intensity of the initial beam
I_x = intensity after passage through x centimeters of sample
e = natural base of logarithms
ρ = density of the absorbing layer
μ/ρ = mass-absorption coefficient

The coefficient μ/ρ is a function of the atomic number and of the wave length as shown by

$$\frac{\mu}{\rho} = \frac{CZ^4\lambda^3 N}{A}$$

where C = constant over a range between characteristic absorption edges
Z = atomic number
λ = wave length
N = Avogadro's number
A = the atomic weight

It is evident that elements of high atomic number, such as uranium and plutonium, absorb more strongly than the light elements in the matrix solution; thus they are ideal subjects for this type of absorption analysis.

(a) *Solutions.* The extent to which a solution of uranium or plutonium absorbs a beam of polychromatic X rays is a function of the following variables:[9] (1) the path length of the X-ray beam through the solution, which is controlled by the dimensions of the sample cell; (2) the energy spectrum of the X-ray beam, which is partly governed by the voltage applied to the X-ray tube; (3) the concentration of the uranium or plutonium in the solution; and (4) the atomic numbers and concentration of the other elements comprising the solution, including the solvent. Data have been reported giving the effect of different elements and tube voltages on the absorption.[9, 11]

In analyses in which an X-ray photometer is used,[9] relative measurements are made. X-ray absorption is measured by attenuating a comparator beam of X rays to reduce its intensity until it is equal to the intensity of an identical beam passing through the sample solu-

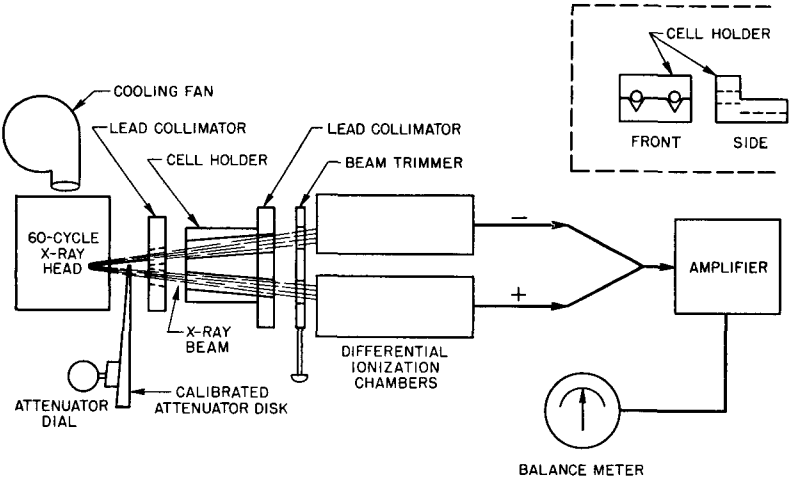


Fig. 16.1—Top view of ionization-chamber X-ray photometer.

tion. Reduction of the intensity of the comparator beam is accomplished in part by means of a reference solution and in part by means of aluminum blocks and a movable wedge-shaped aluminum disk. The absorption is reported in mils of aluminum plus the reference solution. The photometer is calibrated with solutions of known concentrations of solute in the same composition of solvent as the unknown. Since the photometer measures the total absorption of the sample, solvent, solute, and cell, the solution must contain enough uranium or plutonium to give an appreciable absorption relative to that due to the other components. The photometer cannot distinguish between two kinds of atoms present in the same solution; therefore the method is limited to the analysis of solutions containing only one element of relatively high atomic number compared to the other elements present.

Two types of X-ray photometers are used at the Hanford Atomic Products Operation, General Electric Company. These are the fluorescent-screen type and the ionization-chamber type. The fluorescent-screen type is pictured and described in Chap. 2, in Fig. 2.23. A schematic drawing of the ionization-chamber type is given in Fig. 16.1 and is described below.

X rays issue from the X-ray head in a conical beam that is split by a collimator into two distinct and slightly divergent beams. A disk is placed before the collimator so that one of the divergent beams is attenuated. After the X rays have passed the second collimator, they travel through the beam trimmer and into the ionization chamber. Here their electromagnetic radiation is converted into electric current. In the ionization chambers the polarity of the collection voltage is

such that a "difference" current is produced whose magnitude and direction is dependent on the relative intensities of the two beams entering the ion chambers. This difference current is fed to the amplifier and from there to the balance meter. Relative-absorption measurements are made in the same manner as described for the fluorescent-screen type photometer. The X-ray head and tube control systems are also identical.

Four methods of measuring and converting X-ray absorption to chemical concentrations are: (1) aluminum reference method, which is the simplest but least precise; (2) differential method in which the absorption of the sample is matched to a great extent by a standard reference solution of similar composition with only a small thickness of aluminum required to complete the balance; (3) direct comparison method, which is the most accurate but is only valid when the concentrations of the sample and standard are nearly identical; and (4) "criss-cross" method, which is the one most widely used. In the criss-cross method, an aluminum tare is permanently placed in one of the beams not cut by the attenuator disk to permit the measurement of solutions having smaller concentrations than the solution in the "standard" beam. One instrument reading is made with the sample in one of the X-ray beams and the reference solution in the other. A second reading is made after switching the position of the two cells. Solute concentrations can be determined from the appropriate calibration curves. One curve has a positive slope; the other has a negative slope. These characteristics give rise to the name "criss cross." This method minimizes instrumental errors. Another calibration method has been described [12] in which aluminum plates are used instead of solutions. This method cuts the time needed for calibration each day to 15 min.

Cells with path lengths of 12 and 30 mm have been used. This represents a compromise between conditions for optimum precision and practical control laboratory considerations. For one instrument the optimum sample concentration with a 12-mm path was 121 g of uranium per liter and with a 30-mm path it was 41 g of uranium per liter. At these concentrations the overall precision at 12 mm was ± 0.052 per cent, and at 30 mm it was 0.06 per cent.

Because of the interference that is caused by the extraneous materials present in many solutions, it is sometimes necessary to make a chemical separation preceding absorption measurements. Tributyl phosphate (TBP) extractions are widely used. A typical procedure is given for the analysis of plutonium.

Procedure. Determination of Plutonium in Nitrate Solution.[13] Exactly 5 ml of 30 vol.% TBP in high-purity kerosene is pipetted with a 25-sec drainage time into a 10-ml serum bottle. Then a 200-μl sample

in 1.5*N* HNO_3 (approximate concentration of 50 g of plutonium per liter) is pipetted into the bottle, and 1.3 to 1.5 ml of 65 wt.% aluminum nitrate nonahydrate (ANN), which includes pipet rinsings is added. The solution is stirred on a magnetic stirrer for 3 min. The organic layer is transferred to a 12-mm absorption cell. The bridge circuit of the instrument is balanced, the X-ray tube is turned on (primary voltage, 80 volts; amperage, 3 ma), and the two beams are balanced. The standard reference cell containing approximately 15.6 g of uranium per liter dissolved in 30 per cent, TBP solution is placed in one beam and the sample is placed in the other beam, and the beams are balanced. The two cells are exchanged and another reading is made.

Calibration curves are prepared by measuring plutonium standard solutions by the criss-cross method. The extraction procedure is followed with the standards exactly as above. With the calibration curves or the factors thus obtained, the concentration of the unknown sample is calculated.

(b) *Solid Samples.* Solid samples can also be measured on a photometer. The method has been applied in the determination of fuel-element core loadings. Plutonium-bearing fuel plates are fabricated by sandwiching a core of plutonium–aluminum alloy between two layers of aluminum giving approximate overall dimensions of 24 by 2.5 by 0.06 in. The rolling process results in variations in core thickness all along the plate. The ends of the core may taper out or may thicken to exceed the nominal thickness by 20 to 30 per cent. The plutonium content per unit area should not vary by more than 15 per cent from the nominal to be acceptable. Obviously this measurement must be nondestructive. An X-ray photometer [14] was designed to accommodate these fuel plates and to measure the thickness of cores containing 11 and 14 wt.% plutonium–aluminum alloy in the range of 0.010 to 0.030 in. with a sensitivity of +0.0002 in.

A similar method in which the attenuation of gamma-rays from an Am^{241} source is used has been used to measure uranium content in uranium–aluminum alloys.[15] This method has been described in Chap. 5, Sec. 5–1.1(a)(3).

16–1.2 Monochromatic X-ray or Absorption-edge Analysis

Absorption of monochromatic X rays is far less sensitive to impurity elements than is absorption of polychromatic X rays.[16] The method is dependent on the fact that the absorption coefficient for each element changes abruptly at fixed wave lengths that correspond to the so-called "absorption edges" of the given element. The difference in absorption measured at two different wave lengths on either side of an absorption edge is proportional to the concentration of the particular element. In practice, since I_0, the initial intensity, is difficult to determine, measurements are taken with counting equipment with water in the cell at the same two wave lengths. For any one set of

conditions with the same cell and with measurements at the same wave length settings, constants can be calculated. The equation for determining the unknown concentration is

$$C_u = K_1 \log \left(\frac{I_w \lambda_1}{I_s \lambda_1}\right) - K_2 \log \left(\frac{I_w \lambda_2}{I_s \lambda_2}\right) \tag{16.2}$$

where K_1 and K_2 = constants for a given cell length at selected wave lengths λ_1 and λ_2

C_u = concentration of the unknown

I_w and I_s = the intensitives through the cell containing water and sample solution, respectively.

When fixed count measurements[17] are made, the equation becomes

$$C_u = K_1 \log \frac{t_{s1}}{t_{w1}} - K_2 \log \frac{t_{s2}}{t_{w2}} \tag{16.3}$$

where t_1 and t_2 are the times required at λ_1 and λ_2. The constants, K_1 and K_2, are determined by measuring $I_{\lambda 1}$ and $I_{\lambda 2}$ on solutions of two known concentrations, one of which contains impurities, and solving simultaneous equations. All counting times must be corrected for the resolving time of the counting equipment. Elements that seriously interfere would be those with absorption edges very close to the element in question. For example, yttrium and polonium interfere with the uranium L_{III} edge occurring at 0.72 Å.

The measurements taken at λ_1 and λ_2 do not give the intensities that would ideally occur precisely at either side of the absorption edge because of practical instrumental considerations. Because of the wide slit widths needed to obtain sufficient X-ray intensity, the absorption

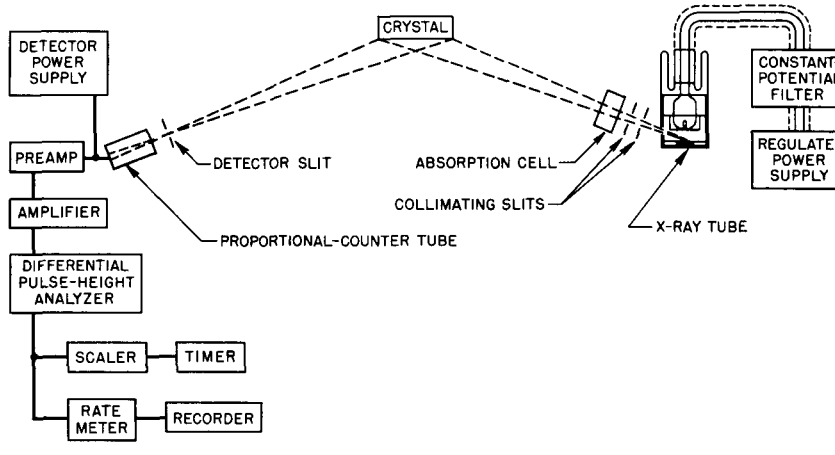


Fig. 16.2—X-ray absorption equipment. [From H. W. Dunn, *Anal. Chem.*, 34: 119 (1962).]

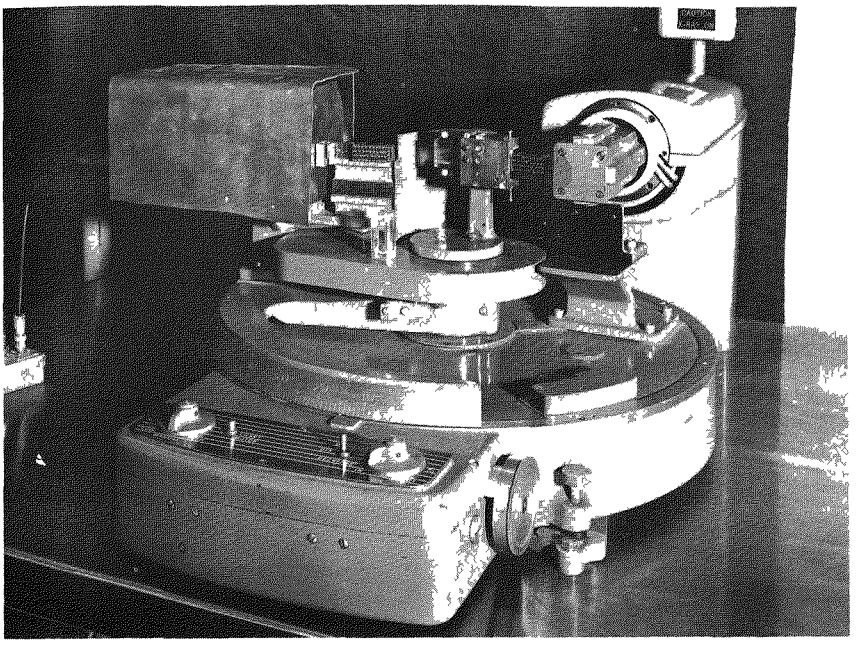


Fig. 16.3—A GE–XRD–3 unit adapted for absorption work at Oak Ridge National Laboratory.

curve obtained by a rate-meter recording does not show the absorption edge to be as sharp as it theoretically is. A method of calculation has been given that extrapolates the measurements at λ_1 and λ_2 back to the long and short wave-length sides of the edge.[18] Calculations made from data taken with zirconium solutions, with accumulated counts of 10 million on either side of the absorption edge, gave a limit of error of 1 per cent (90 per cent confidence) at the concentration level of 1 mg/ml and 5 per cent for concentrations from 0.2 to 1.0 mg/ml.

(a) *Excitation With Primary Beam.* A spectrometer arrangement is necessary to make the required measurements at different wave lengths. The regular X-ray diffraction units with a goniometer and radiation-detection equipment can be easily adapted for use by inserting an analyzing crystal in the usual position of the sample and inserting a sample-cell holder with collimating slits in the path of the X ray between the X-ray tube and the analyzing crystal or between the crystal and the counting unit. A constant-potential filter should be incorporated in the power supply to the X-ray tube. Second-order radiation must be eliminated by keeping the voltage on the tube below the excitation potential of the second-order radiation or, possibly, by differential discrimination.[18] A suitable voltage and current were found to be about 27 kv and 8 ma.[19] A diagram [18] showing the essen-

tial parts is given in Fig. 16.2. Figure 16.3 shows a GE–XRD–3 unit adapted for absorption work at Oak Ridge National Laboratory.[17] Shown mounted right to left are the X-ray tube, the beam slit, sample-cell holder, crystal, Soller slit, detecting slit, and the counter-tube housing. The goniometer protractor scale and the micrometer dial can be seen below. One of the Lucite sample cells is shown on the instrument just below the Soller slit. The X-ray tube is a tungsten-target line-focus tube. The analyzing crystal is a piece of rock salt 1½ by 1⅛ by 1¼ in. cut along the 1 0 0 plane. A scintillation counter is shown, but a proportional counter also can be used.[18] The sample cells are made from solid blocks of Lucite in two sizes, approximately ¾ by ¾ by 2 in. and 1¼ by ¾ by 2 in. The sides of the cell in the beam path are end-milled to 1/16 in. thickness to reduce the attenuation of the X-ray beam by the cell. The cell holder consists of a rectangular brass frame bolted to the beam-slit bracket of the goniometer; the holder has open-end windows and is adjustable for both cell sizes. Thumb screws through the side of the cell holder reproducibly position the cells in the beam.[19] A 0.1° beam slit is used for the small cell, and a 0.3° slit is used for the large cell.

(1) *Determination of Uranium.* Analyses have been made for uranium in aqueous solution,[19] in dibutyl carbitol,[20] and in the presence of yttrium [21] using the L_{II} absorption edge instead of the L_{III} edge. Solutions have been successfully analyzed which range in concentration from 0.5 to 5 mg/ml in the large (1¼ by ¾ by 2 in.) cell and from 2 to 20 mg/ml in the small (¾ by ¾ by 2 in.) cell.[17] For the uranium analysis in the absence of interfering elements such as yttrium, the angles employed for the analysis at the L_{III} edge with a rock-salt analyzing crystal are 14.40° and 14.85°. The procedure given below is used when yttrium, which interferes with the L_{III} edge, is present. The method is considered valid for the analysis of solutions containing 0.0010 g of uranium per milliliter or more. A limit of error (0.95) for a single determination is given as 1.3 per cent at the 10,000-ppm level.

Procedure. Determination of Uranium in the Presence of Yttrium: Evaluation of Constants.[21] Standards were prepared containing 0.0050, 0.0075, 0.0100, and 0.0150 g of uranium per milliliter of 5*M* nitric acid. In addition to the uranium, the two standards of lowest concentration contained approximately 0.04 g of iron and 0.05 g of aluminum per milliliter. X-ray absorption measurements were made on these solutions as described for the samples below. Values of t_{s1} and t_{s2}, t_{w1}, t_{w2}, and C_u were substituted in Eq. 16.3. Each pair of the resulting simultaneous equations was solved for K_1 and K_2. The averages of the values thus obtained were used for the analyses. Typical values obtained were K_1=0.069964 and K_2=0.063845.

Samples. The ¾- by ¾- by 2-in. plastic absorption cell is filled with the solution to be analyzed and placed in the cell holder of the instru-

ment. The time required to accumulate 10^5 counts is recorded for goniometer settings of 11.85° and 12.20° with a slit width of 0.1°. The counting times necessary to accumulate 10^6 counts for distilled water under the same conditions are also determined. (The counting time for water must be divided by 10 to compare it with the sample time.) All counting times are corrected for the resolving time of the counting equipment. The uranium concentration is then obtained by substituting the corrected counting times into the equation, using the previously determined values for K_1 and K_2.

(2) *Determination of Molybdenum.* In the determination of molybdenum in molybdenum-uranium alloys,[22] the uranium is first removed by extraction. With a rock-salt analyzing crystal, a 0.1° slit, and operating conditions of 30 kv and 8 ma on the tube, the angles measured for the K absorption edge are 12.35° and 12.70°. A brief description of this procedure is given in Chap. 5, Sec. 5–1.4(a).

(3) *Determination of Thorium.* Analyses have been made for thorium [23] in the concentration ranges of 100 to 15,000 μg of thorium per milliliter. Lead and uranium in concentrations of 5000 μg/ml do not interfere, but bismuth and strontium do. When the latter elements are present, a TBP extraction of the thorium can be made to eliminate the interference. The thorium L_{iii} absorption edge is used, and measurements are made at 15.25° and 15.60° goniometer settings. The limit of error for a single analysis at the 95 per cent confidence level is ±2.8 per cent for 2000 μg of thorium per milliliter of solution.

(b) *Excitation From Secondary Target.* The desired wave lengths for absorption-edge analysis [24, 25] have been obtained from the secondary radiation from a separate target to furnish two wave lengths that span the desired absorption edge. The use of secondary radiation requires a minimum of instrument modifications and provides high line intensities with no detectable second-order interference. The secondary $K\alpha$ radiation of molybdenum and niobium emitted by a 50 per cent molybdenum–niobium alloy mounted in the sample drawer of a commercial Philips Electronics X-ray spectrograph was used to obtain the desired radiation for the absorption-edge determination of uranium. A similar technique has been worked out for the determination of rhodium, uranium, tantalum, yttrium, cobalt, and cerium.[25] For determining between 0.5 and 40 mg of uranium per milliliter, the relative standard deviation of the method varies from 6 to 0.34 per cent. Yttrium interferes with the analysis. The arrangement of the components is shown in Fig. 16.4. The apparatus is described as follows.[24]

Apparatus. An X-ray spectrograph, with a lithium fluoride analyzing crystal and a scintillation detector with associated high-speed electronics, is modified for absorption-edge analysis (Fig. 16.4). The exit collimator is replaced by a $\frac{1}{8}$-in.-thick lead sheet having a 15- by 15-mm window centered to coincide with the collimator port. The lead window

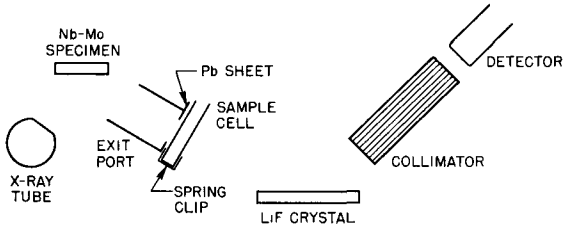


Fig. 16.4—Component arrangement for X-ray absorption-edge determination of uranium. [From E. A. Hakkila, *Anal. Chem.*, **33**: 1013 (1961).]

and spring clips to hold an absorption cell of either a 1- or 3-cm path length in front of the lead window are held in place by the collimator screws. The cell of 1-cm path length is used for analyzing solutions containing up to 40 mg of uranium per milliliter. The longer cell is used for analyzing uranium concentrations in the range of 0.06 to 2 mg/ml. The cells are constructed of Lucite with $\frac{1}{16}$-in.-thick polystyrene windows cemented in place with chloroform. Polystyrene is preferred to Lucite or beryllium as window material because of its greater stability toward nitric acid. The cells are 50 mm wide and 60 mm high with a 20-mm-wide 50-mm-high reservoir. A minimum of 5 ml of sample is required for analysis using the cell of 1-cm path length. The source of secondary radiation is a 50 per cent molybdenum–niobium alloy polished flat on one side and machined to fit into the standard sample cell supplied with the X-ray spectrograph. Either prepared alloys or pelleted oxide mixtures can be used as sources of secondary radiation, but the alloys are preferred because scattering of primary radiation from the X-ray tube is minimized.

Procedure. Samples received as solutions are analyzed as received, or the uranium concentration is adjusted by dilution or evaporation. Solids are dissolved in acid, preferably nitric, and are diluted with water to give uranium concentrations of 10 to 20 mg/ml. If the uranium concentration is high or if impurity elements of high mass-absorption coefficients are present in large amounts, it may be necessary to dilute the sample further so that sufficient count rates can be obtained. If the yttrium concentration is greater than 0.01 mg/ml, it should be removed by precipitation as the fluoride.

A blank solution is prepared to contain approximately 1 to 5 mg/ml of each of the major elements expected in the sample, and the solution is diluted to a total volume of 10 ml with a $2N$ to $5N$ solution of the acid used in sample dissolution. In the same manner, a standard is prepared to contain 20.00 mg of uranium per milliliter.

The X-ray tube, which is operated at 50 kv and 30 ma, is turned on 1 hr before analyses are performed. Then the absorption cell is filled with water, and duplicate measurements are made of the time to accumulate 10^6 counts at the $K\alpha$ peaks for molybdenum and niobium. The measurements are repeated with the sample cell filled with the blank and then with the standard solution. Measurements are made for all samples, with 10^6 or 10^5 counts accumulated. The number chosen is such that the counting time for any one peak does not exceed 10 min. At the conclusion of the analyses, the water and blank-solution measurements are

repeated, and the average times to accumulate 10^6 counts are calculated. All times are corrected for coincidence loss by subtracting 4.0 sec per 10^6 counts taken. Count rates lower than 5000 counts/sec are also corrected for background. Appropriate values for K_1 and K_2 are determined from the blank and standard solutions, and the uranium concentration of each sample is calculated.

The procedure can also be applied without modification to the determination of yttrium in the absence of uranium.

16–2 X-RAY EMISSION SPECTROGRAPHY

16–2.1 Instrumentation

Analysis by X-ray emission is accomplished by measurement of the characteristic secondary fluorescent X rays emitted when X rays from the primary source strike the material in question. For the measurement of the radiation at the selected wave length, the technique requires a spectrograph with an X-ray tube to excite the sample to emit the fluorescent X rays, a crystal analyzer to disperse the X rays, a goniometer to select the angles, and a detector system to measure the intensities of the lines reflected from the crystal at the appropriate angle. The intensity of the fluorescent X ray, measured by counting techniques, is a function of the concentration of the element excited. The components are arranged as shown in Fig. 16.5.

Modern equipment permits a variation in components to meet the requirements of a given problem. X-ray tubes are available with a variety of target materials. Tungsten is the most widely used, but molybdenum [26, 27] has found particular use in the analysis of uranium and thorium. Chromium targets may prove useful in cases where elements of low atomic number must be analyzed.[28] Voltages of up to 100 kv are now available; this can give increased intensities and extend the range of the elements whose K spectrum can be excited. A variety of analyzing crystals with a range of crystal d spacings is

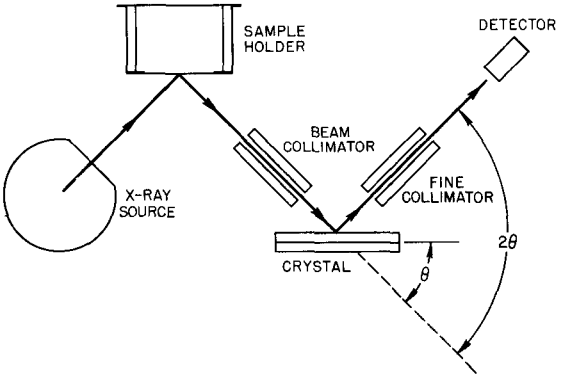


Fig. 16.5—Component arrangement of X-ray emission instrument.

needed to cover the wave lengths to be detected. The relation governed by Bragg's law of diffraction, $n\lambda = 2d \sin \theta$, where n is the order of diffraction, λ is the wave length in angstroms, d is the interplanar spacing of the crystal, and θ is the angle between the incident radiation and the crystal surface. Tables are available which give the wave lengths of the principal lines of all the elements [3, 29-31] including the transuranic ones.[79] The corresponding angles are given for some analyzing crystals.[29] Lithium fluoride is the crystal most widely used since it gives adequate dispersion and can cover a range of elements from potassium through the heavier elements, although not always with the highest possible efficiency. For elements from aluminum through potassium, a crystal of ethylenediamine *d*-tartrate is used. For detection equipment Geiger counters were originally used, but they have been largely replaced by scintillation and proportional counters. These have the advantages of handling higher counting rates and of giving pulses proportional in amplitude to the energy of the X ray absorbed, thus permitting pulse-height discrimination. Scintillation detectors have very good sensitivity to wave lengths from about 2 A and shorter. For long wave lengths flow proportional counters are used in conjunction with helium paths or vacuum spectrographs. Complete discussion of the theories involved which would help one to make an intelligent selection in the use of the various components can be found in recent literature.[1-7]

The use of radioisotopes to replace the X-ray tube as the irradiation source to produce the fluorescent emission has received limited use in analytical applications.[86] The radioisotope source is considerably cheaper than an X-ray tube, and its output and energy distribution are constant. The intensity of radiation, however, is considerably lower than that from a tube source; thus short source–sample–detector distances must be maintained.[87] This short-path requirement eliminates the possibility of using a crystal analyzer; therefore the only energy resolution obtained is that from a proportional counter and a pulse-height analyzer. Analysis is limited to simple mixtures.

16–2.2 Standards

Quantitative results by X-ray emission spectroscopy are almost universally obtained by comparison with standards. When direct comparison standards are used, the best results are obtained when the unknown and the standards are run in a continuous sequence with little time lag and minimized occasions for instrumental fluctuations. A plot of intensity vs. composition will not give a straight line over a wide range of compositions but may show a positive or negative curve due to self-absorption, or absorption by the matrix or other elements present in the sample. A secondary element present may exert a positive effect due to enhancement or a negative effect due to the loca-

tion of its absorption edges. These effects point up the necessity for maintaining the composition of the standards as closely as possible to that of the unknowns. Since the range of compositions being investigated is usually short, standards spanning the range will appear to give a straight line. Absorption and enhancement effects can be minimized by dilution with a material such as starch, by solution with an appropriate solvent, or by fusion into a glass such as with sodium borate.[32] Mathematical approaches to corrections for matrix factors have been given.[1-3, 33-35]

(a) *Direct-comparison Standards.* Standards for use in the analysis of alloys or in the analysis of impurities in a metal sample are difficult to prepare specifically for X-ray standards; therefore they are best obtained from chemically analyzed samples. This situation makes X-ray analysis impractical for a limited number of samples unless analyzed samples are readily available. However, the method is invaluable for routine work. When two or more elements are present which vary independently over an appreciable range, a family of curves may be necessary when it is seen that they affect each other by absorption or enhancement. In the case of powdered samples of simple composition, dry mixes can be made in a mechanical grinder or mixer sometimes with a diluent or binder such as starch or stearic acid. The particle size must be reduced to at least 200 and preferably to 400 mesh to give reproducible results.[36] The mix is usually pelleted in a press to give samples of uniform density. The use of solutions overcomes problems of inhomogeneity of composition and particle size in the preparation of known mixtures, as well as in the preparation of the samples to be analyzed. However, solution techniques have the disadvantage of causing too great a dilution for the analysis of elements of very low concentrations. In the use of direct-comparison standards, generally a working curve is obtained by plotting the concentration vs. the intensity in counts per second of the strongest characteristic peak that is free from interference. Where practical, sufficient counts should be accumulated to attain the desirable degree of precision, considering the standard deviation (insofar as counts alone are concerned) to be $\sqrt{N}$, where N is the total number of counts registered.

(b) *Internal Standards.* Cases where the composition of the samples shows considerable variation can be handled by adding a constant quantity of an internal standard.[36, 37] The internal-standard method is less subject to errors from instrumental fluctuations and from packing densities in powder samples. The element chosen as the internal standard should be close to the unknown element in atomic number so that the absorption and enhancement effects are similar for both elements, but it should not be the cause of interference itself. Since

the internal standard is added in a concentration roughly equal to the element to be determined, its use is best suited to the measurement of elements present in less than 10 per cent concentration so that its introduction will not greatly alter the matrix.[2] A standard curve is made from mixtures containing a representative matrix, a constant concentration of the internal standard, and a range of concentrations of the element in question. A plot is made of the element concentration vs. the ratio of the counts of the element to the internal standard.

(c) *Scattered-Radiation Comparison.* Scattered radiation from the primary source, both coherent and incoherent, can interfere with a desired analytical line, making its measurement impossible. This scatter is particularly serious from a light matrix.[38, 39] However, in some cases a coherently scattered line can be used as an internal standard.[40, 41] Obtaining the ratio of the desired line to a suitable scattered line can correct for instrumental variations and, in some cases, for absorption effects.

16–2.3 Precision of Analysis

The precision of X-ray analysis can not be definitely stated. In addition to counting statistics, a procedure is affected by instrumental variations and adjustments and by variations in sample and standard preparation. A preliminary study of the precision of the X-ray method as affected by several commonplace factors other than counting statistics has been reported by the Task Group on X-ray Fluorescence Spectroscopy,[42] American Society for Testing and Materials. They found that with powder samples a greater error may arise from the preparation of the comparison sample mixes than from all the other sources combined. Individual cases vary greatly, but as a starting point the standard deviation may be considered to be 1 per cent or greater.

16–2.4 Analysis of Solid Metals

In the analysis of metal solids, it must be realized that the physical character of the surface has a large effect on the counts obtained. For this reason all samples and standards must be ground or polished to the same degree to obtain any accuracy in the analysis. Also, since only the surface layer is being irradiated, the analysis may not be representative of the whole sample. Inhomogeneity in an ingot can be measured by taking slices of sample at intervals for analysis.

Chapter 5 presents discussions on the analyses for uranium and plutonium in the aluminum alloys,[43] uranium in zirconium alloys,[44, 45] and molybdenum and ruthenium in uranium alloys;[46] therefore the procedures for these analyses are not repeated here.

Uranium-fissium alloys can be analyzed for zirconium, molybdenum, and ruthenium.[46] The zirconium can be determined in con-

centrations below 0.02 per cent. The zirconium $K\alpha$ intensity shows a linear increase with concentration up to about 0.5 wt.% zirconium. Because of absorption effects, the presence of zirconium in the alloys will cause an error in the molybdenum analysis. This error can be corrected by using a family of curves in which ruthenium is used as a stand-in for zirconium.

16–2.5 Analysis of Powder Samples

The analysis of powder samples offers greater flexibility and choice of technique than is possible with massive samples. A more homogeneous sample can be taken, dilution techniques can be used, an internal standard can be added, and comparison standards can be mixed as the case requires. Particle size must be considered in powder analyses. For reproducible results to be obtained, it has been found necessary to reduce the particle size to below 200 mesh.[36] Grinding and mixing may be done in a mortar and pestle or in a mixer, such as the Spex Industries Mixer Mill. Powder samples may be in the form of powdered metals, oxides, dried residues, or precipitates. The final sample may be pressed into a pellet, packed into a plastic holder, or cast into a glass following a fusion.[32]

(a) *Analysis of Uranium.* Uranium is determined in alloys or sandwiched fuel plates by dissolving either a representative sample or the entire sample, thus overcoming the inhomogeneity possibility present with the solid-sample analysis.[47] At the 65 per cent confidence level, the precision on a single aliquot is ± 0.52 per cent, and on 10 aliquots of solution the precision is ± 0.2 per cent.

Procedure.[47] Five portions of uranium ranging from 6.0 to 8.0 mg in nitric acid solution are accurately measured into 30-ml Vycor crucibles. To each is added a nitric acid solution of aluminum containing the amount to give an aluminum to uranium weight ratio within 20 per cent of that of the samples. Five milliliters of a solution of strontium nitrate [1 g of anhydrous $Sr(NO_3)_2$ per liter] is added by pipet. The solution is evaporated to dryness under infrared lamps placed above and below the crucible. When dried, the residues are ignited to the oxides at 600°C for 1 hr. The oxides are ground for 10 min in a mullite mortar. Methyl cellulose (0.75 g) is added to the oxides in a ¾-by-2-in. plastic vial, and the mixture is blended in a Crescent Dental Manufacturing Co. Wig-L-Bug for 5 min. The entire blend is pressed in a 1-in.-diameter die at 38,000 lb/sq in. pressure for 10 sec. With a tungsten-target X-ray tube operated at 50 kv, and 35 ma, a topaz analyzing crystal, and a scintillation detector with a thallium-activated NaI crystal, the peak positions of the uranium $L\alpha$ and the strontium $K\alpha$ peaks are located at 39.26° 2θ (uranium) and 37.69° 2θ (strontium). These peak positions must be checked daily or each time a standard curve is made simultaneously with the analysis of samples. The time to accumulate 256,000 counts is recorded for each of the lines alternately in duplicate. No background count is taken. A plot is made of the ratio of I_U/I_{Sr} of the standards against the milligrams

of uranium present. For the analysis of the samples, a representative portion of the uranium-aluminum samples is dissolved in 20 vol.% nitric acid which contains 0.1 g of mercuric nitrate per 100 g of sample. In the case of sandwiched fuel plates, the entire fuel plate is dissolved, and the total weight of the dissolved solution is obtained. This solution should contain approximately 50 g of sample per liter. Aliquots of the samples are taken to contain 7±1 mg of uranium. The strontium is added, and the samples are treated exactly the same as the standards described above. From the intensity ratios obtained and from the simultaneously derived standard curve, the milligrams of uranium present in each aliquot is calculated. With enriched-uranium samples a mass correction factor based on the isotopic assay of the sample is applied.

A similar procedure is used to determine the uranium remaining in the cryolite phase[48] after a reduction run of uranium oxide and aluminum metal in the preparation of an aluminum-uranium alloy. The chunks of cryolite are ground to pass a 200-mesh screen. One gram of the powder is weighed and mixed with 15 mg. of strontium nitrate in a Spex Industries Mixer Mill. The use of the internal standard eliminates the need to pack the powder uniformly. The uranium $L\alpha$ and strontium $K\alpha$ peaks are measured, and the ratio of their intensities is plotted against the UO_2 concentration. The calibration curve is nearly a straight line from 0 to 100 per cent UO_2.

In the analysis of UO_2 in bismuth metal[48] (see Chap. 5), the heterogeneous mixture is dissolved in nitric acid and subsequently precipitated. Then it is ignited to the oxides. Since the uranium $L\alpha_1$ line has interference from the bismuth $L\beta_1$ and $L\beta_2$ lines, the measurements are made of the uranium $L\beta_1$ and the bismuth $L\alpha_1$ lines with the bismuth matrix acting as the internal standard.

(b) *Analyses of Beryllium and Beryllium Oxide.* Analyses have been made of both beryllium oxide and beryllium metal for elements occurring either in appreciable amounts or as minor impurities. When both uranium (1 to 10 per cent) and yttrium (1 to 12 per cent) are present in beryllium oxide, X-ray spectroscopy can be used successfully to analyze for each element.[49] Rubidium is added as the internal standard for both elements. A family of curves is necessary for each element. Limits of error at the 95 per cent confidence level for uranium vary from ±4 per cent at the 1 per cent level to ±2.8 per cent at the 9 per cent level and for yttrium from ±7.5 per cent at the 1 per cent level to ±2.5 per cent at the 12 per cent level.

Procedure. All operations involving beryllium oxide should be carried out in a glove box prior to the pressing of the pellets. Into each of two vials is put two ⅜-in. plastic balls, 2.500 g of cornstarch, and 0.010 g of rubidium chloride. The beryllium oxide is ground to pass a 100-mesh screen, and a 0.500-g portion is added to each vial. The vials are shaken in the mixer mill for 20 min. The mixture is trans-

ferred to the pellet die, and the die is encased in a polyethylene bag. The die is placed in a laboratory press and pressed at 20 ton/sq in. pressure. The die is returned to the glove box, and the pellet is removed. The pellet is transferred to a rotating sample holder in the X-ray spectrograph. The tungsten-target tube is operated at 50 kv and 48 ma. With a lithium fluoride analyzing crystal, measurements are made of the yttrium $K\alpha$ (23.81° 2θ), uranium $L\alpha_1$ (26.14° 2θ), and rubidium $K\alpha$ (26.58° 2θ) peaks. A measurement is also made of the background adjacent to each peak. The net count of each peak is determined, and the intensity ratios, uranium/rubidium and yttrium/rubidium, are calculated. The uranium-intensity ratio is compared with the average curve obtained from standard samples to obtain the approximate uranium concentration. The yttrium value is then determined from the appropriate curve based on the uranium concentration, and the proper uranium concentration is read from the curve based on the yttrium concentration.

Calibration. Standard mixes are prepared which contain all the possible combinations of 1, 5, and 9 per cent uranium and 1, 6.5, and 12 per cent yttrium as the oxides in a beryllium oxide matrix. The pellets are prepared in duplicate, and the two intensity ratios are obtained on all nine mixes. The relation between intensity ratio and concentration for each element in the presence of fixed quantities of the other is determined, and curves are plotted. The equations of each curve, in the form of $Y=mX+b$, are calculated. An "average" equation for uranium is calculated to permit an estimate of uranium content so that the proper curve can be selected for yttrium calculations.

The determination of some impurity elements has been reported in relatively pure beryllium-metal powder samples.[50, 51] The low absorption coefficient of beryllium and the low concentration of heavier elements make these analyses possible. With this type of sample, the calibration curves must be made by the measurement of chemically analyzed samples. At the New Brunswick Laboratory, samples were analyzed [51] for nickel (80 to 370 ppm), manganese (80 to 250 ppm), copper (30 to 250 ppm), chromium (70 to 430 ppm), and iron (400 to 2500 ppm). For each of these elements, the $K\alpha$ line was measured, and the ratio of the $K\alpha$ to the $L\alpha$ scattered peak from the X-ray tube was plotted against the concentration of the element. The ranges reported were limited by the standards available. Unpublished work indicates that analyses can also be done for calcium, silicon, and aluminum. For reproducible results to be obtained, all the samples must be of a comparable particle size, preferably at least 200 mesh. The powders are briquetted under a uniform pressure of 80,000 lb/sq in. The samples are measured in a vacuum spectrograph, which is evacuated to less than 550 μ pressure, with a tungsten-target X-ray tube operated at 50 kv and 40 ma, a lithium fluoride analyzing crystal, and a gas-flow proportional counter. Table 16.1 indicates the X-ray intensities obtained under these conditions.

690-457 O—64——79

Table 16.1—X-RAY INTENSITY MEASUREMENTS FROM IMPURITY ELEMENTS IN POWDERED BERYLLIUM METAL[51]

Sample	Impurity elements				
	Nickel	Manganese	Copper	Chromium	Iron
NBL–85:					
Parts per million*	80	80	30	70	400
Net counts per second	3201	490	2215	274	5377
I $K\alpha$/I $WL\alpha$	0. 413	0. 220	0. 224	0. 460	1. 183
NBL–86:					
Parts per million*	200	120	300	200	1400
Net counts per second	6156	693	7513	597	14722
I $K\alpha$/I $WL\alpha$	0. 834	0. 3069	0. 818	0. 675	3. 538
NBL–87:					
Parts per million*	210	215	210	250	1700
Net counts per second	5948	1066	5684	738	15743
I $K\alpha$/I $WL\alpha$	0. 838	0. 516	0. 634	0. 797	4. 284
NBL–88:					
Parts per million*	370	250	250	430	2500
Net counts per second	8250	1226	5686	1126	22675
I $K\alpha$/I $WL\alpha$	1. 300	0. 610	0. 764	1. 146	6. 363

*From certificate of analysis of New Brunswick Laboratory-analyzed samples NBL–85, NBL–86, NBL–87 and NBL–88.

(c) *Analysis of Zircaloy.* Zircaloy-2 has been analyzed[52] for tin (1.25 to 1.65 per cent), iron (0.07 to 0.17 per cent), chromium, 0.06 to 0.14 per cent), and nickel (0.03 to 0.07 per cent). The alloy is converted to the oxide by igniting it in a muffle furnace at 1000°C for 1 hr. The oxides are ground to −300 mesh and then mixed with an equal weight of cellulose powder (Whatman ashless cellulose for chromatography). The mixtures are briquetted at 60,000 lb/sq in. pressure. For standards, 2-g samples of zirconium metal with a known content of iron, chromium, and nickel are dissolved in sulfuric and hydrofluoric acids. The solutions are evaporated to dryness and taken up in dilute nitric acid. Measured additions of tin, iron, chromium, and nickel are made. Tin, iron, and chromium standards are coprecipitated with ammonium hydroxide, filtered, washed, and ignited to the oxides. The nickel standards are precipitated with sodium hydroxide. The oxides are then ground and briquetted in the same manner as the samples. A sample of the starting zirconium metal is carried through the entire procedure to serve as a blank. Measurements are made as described below.

The minor constituents are concentrated by removing the zirconium by extraction with thenoyltrifluoroacetone (TTA) in benzene to increase the sensitivity of the determination.

Procedure.[52] *Extraction of Zirconium.* Approximately 0.5 g of Zircaloy-2 is weighed and dissolved in a mixture of sulfuric and hydrofluoric acids, fumed to dryness, and taken up in 40 ml of 6*N* hydrochloric acid. The solution is transferred to a 125-ml separatory funnel and extracted three times with 40 ml of 1*M* TTA in benzene. The TTA-benzene solution is conditioned with 6*N* hydrochloric acid prior to its use in the extraction. Extraction times are 10 min each.

After the final extraction the aqueous phase is drained into a 150-ml beaker, and three rinses with 6*N* hydrochloric acid are made. To the solution are added 2.00 g of cellulose powder and 20 mg of aluminum as carrier to ensure complete precipitation of the hydroxides. The solution is then taken to the cresol red end point (pH 7.2 to 8.8) with sodium hydroxide solution. After a digestion period of 10 to 15 min, the precipitates are filtered through Whatman No. 41 paper, washed, and dried. The dried mixture of cellulose and hydroxides is then briquetted into a pellet 1 in. in diameter at 60,000 lb/sq in. pressure as in the first method.

Standards. Standards for the extraction method are prepared by mixing suitable aliquots of standard solutions of tin, iron, chromium, and nickel together with 20 mg of aluminum carrier and an arbitrary amount of zirconium (7.5 mg) to represent the unextracted traces. These solutions are precipitated, filtered, dried, and briquetted the same as the samples.

Measurements. A Philips three-specimen spectrograph is used with a specimen spinner and a helium path. Included in the components are a tungsten-target tube operated at 50 kv and 50 ma, a LiF analyzing crystal, a scintillation counter, and an Atomic Instrument Co. model 510 single-channel pulse-height analyzer. Measurements are made at the $K\alpha$ peak for each element by the fixed-count technique, with a minimum of 64,000 total counts accumulated. One or two standards are run with each batch of samples.

On the zirconium oxide pellets, a blank correction is made for tin by counting the blank zirconium standard at the tin Kα peak position. For iron and chromium, backgrounds are determined at positions about 1° to 1.5° removed from the peak positions.

On the pellets containing the concentrated impurities, gross counts at the iron, chromium, and nickel peaks are used since the background is constant. For tin it is necessary to count the background since it varies widely from sample to sample. The pulse-height analyzer is used for the iron, chromium, and nickel counts to reduce the background: it is found to improve the peak to background ratio by a factor of nearly 10. It is not used for the tin determinations because no improvement can be obtained in its peak to background ratio. A helium path is used for all the elements although it is of real advantage only in the case of chromium.

Analyses have been made for 1 to 5 per cent zirconium in mixed oxides of uranium and zirconium.[53] Pellets are made of 1:1 mixtures of oxide and cornstarch. There is some interference to the zirconium $K\alpha$ peak from the uranium $L\beta_6$ peak. The uranium $L\beta_2$ peak is used as an internal standard.

(d) *Analysis of Plutonium.* A method has been reported for the analysis of plutonium in low-level sludges and high-level solids.[54] It is used primarily for samples on which only a reasonable accuracy is needed for process control. The range of the method is from 0.001 to 100 per cent for solid samples. A matrix that is mixed with the solids or sludges to be analyzed is prepared from a mixture of MgO with soupy $Al(OH)_3$ to the consistency of cold cream. A solution of yttrium oxide is added as an internal standard. Approximate amounts of the sample, matrix, and internal standard are mixed in a vial in a mixer mill and then packed into a plastic Caplug (Protective Closures Co., Inc.), covered with two layers of ¼-mil Mylar, and transferred to the X-ray sample holder. A minimum of 12,800 counts for the plutonium and yttrium peaks and 1600 counts for the background are accumulated. Working curves are plotted from the ratio of counts per second of plutonium to net counts per second of yttrium against the plutonium concentration. For low-level sludges containing from 10 to 1820 ppm, the standard deviation is ±9.92 per cent. For high-level oxide samples, the standard deviation is ±0.63 per cent.

16–2.6 Analysis of Solutions

Several factors must be considered when dealing with the analysis of solutions.[55] The primary problem concerns the cell or sample holder, which must be leakproof and must maintain the liquid in a flat plane at the proper position. Various cell designs are given in the literature.[8, 55] Unless the sample is to be irradiated on the top surface, a window that is thin enough to not absorb the X rays must be used in the cell. Liquid evaporation must not be permitted to change the concentration of the solution or to upset the geometry of the beam path. Inverted optics[56] can be used; in this case the X-ray beam strikes the bottom of the cell, which is covered by a ¼-mil Mylar film that forms a transparent watertight window. When inverted optics is used, there is the possibility of damage to the X-ray tube if the cell should leak. Bubble formation at the interface causes errors; even with inverted optics the bubbles may cling to the Mylar window. The addition of a wetting agent to the solution minimizes this problem. Since the solvent has absorption effects, its concentration and composition must be kept constant in any series of samples. Solvents that generally have compositions of elements of low atomic

number cause higher backgrounds due to scatter from the X-ray source than those caused by solids.

The use of solutions offers several advantages, which are ease of mixing and adding internal standards, homogeneity, reduction of interfering adsorption or enhancement effects by dilution, and simple adjustment of concentration to the desired range. Solution techniques, however, are not generally used for the determination of traces of elements because the dilution factor would be too great. Where a concentration of an element is too low, the solution can be evaporated to concentrate the element onto a film or filter paper. Extraction, ion-exchange, or precipitation techniques can also be used for solutions when concentration of an element is necessary.

(a) *Analysis of Uranium and Uranium-containing Mixtures.* Solutions from many sources have been successfully analyzed by X-ray emission. Such sources range from aqueous and organic solvents from ores, feeds, raffinates,[57, 58] and reactor fuels, which may contain many impurities, to alloys containing a few known elements and solutions containing only the element in question and the solvent. Samples containing appreciable impurities are analyzed with the aid of internal standards (usually yttrium or strontium for aqueous solutions and bromine for organic solutions), but simpler solutions can be measured directly by comparison with similar standard solutions.

(1) *Solutions Derived from Reactor-fuel-recovery Processes.* These solutions are examples of the type of sample that can be analyzed directly by measurements at the uranium $L\alpha$ peak.[59, 27] In tests to determine the most efficient components for use in the analysis,[27] it was found that a molybdenum target tube gives a peak to background ratio 2.5 times greater than that given by a tungsten tube. The value of using a LiF analyzing crystal and a scintillation counter with pulse-height analysis was also shown. Errors of about 1 per cent occur when the interfering element to uranium molar ratio is 50 for aluminum, 25 for chlorine, 10 for iron, and 1 for bromine. Molybdenum in a molar ratio of 1 and concentrations of $4\times10^{-3}M$ shows no noticeable enhancement effect. For the reduction of the concentration of such anions as fluoride, chloride, bromide and bromate below the interference level, the sample solution, which contains 7 to 15 mg of uranium, is fumed to dryness with sulfuric acid, the residue is taken up in 1 ml of nitric acid, and the solution is transferred to a 10-ml volumetric flask with water. In samples containing interfering concentrations of such metals as iron, nickel, chromium, aluminum, and zirconium, the uranium is extracted with ethyl acetate as the solvent and aluminum nitrate as the salting agent. The uranium is stripped from the ethyl acetate with water, the water is evaporated to dryness, and the uranium is taken up in nitric acid and diluted to volume

as before. Five standard solutions (1, 2, 3, 4, and $5 \times 10^{-3}M$ uranium) are prepared by dissolving U_3O_8 in nitric acid and diluting the resulting solution to the desired concentrations with $1.6M$ nitric acid. Measurements of the time required to accumulate 102,400 counts with operating conditions of 50 kv and 50 ma are made at the uranium $L\alpha_1$ peak (26.14° 2θ). A plot is made of the counting rate vs. the concentration of each standard.

The above method is used for the determination of uranium in uranium–plutonium–fission-element alloys. In this determination the uranium is separated by extraction with TBP from an HCl medium,[60] as mentioned in Chap. 5.

The analysis for uranium, when it is in combination with aluminum, in solution has been carried out without separation. Procedures are given in Chap. 5 for uranium in uranium–aluminum alloys[61] and in ceramic Al_2O_3–UO_2 fuel elements.[62]

(2) *Solutions With Several Components Present.* When several components are present in appreciable and variable amounts, an internal standard is used to improve the accuracy of the determination. In a pyrochemical process in which heavy-element reactor fuels are dissolved in a mixture of molten potassium and aluminum chlorides and a separation of various elements is achieved by preferential reduction with molten aluminum metal, analyses are done for several components in both the metal and the fused-salt phases.[63] The author of Ref. 63 states that analyses for potassium, uranium, and thorium carried out by X-ray emission are more consistently precise than are determinations by flame photometric, coulometric, and cerate titration methods. Solutions of these samples contain 4 to 16 g of aluminum per liter, 103 to 140 g of chlorine per liter, 6 to 16 g of potassium per liter, 0 to 4 g of thorium per liter, and 0 to 4 g of uranium per liter. The aluminum in these solutions cannot be determined by X-ray analysis because of the almost complete absorption of aluminum fluorescence by the sample. For convenience a gas-flow counter is used for analyzing the potassium, thorium, and uranium since a scintillation counter gives a high noise level at longer wave length from the potassium. A pulse-height analyzer with a 5-volt window is used at each peak. A helium atmosphere is used to avoid the air absorption of the potassium fluorescence. The analyzing crystal is lithium fluoride. The tungsten-target X-ray tube is operated at 55 kv and 40 ma. Calcium was used in the referenced analyses as an internal standard for the potassium, but indium is a better choice. Strontium serves as the internal standard for both the uranium and thorium.

For the determination of the potassium, 2.0 ml of a solution containing 33 g of calcium (as nitrate) per liter is mixed with 10-ml aliquots of the samples. The $K\alpha$ peaks of potassium and calcium are meas-

ured, with a total of 409,600 counts for each accumulated. It is not necessary to measure or correct for the background, which is only 40 counts/sec. The potassium to calcium ratio is calculated. In the range of 3 to 20 g/liter, the precision at the 95 per cent confidence limit for a single determination is ± 0.22 and ± 0.16 g/liter for the average of duplicates.

For the determinations of uranium and thorium, a 10.0-ml sample aliquot is mixed with 2.0 ml of a solution containing 2.4 g of strontium per liter, and the time necessary for the accumulation of 100,000 to 200,000 counts is measured for both the heavy elements and the standard lines. The uranium to strontium ratios are quite constant despite a change in composition, and the thorium to strontium ratios are not significantly affected by large variations in potassium, aluminum, or chloride concentrations. The thorium to strontium ratios do show a decrease with increasing uranium content. A family of curves can be used to avoid this deviation. The lower limit for the practical measurement of uranium and thorium in aqueous solutions by this method without resorting to special techniques is 10^{-4} molar, or 0.024 g/liter. At the 95 per cent confidence level for a single determination, the precision is ± 0.035 g/liter in the range of 0 to 2 g/liter and ± 0.10 g/liter in the range of 2 to 7 g/liter.

A similar technique with strontium used as the internal standard in the analysis of uranium in stainless steel [64] is described in Chap. 5. With yttrium as the internal standard, niobium, zirconium, and uranium [65] can be determined in the presence of each other when the ratio of any two of the metals is not greater than 1 : 5. When uranium is present in large amounts, the uranium is extracted from one test portion before niobium and zirconium are determined, and uranium is determined on another test portion.

Multiple determinations have been reported in another type of sample, a bronze heat-treating material in which certain types of uranium-metal fuel cores are dipped.[66] Analytical methods were needed for the determinations of copper, tin, and uranium in the bronze bath and copper in the tin bath. For these determinations a North American Philips Co., Inc., 100-kv X-ray spectrometer with a tungsten-target tube, a lithium fluoride analyzing crystal, and a scintillation counter was used. It was found that in solutions of bronze containing no uranium, there is a linear relation between copper $K\alpha$ and tin $K\alpha$ intensities and their respective concentrations; but, when varying amounts of uranium are added to test solutions, the linear relation no longer holds. This fact indicates the need for an internal standard. Zinc is used as the internal standard for copper; 3.1 mg of zinc per milliliter of sample solution gives a copper $K\alpha$/zinc $K\alpha$ ratio of unity

at a 50 per cent copper concentration in the original sample. Indium is used as an internal standard for the tin measurement at a concentration of 4.5 mg/ml to give a ratio of unity at a 50 per cent tin concentration in the original sample.

The second-order indium $K\beta_{1,3}$ peak coincides with uranium $L\alpha_1$ peak, but indium $K\alpha$ can be used as an internal standard for the uranium. Since the indium is added in the constant amount, it is not necessary to correct for the indium $K\beta$ interference, and the intensity ratio U $L\alpha_1$ − background/In$K\alpha$ − background gives satisfactory results. Background corrections are also advisable for the tin $K\alpha$/Indium $K\alpha$ measurements, but they are unnecessary to obtain the copper $K\alpha$/zinc $K\alpha$ ratio.

Procedure.[66] A 1.000-g sample of drillings is transferred to a 100-ml volumetric flask and dissolved in 15 ml of HCl (1:1). Five to 10 ml of H_2O_2 is slowly added until the sample is dissolved. A 10-ml portion of the indium–zinc stock solution (45 mg of indium per milliliter and 31 mg of zinc per milliliter) is pipetted into the flask. The solution is boiled until the excess H_2O_2 is decomposed. The solution is then cooled and diluted to the mark. A 10-ml portion of the solution is pipetted into a polyethylene sample cell. The cell is covered with a piece of ½-mil Mylar secured with two O-rings and is placed in the instrument sample holder. The X-ray tube is operated at 50 kv and 10 ma. Each peak is scaled to a fixed count, and the time required is recorded. Standards are prepared by placing the requisite weights of copper, tin, and uranium (each combination totaling 1.000 g) in 100-ml volumetric flasks and by following the method for sample preparation and measurements.

Standard curves are plotted of intensity ratios vs. concentration for each of the three elements in question given above. The following list summarizes the peaks measured and the counts accumulated.

Line	*Goniometer setting 2θ*	*Prefixed count setting*
Tin $K\alpha$	14.06	512,000
Tin background	13.71	64,000
Indium $K\alpha$	14.68	512,000
Indium background	15.25	64,000
Uranium $L\alpha_1$ plus interference	26.14	64,000
Uranium background	25.76	16,000
Copper $K\alpha$	45.02	256,000
Zinc $K\alpha$	41.80	256,000

(3) *Solutions with Traces of Uranium.* When uranium is present in amounts too dilute to determine directly, several methods have been used to concentrate it to a detectable level. Ion-exchange techniques have been applied to sulfate effluents.[67] The use of the batch technique has proved to be preferable to the use of a column from the standpoints of speed and of uniformity of the absorption on the resin to be measured. The lowest concentration of uranium estimated to be practical to analyze by this technique is 0.1 ppm.

Procedure.[67] A 2-g sample of Bio-Rad AG–1X (200- to 400-mesh) anion resin in sulfate form, previously weighed out dry and soaked for at least 30 min in 0.25*M* $(NH_4)_2SO_4$, is added to 500 ml of uranium solution of which the sulfate ion content should not exceed 50 g per liter and the pH should not be lower than 2. The mixture is shaken for 5 min, and the resin is removed by filtering under vacuum on a No. 1 porosity sintered-glass filter crucible. For rapid routine analysis the resin can be washed over into a suitable sample holder with distilled water; and, after the resin has settled for 1 min, the uranium $L\alpha_1$ peak can be counted or recorded on a chart.

If there are interfering coadsorbed elements (iron for instance), the resin is transferred into a sample holder with 5 ml of the internal-standard solution [0.05 per cent $SrCl_2$ in aqueous solution containing 20 g of ethylenediamine tetraacetic acid (EDTA) per liter to prevent precipitation of $SrSO_4$]. Peak counts of the uranium $L\alpha_1$ and the standard element line are taken, along with background counts at convenient angles, for 60 sec. It is advisable to take a few counts at each angle, redistributing the resin bed between counts by swirling. A molybdenum target tube is used at 50 kv and 20 ma with a LiF analyzing crystal.

Precipitation can also be used to concentrate uranium, with the count then being made directly on the collected precipitate. Uranium at a level of 100 ppm in a solution containing thorium is determined by using Alizarin Blue as the precipitant and EDTA as the masking agent for the thorium.[68] The precipitation is carried out at a pH between 2 and 6, and the organic precipitate is filtered off. The filter paper is placed in the sample holder, and the uranium is measured by conventional techniques.

(4) *Rayleigh Scattering Method.* One method of analyzing for uranium (or other high-atomic-number element) in a low-atomic-number medium such as dilute nitric acid has been given.[69] In this method no measurements of the characteristic fluorescent radiation are made. It relies on the increase in Rayleigh scattering with the increase in concentration of the heavy element.[70] The degree of Rayleigh scattering is dependent on the cube of the atomic number; therefore it is increased far less by the presence of the lighter elements than by the presence of the heavy elements. The instruments used are not the usual analytical X-ray equipment but a higher voltage collimated X-ray source and a collimated detector system with a discriminator. The sample is held in the X-ray beam in a thin-wall plastic tube, and the counter is set at a fixed takeoff angle. (In the described work [69] a backscatter angle of 140° was used with an X-ray generator operating at 150 kvp with 0.0425 in. of tin beam filtration and 0.0085 in. of tin detector filtration. The samples contained aluminum or stainless steel as impurities.) The bulk of impurities is removed in an extraction of the uranium. Two hundred milliliters of each unknown is evaporated until salting out occurs; then it is extracted with hexone. Afterwards the uranium is back-extracted into water. The unknowns (uranium and remaining impurities) are

prepared in 250 ml of a 1*N* nitric acid solution. The amounts of aluminum and/or iron remaining with the uranium are determined, and the uranium calibration standards are then corrected for these impurities. The influence of aluminum on the measurement accuracy is shown by comparing two solutions of 8 g of uranium per liter each, one of which also contains 60 g of aluminum per liter. Sixty grams of aluminum increase the signal 5 per cent, which is comparable to that from 1 g of uranium in this concentration range. Similar results are obtained with solutions containing stainless steel. In an actual analysis the uranium concentration in each unknown is roughly estimated by a brief count, and then two standards that are close to the uranium concentration are chosen for more accurate comparison counts to calculate the final concentration. The over-all accuracy of the uranium concentration is stated to be ± 0.7 per cent.

This same principal of measurement of Rayleigh scattering is used in a system with a radioisotope-excited X-ray source instead of a conventional X-ray tube.[71] The source utilizes Kr^{85} β-particle interaction with uranium oxide powder to produce uranium X-ray fluorescence and bremsstrahlung. The inert radioactive gas is physically trapped in a powdered quinol clathrate material. An optimum source mixture for a krypton clathrate activity of 90 mc/g consists of 50 wt.% quinol–krypton clathrate material[88] and 50 wt.% uranium oxide powder. The technique has been applied primarily to the analysis of aluminum–uranium ingots.

(b) *Analysis of Thorium.* Thorium, occurring as an impurity in refined uranium material, has been analyzed in a concentration range of 100 to 1000 ppm following its removal from the uranium matrix.[72] Strontium is added as an internal standard to compensate for uranium that might remain in the solution. A concentration of 175 μg of strontium per milliliter is used because it gives a net intensity (background intensity subtracted from both thorium $L\alpha_1$ and strontium $K\alpha$) of unity at the midpoint of the proposed analytical range. The net intensity is not affected by the presence of 1000 μg of uranium per milliliter in the solution, and 2000 μg causes a change of only 1 per cent in the intensity ratio. The measurements are carried out with a Norelco 100 kv X-ray spectrograph with a tungsten-target X-ray tube operated at 60 kv and 25 ma with a LiF crystal and a scintillation detector.

Procedure.[72] *Determination of Thorium in Refined Uranium Materials.* A series of gravimetrically standardized solutions covering the range from approximately 48 to 962 μg of thorium per milliliter is prepared. These solutions, after the addition of a 10-ml portion of strontium nitrate solution (1.75 mg of strontium per milliliter), are used to establish the final analytical curve.

A uranium sample of sufficient size to contain 1 to 10 mg of thorium is dissolved in nitric acid and diluted to such a volume that the uranium concentration does not exceed 34 g of uranium per liter. The pH of the solution is adjusted to 1.0±0.1, and the solution is equilibrated with a 0.5*M* solution of thenoyltrifluoroacetone (TTA) in xylene by shaking the solutions together in a separatory funnel. A volume of TTA-xylene equal to one-third the volume of the aqueous phase is used. The organic phase is washed with a portion of 0.2*M* HNO_3 equal in volume to twice that of the organic phase. The thorium is then stripped from the organic phase by shaking it with two successive portions of 2.0*M* HNO_3; the volume of each portion is equal to one-fourth that of the organic phase. The two portions of 2.0*M* HNO_3 (now containing thorium) are combined, and 1.00 ml of a standard strontium nitrate solution (1.75 mg of strontium per milliliter) is added. The solution is then evaporated to a volume slightly less than 10 ml. The volume of the cooled solution is adjusted to 10 ml and measured on the X-ray spectrometer to a fixed count of 256,000 at the element peaks of thorium $L\alpha_1$(27.46° 2θ) and strontium $K\alpha$(25.16° 2θ) and to a count of 64,000 at the background chosen for thorium (27.08° 2θ) and strontium (24.73° 2θ). The net intensity ratios are compared to the standard curve.

A similar determination has been made of thorium in uranium, except that the uranium was extracted by tributyl phosphate (TBP), leaving the thorium in the aqueous layer.[73, 74] For such a determination, when 0.1 to 1.0 mg of thorium is present, strontium is added as an internal standard; and the measurements are made.[73] When concentration of the thorium is desirable, the aqueous layer is evaporated to 1 to 2 ml, strontium is added, and the solution is evaporated onto a filter paper.[74] The paper is placed in the sample holder, and the peaks are measured.

Low concentrations of thorium can be concentrated with ion-exchange resins.[75] The AG 50 (WX8 or WX12) cation-exchange resin in the hydrogen form is an efficient absorber of thorium. Successful extraction (99.5 per cent) of 1 ppm of thorium from 500 ml of 0.5 *N* HCl is achieved by shaking the HCl solution for 10 min with 2 g of resin. The resin is then washed into a sample holder with 5 ml of distilled water. When foreign elements that cause interference have been extracted, 5 ml of a standard KBr solution (0.5 g/liter) is added to the resin. After these materials have been mixed thoroughly and the resin particles allowed to settle in the sample holder for about 1 min, the thorium $L\alpha$, and bromine $K\alpha$ peaks are counted. The sensitivity of the method appears to be about 50 μg of ThO_2 on 2 g of resin.

The Amberplex C–1 ion-exchange membrane has been used [76, 77] for removing microgram amounts of thorium from solutions of zirconium and Zircaloy-2. Its use with zirconium metal [76] following the separation of the thorium as the fluoride has been mentioned in Chap. 5.

The procedure suggested [77] for use on Zircaloy-2 employs no preliminary separation.

> *Procedure.* A 1-g sample is dissolved in a mixed acid (20 ml of H_2O, 12 ml of HCl, 4 ml of H_2SO_4, and 4 ml of HBF_4) in a 250-ml beaker with a stream of nitrogen being directed over the surface of the solution to prevent the oxidation of tin. When the sample is dissolved, 50 ml of water and 50 ml of 1 per cent citric acid are added. The pH of the solution is adjusted to 1.8 with NH_4OH. A ½-in. disk of the membrane is placed in the solution, which is stirred with a magnetic stirrer for 24 hr. As the disk is removed from the solution, it is rinsed with a spray of 1 per cent citric acid. After it is dried in a desiccator, the disk is placed in the sample holder, and the thorium $L\alpha_1$ peak is counted.

(c) *Analysis of Plutonium.* Because of the hazards involved in the handling of plutonium, the analysis of a sample in solution form is preferable because of the smaller chance of contaminating the atmosphere and instruments. Solutions can be handled in an open-face hood, whereas powders must be mixed in a glove box. Small sample cells have been used which permit the use of less than 1 mg of plutonium.[78] When the total amount of plutonium used was between 0.4 to 0.8 mg, the standard deviation of a single determination was less than 1 per cent.

As with other solution techniques, the matrix composition must be maintained constant in all the sample and standard solutions. This is especially important when hydrochloric acid rather than nitric is used as the medium. In order to control the acid concentration, the solution or aliquot is evaporated to dryness and taken up in the desired solvent. For the analyses of a large number of samples having matrices whose constituents are known and whose compositions are similar, calibration curves can be made which permit direct analyses. A cell of 0.3-ml capacity, (8 mm in diameter, 7 mm in height, and with a window 0.075 mm thick) is cemented into an aluminum tray large enough to contain the solution if the cell should crack.

Mixtures of uranium, neptunium, and plutonium have been analyzed in ratios of about 1 : 1 : 1, with yttrium used as an internal standard.[79] Rubidium is used as an internal standard for neptunium analysis. Any two of these elements can be analyzed in a ratio of 1 : 8 without any loss of accuracy; but, at a ratio of 1 : 10 low results (5 to 7 percent) are obtained. The analyses are performed with a spectrometer using a platinum target tube operated at 50 kv and 40 ma with a LiF analyzing crystal and solvent matrix of $0.5M$ HNO_3–$0.5M$ HCl. The sample is pipetted into a small plastic cup, which is covered with Mylar to keep the solution in the cup. The entire cup is then covered with Mylar to minimize possible contamination. With a 1000-sec counting time, the standard deviation of a single determination is ± 0.7 per cent.

Table 16.2—PRINCIPAL *L* SERIES X-RAY EMISSION LINES OF URANIUM, NEPTUNIUM, PLUTONIUM, AMERICIUM, AND CURIUM

Emission line	Energy, kev	Wave length, A	Absorption edge, A	Reflection degrees, 2θ LiF
U $L\gamma_1$	20. 163	0. 6148	0. 5919	17. 56
U $L\beta_1$	17. 218	0. 7200	0. 5919	20. 60
U $L\beta_2$	16. 425	0. 7547	0. 7223	21. 60
U $L\alpha_1$	13. 613	0. 9106	0. 7223	26. 14
U $L\alpha_2$	13. 438	0. 9225	0. 7223	26. 49
Np $L\beta_1$	17. 745	0. 6986	0. 5740	19. 97
Np $L\beta_2$	16. 833	0. 7364	0. 7038	21. 07
Np $L\alpha_1$	13. 940	0. 8893	0. 7038	25. 52
Np $L\alpha_2$	13. 758	0. 9010	0. 7038	25. 86
Pu $L\beta_1$	18. 290	0. 6778	0. 5568	19. 38
Pu $L\beta_2$	17. 254	0. 7186	0. 6862	20. 56
Pu $L\alpha_1$	14. 278	0. 8682	0. 6862	24. 90
Pu $L\alpha_2$	14. 083	0. 8802	0. 6862	25. 25
Am $L\beta_1$	18. 845	0. 6578	0. 5403	18. 80
Am $L\beta_2$	17. 672	0. 7015	0. 6692	20. 06
Am $L\alpha_1$	14. 614	0. 8482	0. 6692	24. 32
Am $L\alpha_2$	14. 407	0. 8604	0. 6692	24. 67
Cm $L\beta_1$	19. 393	0. 6392	0. 5244	18. 27
Cm $L\beta_2$	18. 106	0. 6847	0. 6528	19. 58
Cm $L\alpha_1$	14. 961	0. 8286	0. 6528	23. 75
Cm $L\alpha_2$	14. 743	0. 8408	0. 6528	24. 10

Table 16.2 shows the principal *L* series X-ray emission lines of uranium, neptunium, plutonium, americium, and curium.[79]

(d) *Determination of Miscellaneous Elements.* Elements present in minor quantities have been determined in uranyl nitrate solutions. An example is the determination of 0.003 to 0.05 per cent iron in 1.2 to 18 per cent uranyl nitrate solutions.[80] The fluorescent intensity of iron depends upon the concentration of uranium in the solution: therefore, a different working curve is necessary for every 2 per cent gross increase in uranium concentration. It is necessary to know the uranium concentration in order to know which curve to use. If the solutions are too concentrated to analyze for uranium by using the uranium fluorescence lines, the uranium concentration must be related to the background of the iron lines since the background decreases as the uranium concentration increases. Both the uranium and iron are determined by measuring at only three angles. An empirical equation can be developed which eliminates the working curves so that when the uranium concentration in grams of uranium

per gram of solution and the counts per second for iron are known, it is possible to obtain the iron concentration from a single curve.

Attempts to analyze for zirconium in U_3O_8 show that concentration of the zirconium is necessary to analyze for amounts less than 200 ppm.[81] The concentration is carried out by extracting the zirconium from an HCl solution of the uranium into a TTA-xylene solution. The uranium $L\beta_6$ peak cannot be resolved from the zirconium $K\alpha$ peak; therefore all the uranium must be removed. The measurements are made directly on the TTA–xylene solution. The most consistent indication of the zirconium concentration is given by the peak (zirconium $K\alpha$) to background ratio. The samples analyzed can be in the range of 5 to 100 ppm with a limit of error for a single determination at the 95 per cent confidence level of 1.7 ppm.

Procedure.[81] *Determination of Zirconium in U_3O_8.* Ten grams of uranium is converted to UO_3 or UO_2Cl_2 and then dissolved in 30 ml of 6*M* HCl. The solution is transferred to a 125-ml separatory funnel. Twenty-two milliliters of 0.5*M* TTA-xylene is added to the funnel, and the funnel is shaken vigorously for 10 min. The bottom (aqueous) layer is drawn off and discarded. Ten milliliters of 6*M* HCl is added to the funnel, and the funnel is again shaken for 1 min. The bottom layer is again discarded, and the washing with 6*M* HCl is repeated. The organic phase is transferred to a 25-ml volumetric flask and diluted to volume with the TTA-xylene mixture. Ten milliliters of the solution is pipetted into the sample cell (Protective Closures Co. Inc., type EC–28 Caplug), and a ½-mil film of Mylar is fitted over the cell. Measurements are made in duplicate. The tungsten-target X-ray tube with a LiF crystal and a scintillation counter is operated at 60 kv and 25 ma at the zirconium $K\alpha$ peak (22.58° 2θ) to a fixed count of 512,000 and at the zirconium background (23.50° 2θ) to a count of 256,000. The $I(\text{Zr } K\alpha)/I(\text{Zr background})$ ratio is compared to the curve obtained from measuring standard solutions of zirconium in the organic solvent.

The zirconium present in uranium at a somewhat higher concentration (0.1 to 0.5 per cent) has been determined directly with no separations being made.[82] In this case the concentration of the uranium in the solution to be analyzed is kept constant at 10 mg/ml, and the zirconium is determined by measuring the ratio of the zirconium $K\alpha_1$ peak to the uranium $L\beta_2$ peak and comparing it to those of standard solutions.

Examples are reported in which several elements are determined in a solution. In a solution of waste fission products,[83] lead, strontium, and zirconium can be determined in the range of 0.01 to 1 g per liter with rubidium as the internal standard for each element. A method has been reported for determining chromium, iron, nickel, and zirconium in uranium solutions.[84] This analysis is accomplished by making a single extraction with TBP to remove the uranium. Oxalate is added to prevent extraction of zirconium. The sensitivity is 100 ppm.

X-ray analysis has also been employed where extensive separation of the individual elements being analyzed has been carried out before their determinations. One such case is the analysis of solutions of uranium-base fissium alloys for zirconium, molybdenum, ruthenium, rhodium, and palladium.[85] The uranium present causes direct interference with the molybdenum and rhodium peaks. Attenuation of the characteristic X-ray occurs in the case of zirconium and ruthenium. A separation approach appears to be simpler than a procedure for compensating for the interferences. After the sample has been dissolved in aqua regia, the palladium is extracted with dimethylglyoxime. Zirconium and rhodium are separated from the uranium, molybdenum, and ruthenium by passing the aqueous portion through an anion-exchange column. Further extractions are used to separate the individual elements before they are measured.

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