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# THE CHEMICAL AND SPECTROCHEMICAL PRODUCTION ANALYSIS OF $ThO_2$ AND $^{233}UO_2$-$ThO_2$ PELLETS FOR THE LIGHT WATER BREEDER REACTOR CORE FOR SHIPPINGPORT

(LWBR Development Program)

JUNE 1975

MASTER

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BETTIS ATOMIC POWER LABORATORY
PITTSBURGH, PENNSYLVANIA
Operated for the U. S. Energy Research and Development Administration by
WESTINGHOUSE ELECTRIC CORPORATION

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# CONTENTS

## CONTENTS (Cont)

## CONTENTS (Cont)

# CONTENTS (Cont)

# CONTENTS (Cont)

# CONTENTS (Cont)

# CONTENTS (Cont)

## CONTENTS (Cont)

# CONTENTS (Cont)

# CONTENTS (Cont)

# LIST OF ILLUSTRATIONS

# LIST OF ILLUSTRATIONS (Cont)

# LIST OF TABLES

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**The Bettis Atomic Power Laboratory has utilized wet chemical, emission spectrochemical, and mass spectrometric analytical techniques for the production analysis of the $ThO_2$ and $^{233}UO_2$-$ThO_2$ (1 to 6 w/o $^{233}UO_2$) pellets for the Light Water Breeder Reactor (LWBR) core for Shippingport. Proof of the fuel breeding concept necessitates measurement of precise and accurate chemical characterizations of all fuel pellets before core life.**

**Chemistry's efforts toward this goal are presented in three main sections: (1) general discussions relating the chemical requirements for $ThO_2$ and $^{233}UO_2$-$ThO_2$ core materials to the analytical capabilities, (2) technical discussions of the chemical and instrumental technology applied for the analysis of aluminum, boron, calcium, carbon, chloride plus bromide, chromium, cobalt, copper, dysprosium, europium, fluoride, gadolinium, iron, magnesium, manganese, mercury, molybdenum, nickel, nitrogen, samarium, silicon, titanium, vanadium, thorium, and uranium (total, trace, and uranium VI), and (3) a formal presentation of the analytical procedures as applied to the LWBR Development Program.**

# THE CHEMICAL AND SPECTROCHEMICAL PRODUCTION ANALYSIS OF $ThO_2$ AND $^{233}UO_2$-$ThO_2$ PELLETS FOR THE LIGHT WATER BREEDER REACTOR CORE FOR SHIPPINGPORT

**(LWBR Development Program)**

**J.F. Bukowski and E.D. Hollis**

## I. INTRODUCTION

The chemistry required for the production analysis of the $ThO_2$ and $^{233}UO_2$-$ThO_2$ (1 to 6 w/o $^{233}UO_2$) pellets for the Light Water Breeder Reactor (LWBR) core for Shippingport necessitated the establishment of 16 individual analytical procedures. These procedures involve the combined technologies of (1) wet chemistry, (2) optical emission spectroscopy, and (3) spark-source mass spectroscopy applied for the analysis of approximately 25 attributes. This report discusses wet chemical and optical emission spectrographic techniques.

The technology applied at the Bettis Atomic Power Laboratory for the chemical and instrumental analysis of LWBR core materials is presented and discussed. Reflected in these descriptions are the technical efforts of (1) the Bettis Analytical and Spectrochemical Analysis Laboratory and (2) the Bettis Operational Chemistry Laboratory. The technology presented includes new techniques, which were necessitated by the chemical and physical properties of the $ThO_2$ and $^{233}UO_2$-$ThO_2$ pellet materials, as well as reapplications or modifications to basic techniques that were previously applied to other nuclear materials programs at the Bettis Atomic Power Laboratory and/or throughout the industry.

Structurally, this report presents (1) a brief background discussion of the relationship, requirements, and responsibilities of Chemistry to the LWBR Development Program, (2) a discussion of the technical concepts applied in each chemical or instrumental analysis, and (3) actual copies of each analytical procedure as used during production analysis.

The mention of proprietary instruments, reagents, apparatus, or materials within this document does not imply endorsement by Westinghouse, the United States Energy Research and Development Administration, or the persons responsible for its preparation. The identification of proprietary items was done only for the convenience of the reader and for clarity of the report. Items equivalent to those mentioned may be substituted as applicable.

## II. BACKGROUND

Included in this section are the highlights of the LWBR material chemistry requirements and their relationship to the analytical responsibilities of the Bettis Chemistry Laboratories.

### A. Role of Chemistry in the LWBR Development Program

A goal of the LWBR Development Program is to develop basic technology that can be applied to confirm that the fuel utilization of light water reactors can be significantly improved. A step in this program is to show by operation of the LWBR core at Shippingport that breeding can be achieved using a $^{233}U$/thorium fuel system. A prime factor in proof of breeding is measurement of the chemical composition of the core before operation.

With this goal in mind, the vital role played by Chemistry in this program is quite obvious. A complete and accurate chemical characterization of all LWBR core fuel pellets is imperative, and high purity core components are essential. The presence of trace impurities must be minimized, and if present, these impurities must be quantitatively determined. The presence of neutron absorbing trace impurities can suppress the breeding reaction; consequently, such impurities must be identified and included in all data related to this program. Of significance is the requirement for an accurate and precise knowledge of the quantity of uranium present at the beginning of core life.

## B. Specifications

A series of specifications has been established for ensuring the production of the required core. These specifications can be categorized as (1) material specifications and (2) chemical laboratory specifications. The material specifications govern the quality of the fuel pellets, while the chemical laboratory specifications govern the quality of the analytical data obtained during core production.

The specifications most pertinent to the capabilities required of the analytical procedures discussed in this report are extracted from their individual documents and condensed in Tables 1 through 4. Tables 1 and 3 have been included only to indicate the laboratory qualification specifications to which raw material subcontractor laboratories are controlled.

The Bias Approval Limits (BAL) and Relative Precision Approval Limits (RPAL) for laboratory qualification in Tables 1 through 4 are only applicable at and above the Minimum Acceptable Reporting Values (MARV). The laboratory reports actual values between the Minimum Level of Detection (MLD) and the MARV concentrations to facilitate calculating the Neutron Poison Equivalence (NPE) required by the product specifications. MLD values are used in calculating the NPE when analytical results are less than the MLD. The total NPE of each material is computed by summing the products obtained from multiplication of the NPE factor of each listed impurity by the parts per million of that impurity present. No impurity should exceed the indicated maximum individual impurity limit specified in Tables 1 through 4.

## C. Laboratory Responsibility

To satisfy the specification requirements described in Section II.B, a quality assurance program was established which provided chemical analysis of pellets and powder for LWBR. The chemical analyses and techniques of subcontractors were verified and overinspected.

## D. Selection of Analytical Techniques

The selection of the analytical techniques utilized for the analysis of each attribute in the $ThO_2$ and $^{233}UO_2$-$ThO_2$ pellet specifications (Tables 2 and 4) was based on consideration of (1) relative efficiency, (2) precision and accuracy, and (3) sensitivity. A tabulation of the final analytical technique selected for each attribute is included in Table 5.

## E. Laboratory Facility Requirements

Due to the different radiological control requirements for $ThO_2$ and $^{233}UO_2$ materials, two types of analytical laboratory facilities were required for the complete production chemical analyses. The Analytical and Spectrochemical Analysis Laboratory applied limited confinement devices such as the box shown in Figure 1 for the chemical analysis of the $ThO_2$-bearing materials, while the Operational Chemistry Laboratory applied total confinement such as that shown in Figure 2 for the chemical analysis of the $^{233}UO_2$-bearing materials. Another comparison of the two facilities and the differing sample confinement requirements is shown in Figures 3 through 8, which show the carbon, nitrogen, and pyrohydrolysis operations of the two facilities.

The requirement for the two types of facilities resulted in the establishment of equivalent analytical procedures for both facilities and duplication of analytical equipment in the facilities. A complete set of analytical procedures for each facility is included in Appendices A through E to this report.

# III. TECHNICAL DISCUSSIONS OF ANALYTICAL PROCEDURES

## A. General

The detailed emission spectrochemical and wet chemical procedures applied by the Bettis Operational Chemistry and Analytical and Spectrochemical Laboratories for the production analysis of the $ThO_2$ and $^{233}UO_2$-$ThO_2$ pellet materials are included in Appendices A through E to this report. With this in mind, the technical discussions included in this section are intended only to present a brief procedural summary, pertinent developmental information, and the statistically determined accuracies and precisions of each procedure. Since considerable duplication resulted from applying identical technologies by both laboratories, all technical discussions are representative of this combined effort.

### 1. Pellet Grinding

For efficiency and maximum analytical accuracy, the analytical laboratories determined that pellet samples should be in a finely ground ($\approx$100 to 200 mesh) powder form prior to all chemical or spectrochemical analyses.

The grinding of the pellet samples to the prescribed consistency accomplishes (1) sample homogenization, (2) increased efficiency by reducing dissolution times for wet chemistry procedures, and (3) stabilization of spectrochemical analyses.

Initially, a totally manual technique was utilized for grinding LWBR development samples and initial LWBR $ThO_2$ production samples. This technique consisted of hand grinding with a standard type zirconium mortar and pestle as illustrated in Figure 9. The acquisition of automatic grinders, also illustrated in Figure 9, led to the current practice, which incorporates a preliminary coarse hand grinding of a pellet sample followed by a period of automatic pulverization. This automatic grinding technique is included in Appendix E.

Due to the extreme hardness of the $ThO_2$ and $^{233}UO_2$-$ThO_2$ high-fired pellets, a vigorous grinding technique is required. This results in the physical scoring of the grinding apparatus and subsequent sample contamination. Due to this unavoidable scoring and the fact that zirconium was not a attribute requiring control by the LWBR material specifications, high purity zirconium was selected as the most suitable material for the grinding operations. Only the total uranium method is affected by the trace contributions of the zirconium in the sample.

An accurate sample weight is necessary when considering the relative precision (0.25 percent) and relative bias (0.15 percent) requirements for the total uranium analysis. To eliminate sample contamination with zirconium, a Plattner mortar and pestle was chosen for grinding samples for total uranium analyses. The iron contamination from this grinding operation is removed by passing the sample vial through the magnetic field of an adjustable gap magnet. The mortar and pestle and the magnet are shown in Figure 10. (The micrometer shown is used for pellet identification only.)

After initial crushing of the pellet in either a zirconium or a Plattner mortar, agate may be used in the automatic grinding operation. Caution should be applied when using agate, since silicon contamination of the sample may result.

Other materials such as mullite, steel, and tungsten carbide were investigated and rejected for application to impurity analyses. The rejections were based on evidence that these materials contribute considerable contamination in the form of impurity elements such as aluminum, iron, nickel, chromium, and cobalt, all of which are significant to LWBR nuclear performance.

## B. Wet Chemical Procedures (see Appendices C and D)

### 1. Total Uranium (see Appendix D, Section I)

Total uranium determinations are performed on $^{233}UO_2$ powder and $^{233}UO_2$-$ThO_2$ powder or pellets. $^{233}UO_2$ powder can be dissolved in either a nitric-hydrofluoric or a phosphoric-sulfuric acid solution. $^{233}UO_2$-$ThO_2$ pellets are dissolved in a nitric-hydrofluoric acid solution, while the powder form is dissolved in a phosphoric-sulfuric acid solution.

If the sample is dissolved using the nitric-hydrofluoric acid, a mixture of the phosphoric-sulfuric acid is added. After dissolution, the nitric and hydrofluoric acids are removed by heating to strong fumes of sulfur trioxide. Samples dissolved using phosphoric-sulfuric acid are taken to strong fumes of sulfur trioxide to remove excess water present from the mixed acid. The subsequent addition of water to the cooled sample hydrolyzes any meta or pyrophosphates. The uranium is reduced to the tetravalent state using the Davies-Gray reduction method (Appendix D, Section I). Upon sample dilution, the ferric sulfate oxidizes the tetravalent uranium to the hexavalent state with a corresponding formation of ferrous iron. The ferrous iron is stoichiometrically oxidized to ferric iron by adding standard ceric to a potential of 800 to 820 millivolts (Calomel reference-platinum indicator electrode system). Ferrous ammonium sulfate is used for the back titration, and 5,6 dimethylorthophenanthroline ferrous sulfate is used as an indicator to verify the end point potential.

The analysis of samples for total uranium has been established as a two-day production operation. This excludes time necessary for grinding, salvaging, and scrapping of samples. The glove box facility, illustrated in Figure 11, was designed for the analysis of five samples, two controls, and a blank as comprising one set of analyses. The first day involves weighing and dissolution of the sample set, while the reduction, titration, and data evaluation are completed on the second day.

Duplicate control standards, with verified uranium concentrations, are analyzed with each sample set. The recovery and range of the duplicate controls are used to accept or reject all sets of data. The acceptable limits for the mean and range of the duplicate controls are 99.65 to

100.35 and 0 to 0.70, respectively. Values obtained on samples accompanying controls that fall outside of these limits are invalidated, and the sample set is reanalyzed. Control charts are maintained on a daily basis to verify day-to-day control and to indicate abnormal method variances. The samples must have a relative precision (1s) of 0.25 percent and a relative bias of 0.15 percent to meet the core specifications.

The milliequivalent weight of uranium is verified by using the appropriate isotopic assay of the $^{233}UO_2$. The isotopic abundance is determined using mass spectrometric analysis.

### 2. Nitrogen—Spectrophotometric (see Appendix C, Section I and Appendix D, Section II)

Ground samples are dissolved in a phosphoric-sulfuric acid mixture in Erlenmeyer flasks. After transferring to distillation flasks and adding sodium hydroxide to make the solutions basic, these solutions are steam distilled and the ammonia is collected in the condensate. Considering the processes used for production of $ThO_2$ and $^{233}UO_2$-$ThO_2$, that is, calcination ($ThO_2$ only) and high temperature hydrogen sintering, nitrogen as oxides is not expected to be present. Because the concentration of nitrogen in the sample is usually low, photometric absorbance measurements of the color produced by the reaction between ammonia and Nessler reagent are used for the final determination rather than a titrimetric technique. Experiences at the Bettis Laboratory have highlighted the following areas of the procedure requiring particular attention.

The selection, treatment, and use of reagents must be carefully considered with respect to purity. If the combined nitrogen contribution from the reagents used exceeds 10 to 15 micrograms, the ability to detect photometrically low levels of nitrogen with a sufficient degree of accuracy is decreased. Since numerous organic and inorganic ions interfere with the Nessler color system, all water used must be deionized.

Those areas of the procedure where nitrogen may be lost must be controlled. During dissolution, samples requiring high heat and/or lengthy solution times are to be protected using air condensers. Prior to distillation, the addition of sodium hydroxide should proceed slowly to prevent any mixing of the two distinct layers. Distillation rates should be such that the steam carrying the ammonia is condensed. Before measuring the absorbance, the distilled solutions should be Nesslerized within a reasonable length of time and color development allowed to proceed for a standard period of time.

The relative precision and relative bias of the procedure are approximately ±10 percent at the 10-ppm level.

The spectrophotometric nitrogen technique is the production analysis method used at the Bettis Laboratory by Operational Chemistry. The method discussed in the next section is applied as a part of the laboratory overinspection performed by the Analytical and Spectrochemical Analysis Laboratory.

### 3. Nitrogen—Ammonia Gas Detecting Electrode (see Appendix C, Section II)

The recent introduction of an ammonia gas-sensing electrode suggested the feasibility of utilizing it for the determination of nitrogen in LWBR fuel materials. The only significant difference from the spectrophotometric method is in the measurement technique of the nitrogen.

The electrode consists of a flat window glass electrode that is $H^+$ sensing and a reference electrode. The reference electrode is inside a plastic tube with one end closed by a unique hydrophobic membrane permeable only to ammonia gas. The plastic tube is filled with an electrolyte reactive to the ammonia gas. When the gas passes through the membrane, the chemical equilibrium of the electrolyte is shifted, causing a change in $H^+$ concentration. This change is sensed by the glass electrode, producing a definite EMF with respect to the internal reference electrode. This EMF is directly proportional to the concentration of ammonia in the sample solution after distillation. The nitrogen in samples is present as ammonium ion after dissolution and/or distillation and is converted to ammonia gas by adjustment of sample solutions to a pH of 12 or greater just prior to concentration measurements. The electrode response is linear and Nernstian from a molarity of $10^{-6}$ to $10^{-1}$, providing more than the required sensitivity to meet the detection limits specified for the LWBR fuel materials.

There is only minimal time saving using this method as compared with a spectrophotometric determination using Nessler reagent. However, there is considerable space saving for glove box operations since the measuring instrument (high impedance voltmeter) can be located outside the glovebox. There is also a further saving since the same measuring instrument can be used for fluoride and chloride plus bromide analysis.

The relative precision and relative bias are approximately ±10 percent, which is comparable with the spectrophotometric determination of nitrogen.

### 4. Trace Uranium (see Appendix C, Section III and Appendix D, Section III)

Ground samples containing microgram quantities of uranium are dissolved in a mixture of hydrofluoric and nitric acids. The sample solution is taken to dryness, the salts are dissolved in nitric acid, and the resulting solution is transferred to a polyethylene bottle with water. An acid-deficient solution of aluminum nitrate, containing tetra-n-propylammonium hydroxide, is added as a salting agent. The use of quaternary or tertiary amines as complexing agents is desirable since under these conditions thorium or the rare earths are not quantitatively extracted (Reference 1). The relative amount of each reagent in the final solution is controlled to maintain an acidity that is low enough to prevent either the decomposition of the methyl isobutyl ketone or the extraction of the thorium (Reference 1), but high enough to keep the thorium and uranium in solution.

Exactly 10.0 milliliters of methyl isobutyl ketone are added, and the uranium is extracted as the soluble tetra-n-propylammoniumuranyltrinitrate (Reference 2).

An aliquot of the organic phase is evaporated on a pellet of 98 percent sodium fluoride, 2 percent lithium fluoride in a small platinum dish, and the mixture fused into a button. The characteristic uranium fluorescence emitted from the button under ultraviolet light is measured with a fluorimeter, and the uranium value is determined from a calibration curve. The flux for each pellet should be measured as reproducibly as possible, and fusion time and fusion temperature should not vary from sample to sample.

High carbonate fluxes, pure sodium fluoride, or other sodium fluoride-lithium fluoride mixtures may be used, but the selected mixture maximizes the uranium fluorescence and allows the analysis of a large number of samples at one time. In addition, this mixture is optimal for use in the Galvanek-Morrison fluorimeter.

The relative precision and relative bias of the method are both within ±10 percent at the 3-ppm uranium level.

### 5. Thorium (see Appendix C, Section IV and Appendix D, Section IV)

Samples of $ThO_2$ may be dissolved by two different techniques: (1) dissolution with nitric-hydrofluoric acid, or (2) fusion with sodium pyrosulfate or fused sodium bisulfate. If dissolution by fusion is chosen, the particle size of the crushed thoria should be smaller than 100 mesh.

For production analysis, a nitric-hydrofluoric acid dissolution is utilized. Boric acid is added to the sample after dissolution to remove the hydrogen fluoride as boron trifluoride, thus preventing a fluoride interference in the oxalate precipitation. The solution is then evaporated to a moist paste. After dissolution of the thorium nitrate in a weak hydrochloric acid solution, thorium is precipitated as the oxalate with an excess of oxalic acid. It is then filtered, ignited to $ThO_2$, and weighed.

Precipitation with salts of oxalic acid, such as ammonium oxalate or the alkali oxalates, is undesirable since soluble and insoluble double salts may form and some thorium oxalate thus formed may dissolve (References 1 and 3). These and other reactions would compromise the validity of the results. Precipitation in a weakly acidic solution is necessary, not only to ensure the formation of a voluminous precipitate, but also to dissolve soluble oxalates of impurity elements. Under the conditions given, niobium, tantalum, the lanthanides, yttrium, and scandium precipitates are weighed as their oxides with $ThO_2$. However, the concentration of these elements in LWBR $ThO_2$ is not significant. In the presence of a large excess of oxalic acid, uranium and zirconium do not interfere. The alkaline earths and transition metals do not interfere unless present in high concentrations (Reference 1).

The nitric-hydrofluoric acid dissolution technique was utilized for production analysis since fusion dissolution requires an ammonium hydroxide precipitation, which increases analysis time. Sulfate ions present from the fusion dissolution not only prevent the quantitative precipitation of thorium as the oxalate, but also necessitate the use of higher ignition temperatures (Reference 3). Therefore, the sulfate ions must be removed by a preliminary precipitation of hydrous oxides of thorium with ammonium hydroxide. Precipitation is carried out in a hot solution (80 to 90°C) to facilitate the formation of an easily filtered, crystalline precipitate (References 1 and 3).

The relative precision and relative bias for high purity $ThO_2$ are well within ±0.5 percent.

### 6. Carbon (see Appendix C, Section V and Appendix D, Section V)

Carbon is determined by combustion of powdered samples in an induction-heated crucible at approximately 1600°C in the presence of low carbon iron, copper, or tin. This combustion converts the carbon or carbides present in the samples to carbon dioxide. The carbon dioxide is separated from the other combustion gases by gas chromatography on a molecular sieve and an alumina column using a helium carrier gas stream. The amount of carbon dioxide is determined by measuring the change in the thermal conductivity of the helium carrier gas as the carbon dioxide is eluted from the column. This measurement is made automatically, and the carbon content of the sample is read out directly in micrograms on a digital voltmeter.

Any carbon monoxide formed is converted to carbon dioxide in a heated catalyst furnace. The sulfur gases and any halides present are absorbed in a trap containing manganese dioxide and silver wire. Moisture is removed in an anhydrone trap.

All components are combined in one instrument, which is calibrated by analyzing National Bureau of Standards carbon steel standards. Carbon can be determined in the range of 10 to 2000 ppm with a relative precision and relative bias of ±10 percent based on a 0.5-gram sample.

### 7. Fluoride (see Appendix C, Section VI and Appendix D, Section VI)

Fluoride must be separated from $ThO_2$ and $^{233}UO_2$-$ThO_2$ before chemical analysis is possible. The most effective separation method is by pyrohydrolysis in an all quartz system at 1050°C with a steam flow rate of 2 milliliters per minute. The fluoride is condensed as hydrofluoric acid, and the fluoride content of the sample is determined using a fluoride specific ion electrode.

The electrode utilizes a lanthanum fluoride crystal through which only fluoride ions can migrate. The crystal is sealed into the end of a plastic tube that is filled with a reference solution. When the crystal is exposed to the solution containing fluoride ions, the ions migrate to the interior of the electrode and change the equilibrium conditions. A definite potential, proportional to the fluoride ion activity of the sample solution, is developed between the crystal and the reference solution and is measured with respect to an external reference electrode. The fluoride ion content of samples is determined from a calibration curve relating the fluoride ion concentration of standards to the measured potential. Although the electrode responds only to changes in fluoride ion activity, the fluoride ion concentration is proportional to this activity, and thus an empirical curve can be used. The determination of fluoride ion with this electrode is the most specific method for determining the activity of an ion in solution.

The only problems that can arise in electrode operation are when there is a variation in total ionic strength from sample to sample or when the fluoride ion is complexed by a cation such as aluminum. Both of these problems are resolved by use of a total ionic strength buffer that negates variations in ionic strength, preferentially complexes the ions which complex fluoride, and adjusts the pH to a range where complexation is at a minimum.

Fluoride can be determined in the range of 2 to 50 ppm with a relative precision and relative bias of ±10 percent based on a 1-gram sample.

### 8. Chloride plus Bromide (reported as chloride)—Colorimetric (see Appendix C, Section VII and Appendix D, Section VII)

Chloride and bromide must be separated from $ThO_2$ and $^{233}UO_2$-$ThO_2$ before analyses for these elements can be made. As in the case for fluoride, a pyrohydrolytic separation is used to condense the chloride as hydrochloric acid. The chloride reacts with mercuric thiocyanate, releasing thiocyanate ions since chloride forms more stable complexes with mercury than thiocyanate does. The freed thiocyanate ions in turn combine with ferric ions previously added to the solution to form the red ferric thiocyanate complex ion. The chloride plus bromide content of the samples is read from a calibration curve relating the chloride concentration of standard solutions to the measured color intensity of the ferric thiocyanate.

A potential difficulty with this method, or any trace chloride method, is chloride contamination. Such contamination is kept under control by careful handling procedures, cleaning of all apparatus, use of high purity reagents, and limiting the use of chloride-containing solutions in the immediate sample analysis area.

Chloride can be determined in the range of 3 to 50 ppm with a relative precision and relative bias of 10 to 15 percent.

This colorimetric procedure is used for production analysis by Operational Chemistry. The specific ion electrode technique for the determination of chloride and fluoride, which is discussed in the next section, is a procedure used for overinspection of Operational Chemistry by the Analytical and Spectrochemical Analysis Laboratory.

### 9. Chloride plus Bromide and Fluoride—Specific Ion Electrode (see Appendix C, Section VIII)

Chloride and fluoride are separated from $ThO_2$ and $^{233}UO_2$-$ThO_2$ by pyrohydrolysis and condensed into glacial acetic acid. The chloride is directly determined in this medium by measuring the EMF between a chloride ion electrode and a double junction reference electrode. After buffering the solution to a pH of 4.5 with sodium acetate, the fluoride concentration is measured by using a fluoride ion electrode and the same reference electrode as used for the chloride analysis.

The chloride specific ion electrode utilizes a mixed solid-state crystal of silver sulfide and silver chloride as the sensing element. The crystal responds only to silver ions; however, a small concentration of silver ions is always present due to the slight solubility of the silver chloride in the membrane. When the crystal is exposed to a solution containing chloride ions, the equilibrium at the membrane surface is shifted, causing silver ions to migrate into the crystal until a new equilibrium is established. At this time a definite EMF is produced between the outer and inner membrane surfaces. The electrode is filled with a reference solution and contains an internal reference electrode where a fixed EMF is developed. The external EMF's are measured with respect to an external reference electrode and are proportional to the chloride concentration of the sample solution.

Since the acetate medium used for chloride electrode measurements is also ideal for fluoride electrode measurements, a combined method was developed. The main problem was neutralization of the acetic acid to a pH of 4 to 5 necessary for optimum fluoride measurement conditions. This was accomplished with a 30-percent sodium acetate solution, which serves a dual function by also producing an ideally buffered medium for the fluoride specific ion electrode. The distillation system used must have no rubber in contact with the steam or water since the sulfur present in the rubber provides the most serious interference with the chloride electrode.

Relative precision and relative bias values of ±10 percent are attainable at the minimum levels of detection for chloride plus bromide and fluoride. These values are comparable with those obtained using the independent methods. However, a considerable time saving is realized with the combining of the methods.

### 10. Uranium VI (see Appendix C, Section IX and Appendix D, Section VIII)

$UO_2$ and $UO_2$-$ThO_2$ can oxidize in air by chemical combination of uranium with oxygen to form $UO_{2+x}$-$ThO_2$. Several gravimetric methods based on either reduction of the $U^{+6}$ to $U^{+4}$ or stoichiometric oxidation of the $U^{+4}$ to $U^{+6}$ have been used. However, the small weight changes produced and very large sample sizes (10 to 15 grams) required are not applicable to production analysis operations.

Polarography was found to be the most sensitive means of determining small amounts of $U^{+6}$. In the polarographic determination, the $U^{+6}$ is reduced to $U^{+4}$ at the surface of mercury drops falling from a capillary tube. At a definite voltage versus a reference electrode the diffusion current produced during this reduction is measured. This diffusion current is proportional to the concentration of $U^{+6}$ in the solution. Classical polarography with slow voltage scanning and mechanical recording of polarograms provides sufficient sensitivity for most concentrations by careful measurement, but the sensitivity limit is nearly reached at the 1.5- to 2.0-percent $UO_2$-$ThO_2$ level. A relatively new scanning technique involving a rapid voltage scan during the life of one mercury drop provides approximately a fourfold sensitivity increase. This technique uses a storage oscilloscope for recording the scan as a peak-shaped polarogram rather than the stepped polarogram of conventional polarography. The peak current is proportional to the concentration of the $U^{+6}$ in solution. In addition to improving sensitivity, this technique provides better resolution of ions, which may reduce at potentials close to $U^{+6}$. The dropping mercury electrode system is shown in Figure 12.

The main concern with the analysis is the prevention of any appreciable oxidation of the $U^{+4}$ produced during the dissolution step. Concentrated phosphoric acid will dissolve $UO_2$ and $UO_2$-$ThO_2$ with negligible oxidation of the $U^{+4}$ due to the formation of extremely stable tetravalent uranium complex ions. This is excellent for $UO_2$, but the thorium in $UO_2$-$ThO_2$ readily precipitates as a phosphate, especially with prolonged heating of the solution. A mixture of concentrated sulfuric and phosphoric acids will dissolve the material with minimal precipitation, but oxygen must be excluded since $U^{+4}$ will oxidize in the presence of oxygen in the sulfuric medium.

The relative precision and relative bias of the method are well within the requirements listed in Tables 3 and 4. The O/U ratio is determined by calculating the fraction of $U^{+6}$ present in the uranium; this fraction represents the excess oxygen over the 2.00 ratio of pure $UO_2$.

## C. Optical Emission Spectrochemical Procedures (see Appendices A and B)

### 1. Carrier Distillation and Buffer Applications

The single technology most common to all of the procedures discussed is the application of the classical carrier-distillation and/or buffered excitation spectrochemical concepts. These concepts were first described by B. F. Scribner and H. R. Mullins in 1946 (Reference 4) and have experienced considerable popularity for application to the analysis of nuclear related materials.

These spectrochemical approaches have been successfully applied to numerous nuclear materials such as zirconium, hafnium, and uranium. A brief explanation of the theory involved in a buffer and/or carrier-distillation technique is described in the following paragraphs.

The carrier is intimately blended with the powdered sample, and when this resultant mixture is heated or burned in a high amperage electrical discharge, the elements to be determined are selectively distilled from the sample after thermochemical reaction with the carrier. This elemental atomic vapor is then excited in the arc stream, and the characteristic radiations from the individual elements of interest are recorded. This process results in minimal excitation of the sample base material and, therefore, a great suppression in its production of interfering spectral lines.

Buffering is another means of suppressing the excitation of the sample base material. This can be accomplished by the carrier itself or by a specially introduced buffer material. Spectrochemical buffering provides arc stabilization through temperature control of the sample excitation. The addition of a buffer material with a boiling point below that of the sample material but higher than the boiling points of the elements of interest is desirable. Under these conditions, the temperature of the sample excitation will only reach that of the buffer boiling point and remain in that range as long as the buffer physically remains in the arc. This results in a stable sample excitation with excitation of the lower boiling impurity elements of interest, but only minimal base material excitation.

The combined buffering and carrier distillation principles are the prime factors contributing to the grouping of elements into individual procedures as shown in Appendices A and B.

### 2. Sample Granularity Requirements

Each of the emission spectrochemical procedures applied for LWBR $ThO_2$ and $^{233}UO_2$-$ThO_2$ production analysis requires the sample to be in a finely ground powder form ($\approx$ 200 mesh) prior to analysis. Specifically, this requires a powder capable of passing through a 200-mesh nylon screen after grinding. The means of achieving this consistency were previously discussed in Section III.A.1.

The 200-mesh sample consistency provides (1) an intimate blend of the sample with the carrier and/or buffer and (2) a consistent sample excitation. Both of these characteristics permit a precise and accurate distillation of the impurity elements being analyzed during spectrographic sample excitation. Inhomogeneous blending of the sample with the carrier and inconsistent sample grain size can cause a sporadic elemental evolution and eliminate the smooth evolution required for precision and accuracy.

### 3. Spectrochemical Standardization

The standards utilized for calibration of the spectrochemical procedures are all synthetically prepared and evaluated by the Bettis Laboratory. This preparation, with the exception of the standards for the analysis of the rare earth elements, is accomplished by dry-blending high purity element oxides, carbonates, metallic powders (boron only), etc. with high purity $ThO_2$ materials. This technique provides standards of a granularity similar to that of the dry ground samples to ensure similar sample excitation conditions in the spectrographic arc. The end results are precision and accuracy improvements and the minimization of potential bias situations that could arise through differences in standard and sample excitations. The rare earth standards are prepared by a solution-precipitation technique which resembles the sample dissolution technique of the rare earth procedure. The end results are samples and standards with similar excitation potentials in the spectrographic arc.

Since the $^{233}UO_2$-$ThO_2$ production samples contain varying quantities of $^{233}UO_2$ from approximately 1.2 to 6.0 w/o, the obvious question of the relative effect this $^{233}UO_2$ has on the procedures was investigated. The results of these investigations revealed no significant spectrochemical differences between pure $ThO_2$ samples and $ThO_2$ samples containing up to 10 w/o $^{233}UO_2$. Consequently, all procedures utilized for $ThO_2$ analyses are also equally applicable to $^{233}UO_2$-$ThO_2$ materials. The need to have a separate set of $^{233}UO_2$-$ThO_2$ spectrochemical standards was therefore eliminated.

A minimum of five individual standards, each represented by duplicate spectrochemical excitations, was analyzed with every group of $ThO_2$ or $^{233}UO_2$-$ThO_2$ samples. These standards are utilized to plot an analytical curve for each impurity element of interest. From these curves the sample impurity concentrations are determined. The standards utilized must include one standard containing the elements of interest at the minimum level of detection specified in Tables 1, 2, and 4. Additional standards necessary to cover the procedural scope adequately must also be included.

All sets of standards are prepared by a successive dilution technique, which begins with a high standard (containing all elements of interest at 0.5 or 1 w/o concentration levels) and is followed by a series of dilutions with high purity $ThO_2$. Each individual standard is homogenized by hand blending using a zirconium mortar and pestle followed by a period of automatic tumbling (minimum 20 minutes per standard).

After a set of standards is prepared to nominal impurity element concentrations by using high purity $ThO_2$, the elemental contents are evaluated. The standards are analyzed spectrographically in triplicate using the appropriate spectrochemical procedures (Appendices A and B). The results of the analysis of the new standards are then compared with the analysis of the previous standard set to confirm the values of the new set.

The residual concentrations of the elements of interest present in the high purity $ThO_2$ are established by a plotting-extrapolation technique. If residuals for any of the individual elements are found, they are added to the nominally calculated concentrations of the standards.

The triplicate determinations are then plotted as individual analytical curves for each of the elements and compared with an analytical plot of the previous standard set. If all analytical curves for the new and old standard sets agree within the expected precision and bias of the procedure, the new standards are accepted for routine use.

Though lengthy, the standardization practices discussed herein are considered essential since all analytical data are completely dependent on their adequacy.

### 4. Aluminum, Silicon, and Magnesium (see Appendix A, Section I and Appendix B, Section I)

Aluminum and silicon in $ThO_2$ and $^{233}UO_2$-$ThO_2$ are determined using a single procedure.

These two elements are paired due to their refractory nature and similar spectrochemical excitation characteristics. A mixture of one part barium fluoride plus one part powdered graphite is intimately blended with the sample. This blend is excited, in duplicate, using a high amperage electrical discharge. The refractory characteristics of these elements make their complete removal or distillation from the thorium and/or uranium base material difficult. Buffer techniques prove the most effective and reproducible for the excitation of these elements.

The aluminum/silicon procedure detailed in Appendix B, Section I is also applicable to the determination of magnesium. A 10-percent transmission filter must, however, be placed at the camera to decrease the intensity of the sensitive spectral lines at 2802.70 and 2795.53 angstroms.

It should be noted that magnesium may also be determined using the general impurities procedure detailed in Appendix A, Section VI.

Precision and bias were statistically evaluated using synthetically prepared standards containing aluminum, silicon, and magnesium and are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Aluminum | 75 ppm | ± 8.1% | ±0.53% |
| Silicon | 75 ppm | ± 7.9% | −2.1% |
| Magnesium | 50 ppm | ±15.2% | +5.8% |

### 5. Boron (see Appendix A, Section II and Appendix B, Section II)

The analysis for boron in $ThO_2$ and $^{233}UO_2$-$ThO_2$ is performed by a separate spectrochemical procedure. The analysis involves the intimate blending of a carrier-buffer mixture (eight parts silver chloride plus one part barium fluoride plus one part powdered graphite) with the samples and standards. The success of this carrier-buffer mixture is attributed to both carrier distillation and buffering principles. Boron is an extremely volatile element with a relatively low excitation potential. Consequently, the silver chloride present adequately performs the carrier-distillation function. The addition of the barium fluoride and graphite stabilizes the boron distillation process and increases the analytical precision.

The instrument used for boron analyses must have a high optical speed in the wavelength region of 2500 angstroms to permit detection below 0.25 ppm. Spectrographs having long optical paths may not be able to meet this level of detection. The spectrograph chosen should also have a reciprocal linear dispersion of at least 2.5 angstroms per millimeter to resolve the iron interference present on the boron 2497.73-angstrom line.

Precision and bias, established on synthetically prepared samples containing boron at the Bettis lower reporting limit, are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Boron | 0.25 ppm | ±18.5% | +6.9% |

### 6. Calcium (see Appendix A, Section III and Appendix B, Section III)

Calcium is determined utilizing the intimate blending of a carrier-buffer mixture of barium fluoride and graphite (1:1) with the powdered sample. In this procedure the addition of barium fluoride and graphite theoretically performs a combined carrier action due to the spectrochemical similarity of barium fluoride to calcium and a buffering action from the graphite.

Addition of calcium to $ThO_2$ powder was made to improve pellet characteristics. Analysis of these new powder materials verified the presence of calcium, but pellets produced from these same powders showed extremely low spectrographic calcium values. The conclusion was reached that the spectrochemical technique was not releasing the calcium from the pellet lattice. At that time, the samples were excited in 7-millimeter-deep electrodes with a 12-ampere electrical discharge for 80 seconds. Investigations indicated the need for an extension of sample excitation time from the original 80 seconds to 150 seconds to completely distill the calcium. This procedure is detailed in Appendix A, Section III.

Complete distillation of the calcium from $ThO_2$ samples has also been attained by an alternate procedure. This procedure utilizes 4-millimeter-deep sample electrodes and a 16-ampere sample excitation. This results in complete distillation of the calcium during a 105-second burn period. The procedure is detailed in Appendix B, Section III.

Precision and bias, established on synthetically prepared samples containing calcium at the Bettis lower reporting limit, are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Calcium | 25 ppm | ±18.2% | +0.36% |

### 7. Molybdenum (see Appendix A, Section IV and Appendix B, Section IV)

Molybdenum is analyzed utilizing a gallium oxide buffer type technique. The gallium oxide is intimately blended with the powdered sample, and this mixture is pressed into center-post graphite electrodes. The press-packed electrodes are then excited using a low amperage (8 amperes) electrical discharge.

Essentially, the gallium oxide buffers the sample excitation temperature below the molybdenum carbide formation stage, and the low amperage assists in maintaining this low temperature burn. The pressing technique presents the sample more readily to the excitation arc before the molybdenum can combine with the carbon from the graphite electrode. The center-post electrode stabilizes the discharge and excitation.

This carbide formation tendency and the related spectrochemical sensitivity reduction were noted at Bettis when common carriers such as silver chloride and barium fluoride were attempted, and also when higher amperage techniques were used during method development.

Precision and bias, established on synthetically prepared samples containing molybdenum at the Bettis lower reporting limit, are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Molybdenum | 5 ppm | ±20.8% | +3.2% |

### 8. Mercury (see Appendix A, Section V and Appendix B, Section V)

A separate spectrochemical procedure for the analysis of mercury is required due to the low boiling point (350°C) of this element coupled with the low LWBR reporting limit of 1 ppm.

This high volatility-low boiling property of mercury normally results in its rapid evolution from a sample during a spectrochemical excitation. When standard spectrochemical excitations are utilized, this evolution is so rapid that the emission from the mercury cannot be quantitatively measured, particularly in ppm concentrational ranges. Consequently, spectrochemical techniques are required which impede this volatilization process and extend the period that the mercury atom is present in the arc stream during spectrographic excitation.

The Bettis procedure incorporates the use of a 5-ampere a-c arc type excitation coupled with the use of a graphite boiler cap covering the sample charge in the electrode. This low amperage a-c discharge results in a relatively cool sample burn since a-c is an intermittent type discharge with a cooling period every half cycle. Since amperage increase in a spectrochemical discharge is synonomous with heat increase, the low amperage used encourages a cooler burn. The boiler cap provides gradual mercury evolution during the excitation.

Precision and bias, established on synthetically prepared samples containing mercury at the Bettis lower reporting limit, are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Mercury | 1 ppm | ±14.5% | 0% |

### 9. General Impurity Elements (Chromium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Titanium, and Vanadium) (see Appendix A, Section VI and Appendix B, Section VI)

The nine elements listed above are analyzed by a single spectrochemical procedure due to their similar spectrochemical excitation characteristics. This procedure incorporates a silver chloride carrier technique that involves the intimate blending of the silver chloride with the sample. The total excitation period established is such that all of the elements of interest are completely distilled into the spectrochemical arc stream. This process results in minimal excitation of the thorium and/or uranium base material and, thus, increased sensitivity with minimization of interfering thorium or uranium background.

Precision and bias, established on synthetically prepared samples containing all of the general impurity elements at their individual Bettis lower reporting levels, are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Chromium | 5 ppm | ±26.6% | 0 % |
| Cobalt | 2.5 ppm | ±20.8% | +13.6% |
| Copper | 5 ppm | ±28.2% | −4.2% |
| Iron | 10 ppm | ±29.9% | +6.9% |
| Magnesium | 10 ppm | ±15.8% | +4.1% |
| Manganese | 2.5 ppm | ±53.7% | +2.8% |
| Nickel | 5 ppm | ±17.8% | +3.3% |
| Titanium | 5 ppm | ±20.5% | +15.7% |
| Vanadium | 5 ppm | ±24.9% | −0.5% |

### 10. Dysprosium, Europium, Gadolinium, and Samarium (see Appendix A, Section VII and Appendix B, Section VII)

The analysis of these rare earth elements in $ThO_2$ involves a combined chemical concentration and a thorium elimination technique coupled with an emission spectrochemical analysis of the separated material.

There is a twofold need for the chemistry portion of this procedure. One need is the elimination of spectrochemical interferences from the thorium and the second is the sufficient concentration of the rare earths to ensure adequate sensitivity to meet the LWBR specification requirements. Both of these goals are accomplished by an ion-exchange separation of the rare earth elements from the thorium and by the concentration of the rare earths from a 2-gram sample onto a 10-milligram quantity of lanthanum oxide.

Lanthanum acts as a carrier to physically collect the separated trace rare earth elements. Without this carrier addition, the microquantities of the separated rare earth elements would be difficult to recover quantitatively.

The samples may be dissolved in either a nitric-hydrofluoric acid mixture or in a nitric acid media with the addition of a few drops of dilute hydrofluoric acid to catalyze the dissolution process. The samples are taken to dryness, redissolved in nitric acid, and passed through an anion exchange column. The column allows the rare earths to pass but retains the thorium. The rare earth elements and lanthanum are then precipitated as fluorides with a hydrofluoric acid addition. The fluoride precipitate is then filtered and oxidized. This oxidation step is required since the rare earth elements and lanthanum are more stable as oxides in a spectrochemical excitation than in their fluoride forms. At this stage the separations are ready for spectrochemical analysis.

The spectrochemical portion of this procedure first involves the intimate blending of the oxide separations with equal quantities of high purity powdered graphite, which acts as a buffer. One-half portions of this mixture are physically pressed into duplicate electrodes which are excited in a controlled atmosphere of 80 percent argon and 20 percent oxygen. The "atmo-jet" apparatus used for spectrographic excitation of rare earth oxides is shown in Figure 13. The argon-oxygen controlled atmosphere is utilized to reduce the formation of cyanogen (CN) bands. In the case of a rare earth analysis, these bands must be suppressed since most sensitive rare earth wavelengths are in this band region. The presence of these CN bands would seriously interfere with this analysis.

During spectrographic analysis, the lanthanum acts as an internal standard to increase the precision and accuracy of the analysis. The lanthanum internal standard is utilized in the analytical calculation portion of the procedure to compensate for any variations that may have occurred during the sample excitations.

Analytical standards containing dysprosium europium, gadolinium, and samarium are prepared by solution-precipitation techniques with each group of samples analyzed for rare earths. A total of five standards and one control sample are normally included on each spectrographic plate. The control sample, which is a production type sample spiked with the rare earth elements, is analyzed in a manner identical to that of the samples.

Analytical curves are plotted, using the analytical standards, for each of the rare earth elements. The control sample recovery values for each element obtained from these curves are used as confirmation that the production sample data from that sample set are valid.

Precision and bias were statistically evaluated for the rare earth determinations in $ThO_2$ and are as follows:

| Element | Concentration Level | Relative Precision | Relative Bias |
|---|---|---|---|
| Dysprosium | 0.42 ppm | ±14.0% | −5.4% |
| Europium | 0.11 ppm | ±16.9% | +1.9% |
| Gadolinium | 0.70 ppm | ± 9.8% | −2.5% |
| Samarium | 0.60 ppm | ±21.7% . | −0.4% |

## IV. ACKNOWLEDGMENTS

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## TABLE 1. LABORATORY QUALITY CONTROL AND MATERIAL SPECIFICATIONS FOR $ThO_2$ POWDERS

| | Laboratory Quality Control | | | | Material Quality Control | |
|---|---|---|---|---|---|---|
| **Attribute** | **RPAL** | **BAL** | **MLD** | **MARV** | **NPE** | **SPEC** |
| Thorium | 0.5% | 0.5% | N.A. | N.A. | N.A. | >87.0% |
| **Impurity** | % | % | ppm | ppm | | ppm |
| Aluminum | 25 | 25 | 75 | 100 | 0.01 | 100 |
| Boron | 25 | 25 | 0.25 | 0.5 | 30.0 | 1 |
| Calcium | 25 | 25 | 25 | 35 | 0.07 | 150 |
| Carbon | 25 | 25 | 50 | 100 | N.A. | 500 |
| Chloride + Bromide | 25 | 25 | 3 | 7.5 | 1.2 | 15 |
| Chromium | 25 | 25 | 5 | 50 | 0.07 | 80 |
| Cobalt | 25 | 25 | 2.5 | 5 | 1.0 | 10 |
| Copper | 25 | 25 | 5 | 10 | 0.09 | 10 |
| Fluoride | 25 | 25 | 10 | 10 | N.A. | 20 |
| Iron | 25 | 25 | 10 | 50 | 0.06 | 75 |
| Magnesium | 25 | 25 | 10 | 50 | 0.03 | 50 |
| Manganese | 25 | 25 | 2.5 | 5 | 0.34 | 5 |
| Mercury | 25 | 25 | 1 | 2 | 1.13 | 2 |
| Molybdenum | 25 | 25 | 5 | 25 | 0.11 | 25 |
| Nickel | 25 | 25 | 5 | 50 | 0.11 | 50 |
| Nitrogen | 25 | 25 | 10 | 15 | 0.11 | 40 |
| Silicon | 25 | 25 | 75 | 100 | 0.02 | 100 |
| Titanium | 25 | 25 | 5 | 10 | 0.16 | 15 |
| Uranium | 25 | 25 | 2 | 5 | N.A. | 10 |
| Vanadium | 25 | 25 | 5 | 10 | 0.13 | 10 |
| Dysprosium | 50 | 50 | 0.25 | 0.5 | 6.2 | 1.6 |
| Europium | 50 | 50 | 0.07 | 0.14 | 14.0 | 0.71 |
| Gadolinium | 50 | 50 | 0.25 | 0.5 | 3.2 | 3.1 |
| Samarium | 50 | 50 | 0.25 | 0.5 | 4.1 | 2.4 |

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**RPAL = Relative Precision Approval Limit**
**BAL = Bias Approval Limit**
**MLD = Minimum Level of Detection**
**MARV = Minimum Acceptable Reporting Value**
**NPE = Neutron Poison Equivalent**
**SPEC = Specification Limit**
**N.A. = Not Applicable**

## TABLE 2. LABORATORY QUALITY CONTROL AND MATERIAL SPECIFICATIONS FOR HIGH DENSITY $ThO_2$ PELLETS

| | Laboratory Quality Control | | | | Material Quality Control | |
|---|---|---|---|---|---|---|
| **Attribute** | **RPAL** | **BAL** | **MLD** | **MARV** | **NPE** | **SPEC** |
| Thorium | 0.5% | 0.5% | N.A. | N.A. | N.A. | 87.6-88.4% |
| **Impurity** | % | % | ppm | ppm | | ppm |
| Aluminum | 25 | 25 | 75 | 100 | 0.01 | 500 |
| Boron | 25 | 25 | 0.25 | 0.5 | 30.0 | 1 |
| Calcium | 25 | 25 | 25 | 35 | 0.07 | 150 |
| Carbon | 25 | 25 | 50 | 100 | N.A. | 200 |
| Chloride + Bromide | 25 | 25 | 3 | 7.5 | 1.2 | 15 |
| Chromium | 25 | 25 | 5 | 50 | 0.07 | 100 |
| Cobalt | 25 | 25 | 2.5 | 5 | 1.0 | 10 |
| Copper | 25 | 25 | 5 | 10 | 0.09 | 40 |
| Fluoride | 25 | 25 | 10 | 10 | N.A. | 20 |
| Iron | 25 | 25 | 10 | 50 | 0.06 | 300 |
| Magnesium | 25 | 25 | 10 | 50 | 0.03 | 100 |
| Manganese | 25 | 25 | 2.5 | 5 | 0.34 | 10 |
| Mercury | 50 | 50 | 1 | 2 | 1.13 | 2 |
| Molybdenum | 25 | 25 | 5 | 25 | 0.11 | 100 |
| Nickel | 25 | 25 | 5 | 50 | 0.11 | 200 |
| Nitrogen | 25 | 25 | 10 | 15 | 0.11 | 25 |
| Silicon | 25 | 25 | 75 | 100 | 0.02 | 300 |
| Titanium | 25 | 25 | 5 | 10 | 0.16 | 20 |
| Uranium | 25 | 25 | 2 | 5 | N.A. | 25 |
| Vanadium | 25 | 25 | 5 | 10 | 0.13 | 25 |
| Dysprosium | 50 | 50 | 0.25 | 0.5 | 6.2 | 1.6 |
| Europium | 50 | 50 | 0.07 | 0.14 | 14.0 | 0.71 |
| Gadolinium | 50 | 50 | 0.25 | 0.5 | 3.2 | 3.1 |
| Samarium | 50 | 50 | 0.25 | 0.5 | 4.1 | 2.4 |

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**RPAL** = Relative Precision Approval Limit
**BAL** = Bias Approval Limit
**MLD** = Minimum Level of Detection
**MARV** = Minimum Acceptance Reporting Value
**NPE** = Neutron Poison Equivalent
**SPEC** = Specification Limit
**N.A.** = Not Applicable

## TABLE 3. LABORATORY QUALITY CONTROL AND MATERIAL SPECIFICATIONS FOR $^{233}UO_2$ POWDERS

| | Laboratory Quality Control | | | | Material Quality Control | |
|---|---|---|---|---|---|---|
| **Attribute** | **RPAL** | **BAL** | **MLD.** | **MARV** | **NPE** | **SPEC** |
| Total Uranium | 0.25% | 0.15% | N.A. | N.A. | N.A. | ≥86.5 w/o |
| O/U ratio $(U^{+6})$ | 1.0 % | 1.0 % | 2.01 | 2.02 | N.A. | N.A. |
| **Impurity** | **%** | **%** | **ppm** | **ppm** | | **ppm** |
| Aluminum | 80 | 80 | 40 | 50 | 0.01 | 200 |
| Boron | 80 | 80 | 0.6 | 0.75 | 30.0 | 3 |
| Calcium | 80 | 80 | 10 | 15 | 0.07 | 50 |
| Carbon | 80 | 80 | 50 | 100 | N.A. | 500 |
| Chloride + Bromide | 80 | 80 | 6 | 7.5 | 1.2 | 15 |
| Chromium | 80 | 80 | 25 | 30 | 0.07 | 100 |
| Cobalt | 80 | 80 | 4 | 5 | 1.0 | 15 |
| Copper | 80 | 80 | 6 | 8 | 0.09 | 40 |
| Fluoride | 80 | 80 | 9 | 18 | N.A. | 30 |
| Iron | 80 | 80 | 60 | 80 | 0.06 | 400 |
| Magnesium | 80 | 80 | 20 | 25 | 0.03 | 100 |
| Manganese | 80 | 80 | 4 | 5 | 0.34 | 20 |
| Mercury | 80 | 80 | 5 | 7.5 | 1.13 | 30 |
| Molybdenum | 80 | 80 | 10 | 15 | 0.11 | 100 |
| Nickel | 80 | 80 | 20 | 30 | 0.11 | 200 |
| Nitrogen | 80 | 80 | 10 | 15 | 0.11 | 50 |
| Silicon | 80 | 80 | 70 | 100 | 0.02 | 200 |
| Titanium | 80 | 80 | 4 | 5 | 0.16 | 20 |
| Vanadium | 80 | 80 | 10 | 15 | 0.13 | 50 |
| Plutonium | 80 | 80 | 10 | 15 | N.A. | 25 |
| Thorium | 80 | 80 | 50 | 100 | N.A. | 500 |

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RPAL = Relative Precision Approval Limit
BAL = Bias Approval Limit
MLD = Minimum Level of Detection
MARV = Minimum Acceptance Reporting Value
NPE = Neutron Poison Equivalent
SPEC = Specification Limit
N.A. = Not Applicable

## TABLE 4. LABORATORY QUALITY CONTROL AND MATERIAL SPECIFICATIONS FOR $^{233}UO_2$-$ThO_2$ SINGLE-FIRED PELLETS

| | Laboratory Quality Control | | | | Material Quality Control | |
|---|---|---|---|---|---|---|
| **Attribute** | **RPAL** | **BAL** | **MLD** | **MARV** | **NPE** | **SPEC** |
| Total Uranium | 0.25% | 0.15% | N.A. | N.A. | N.A. | N.A. |
| O/U ratio $(U^{+6})$ | 4.0% | 4.0% | 2.02 | 2.02 | N.A. | N.A. |
| **Impurity** | **%** | **%** | **ppm** | **ppm** | | **ppm** |
| Aluminum | 25 | 25 | 75 | 100 | 0.01 | 500 |
| Boron | 25 | 25 | 0.25 | 0.5 | 30.0 | 1 |
| Calcium | 25 | 25 | 25 | 35 | 0.07 | 70 |
| Carbon | 25 | 25 | 50 | 100 | N.A. | 200 |
| Chloride + Bromide | 25 | 25 | 6 | 7.5 | 1.2 | 15 |
| Chromium | 25 | 25 | 5 | 50 | 0.07 | 100 |
| Cobalt | 25 | 25 | 2.5 | 5 | 1.0 | 10 |
| Copper | 25 | 25 | 5 | 10 | 0.09 | 40 |
| Fluoride | 25 | 25 | 10 | 10 | N.A. | 20 |
| Iron | 25 | 25 | 10 | 50 | 0.06 | 300 |
| Magnesium | 25 | 25 | 10 | 50 | 0.03 | 100 |
| Manganese | 25 | 25 | 2.5 | 5 | 0.34 | 10 |
| Mercury | 50 | 50 | 1 | 2 | 1.13 | 2 |
| Molybdenum | 25 | 25 | 5 | 25 | 0.11 | 100 |
| Nickel | 25 | 25 | 5 | 50 | 0.11 | 200 |
| Nitrogen | 25 | 25 | 10 | 25 | 0.11 | 50 |
| Silicon | 25 | 25 | 75 | 100 | 0.02 | 300 |
| Titanium | 25 | 25 | 5 | 10 | 0.16 | 20 |
| Vanadium | 25 | 25 | 5 | 10 | 0.13 | 25 |

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RPAL = Relative Precision Approval Limit
BAL = Bias Approval Limit
MLD = Minimum Level of Detection
MARV = Minimum Acceptable Reporting Value
NPE = Neutron Poison Equivalent
SPEC = Specification Limit
N.A. = Not Applicable

## TABLE 5. TABULATION OF PELLET TYPE ANALYZED, RANGE REQUIRED BY SPECIFICATIONS, AND TECHNIQUE SELECTED FOR EACH ATTRIBUTE AND IMPURITY

| Attribute | Pellet Type | Range Required by Specifications | Technique |
|---|---|---|---|
| Thorium | $ThO_2$ only | 87.6 to 88.4% | Wet chemistry |
| Uranium (trace) | $ThO_2$ only | 2 to 25 ppm | Wet chemistry |
| Uranium (total) | $^{233}UO_2$-$ThO_2$ only | Actual value | Wet chemistry |
| Uranium (O/U ratio) | $^{233}UO_2$-$ThO_2$ only | Actual value | Wet chemistry |
| Uranium (isotopic) | $^{233}UO_2$-$ThO_2$ only | Actual value | Mass spectrometry |

| Impurity | Pellet Type | Range Required by Specifications | Technique |
|---|---|---|---|
| Aluminum | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 75 to 500 ppm | Optical emission |
| Boron | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 0.25 to 1.0 ppm | Optical emission |
| Calcium | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 25 to 150 ppm | Optical emission |
| Carbon | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 50 to 200 ppm | Wet chemistry |
| Chloride + Bromide | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 3 to 15 ppm | Wet chemistry |
| Cobalt | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 2.5 to 10 ppm | Optical emission |
| Chromium | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 100 ppm | Optical emission |
| Copper | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 40 ppm | Optical emission |
| Fluoride | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 10 to 20 ppm | Wet chemistry |
| Iron | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 10 to 300 ppm | Optical emission |
| Magnesium | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 10 to 100 ppm | Optical emission |
| Manganese | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 2.5 to 10 ppm | Optical emission |
| Mercury | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 1.0 to 2.0 ppm | Optical emission |
| Molybdenum | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 100 ppm | Optical emission |
| Nickel | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 200 ppm | Optical emission |
| Nitrogen | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 10 to 50 ppm | Wet chemistry |
| Silicon | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 75 to 300 ppm | Optical emission |
| Titanium | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 20 ppm | Optical emission |
| Vanadium | $ThO_2$, $^{233}UO_2$-$ThO_2$ | 5 to 25 ppm | Optical emission |
| Dysprosium | $ThO_2$ only | 0.25 to 1.6 ppm | Optical emission |
| Europium | $ThO_2$ only | 0.07 to 0.71 ppm | Optical emission |
| Gadolinium | $ThO_2$ only | 0.25 to 3.1 ppm | Optical emission |
| Samarium | $ThO_2$ only | 0.25 to 2.4 ppm | Optical emission |

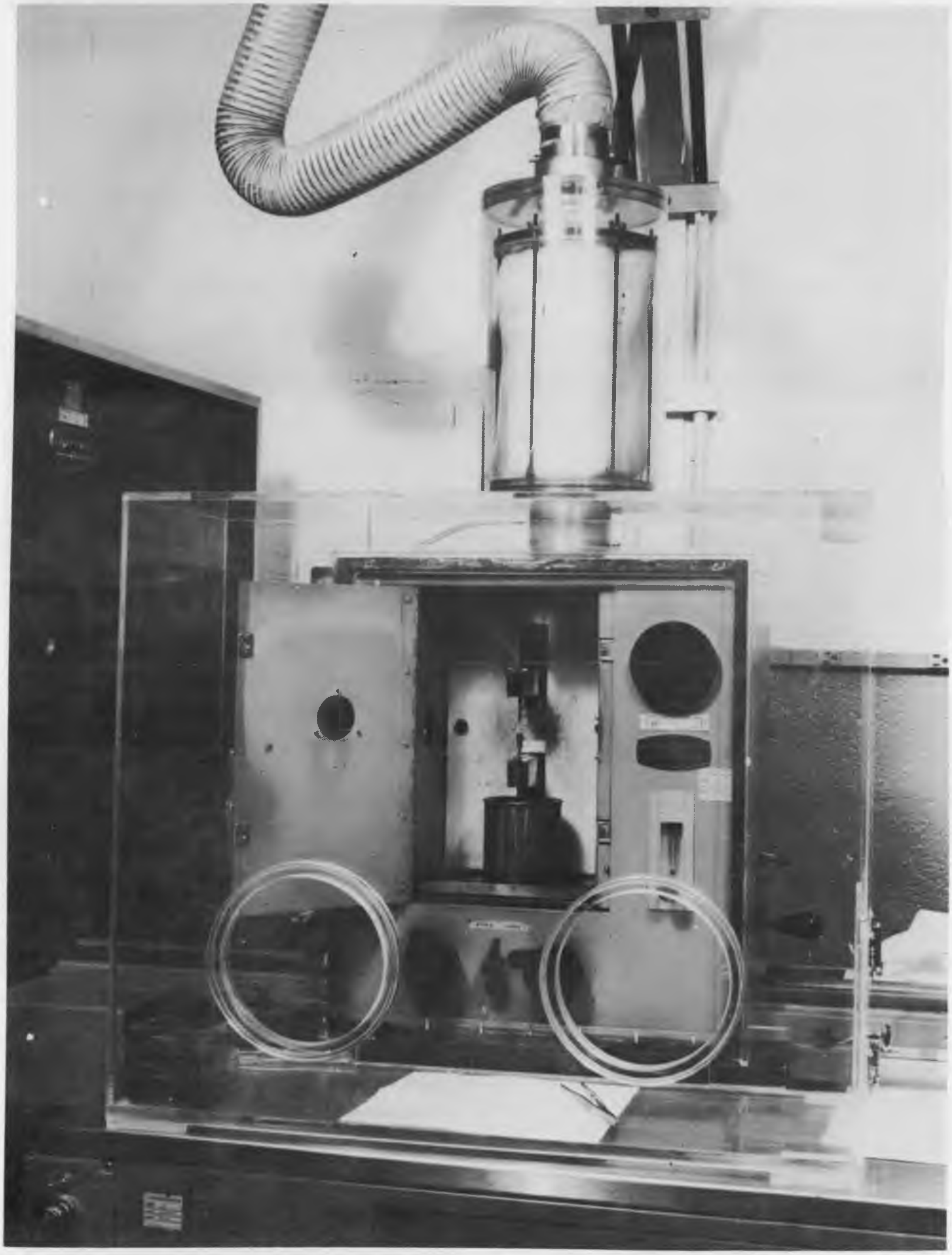

Figure 1. Limited Confinement Glove Box for Emission Spectrographic Impurity Analyses of $ThO_2$ (Analytical and Spectrochemical Analysis Laboratory)

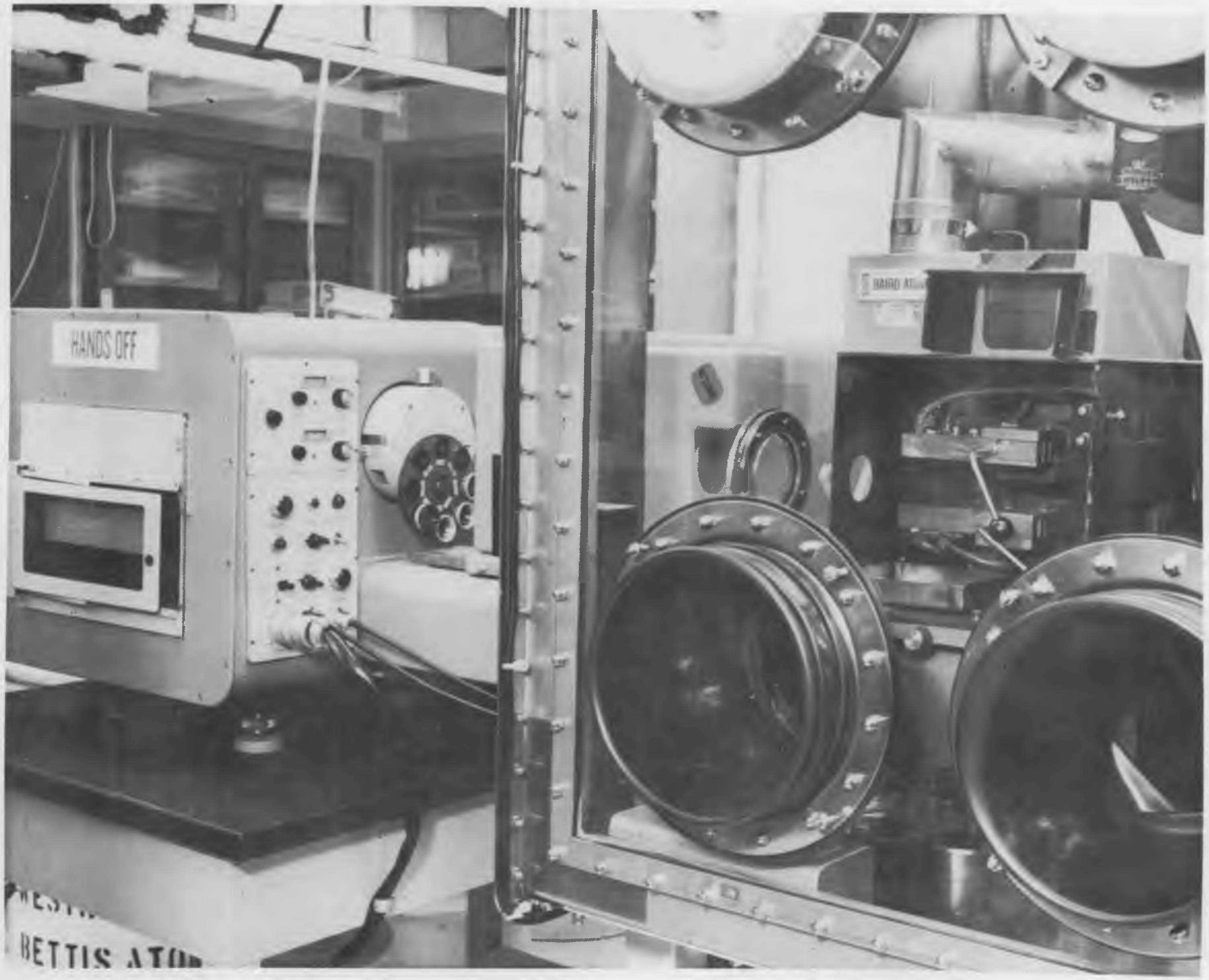

Figure 2. Total Confinement Glove Box for Emission Spectrographic Impurity Analyses of $ThO_2$ and $^{233}UO_2$-$ThO_2$ (Operational Chemistry Laboratory)

Figure 3. Instrumentation for Determination of Carbon in $ThO_2$ (Analytical and Spectrochemical Analysis Laboratory)

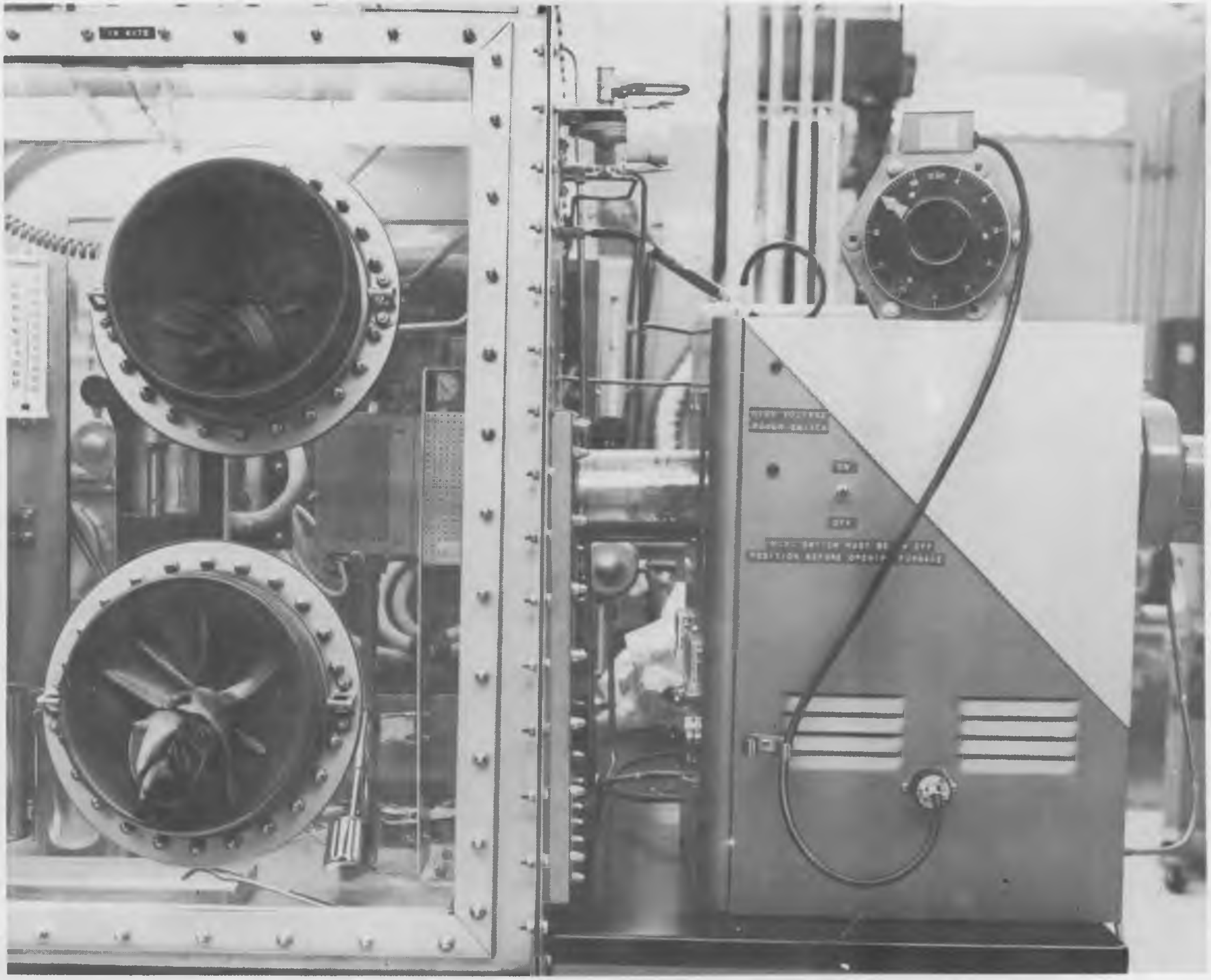

**Figure 4.** Instrumentation for Determination of Carbon in $ThO_2$ and $^{233}UO_2$-$ThO_2$ (Operational Chemistry Laboratory)

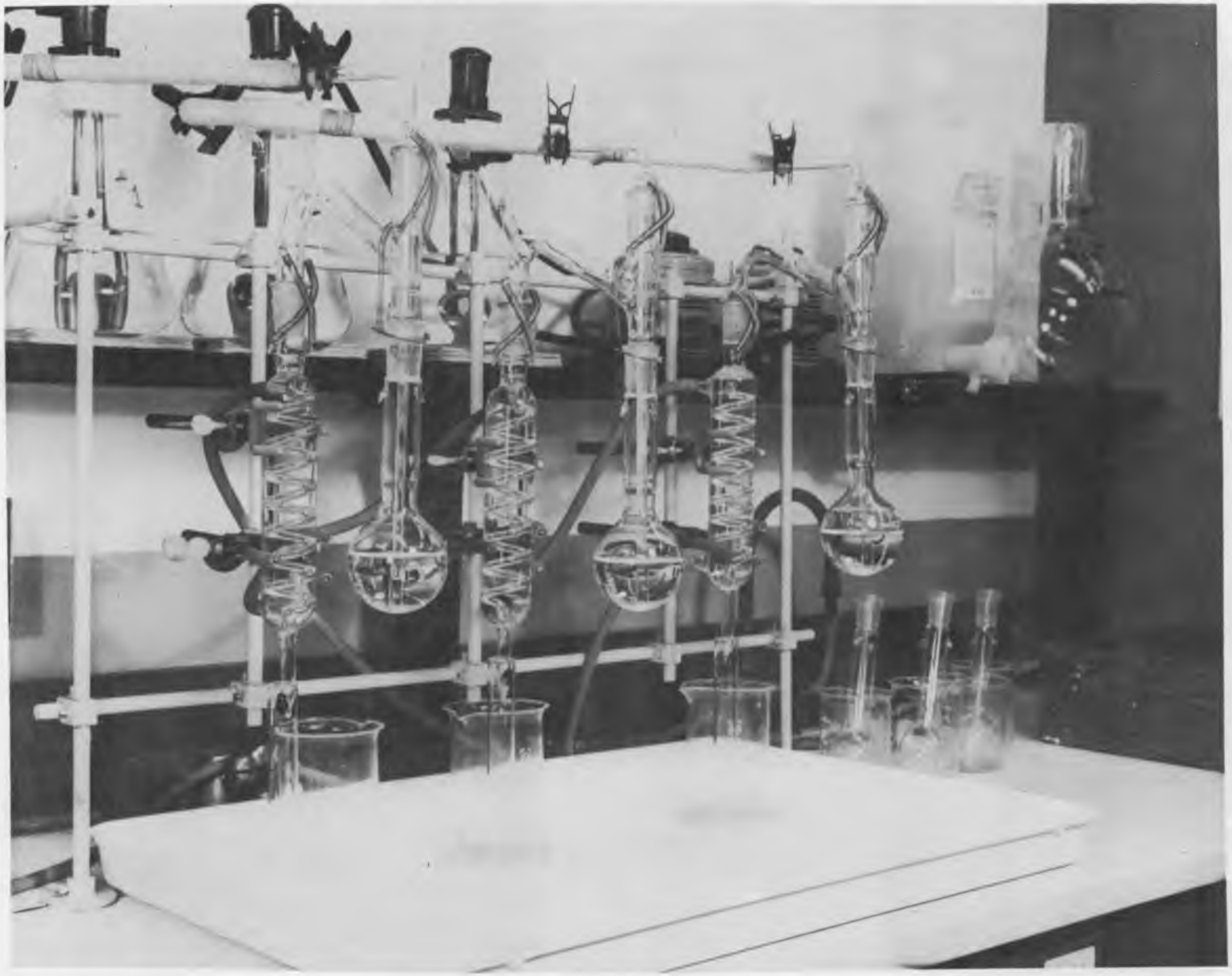

Figure 5. Distillation Apparatus for Determination of Nitrogen in $ThO_2$ (Analytical and Spectrochemical Analysis Laboratory)

Figure 6. Distillation Apparatus for Determination of Nitrogen in $ThO_2$ and $^{233}UO_2$-$ThO_2$ (Operational Chemistry Laboratory)

Figure 7. Pyrohydrolysis Unit for Steam Distillation of Chloride and Fluoride from $ThO_2$ (Analytical and Spectrochemical Analysis Laboratory)

Figure 8. Pyrohydrolysis Unit for Steam Distillation of Chloride and Fluoride from $ThO_2$ and $^{233}UO_2$-$ThO_2$ (Operational Chemistry Laboratory)

Figure 9. Zirconium Mortar and Pestle and Automatic Grinder Used for Pellet Pulverization

Figure 10. Plattner Mortar and Pestle and Adjustable Gap Magnet Used for Total Uranium Sample Preparation

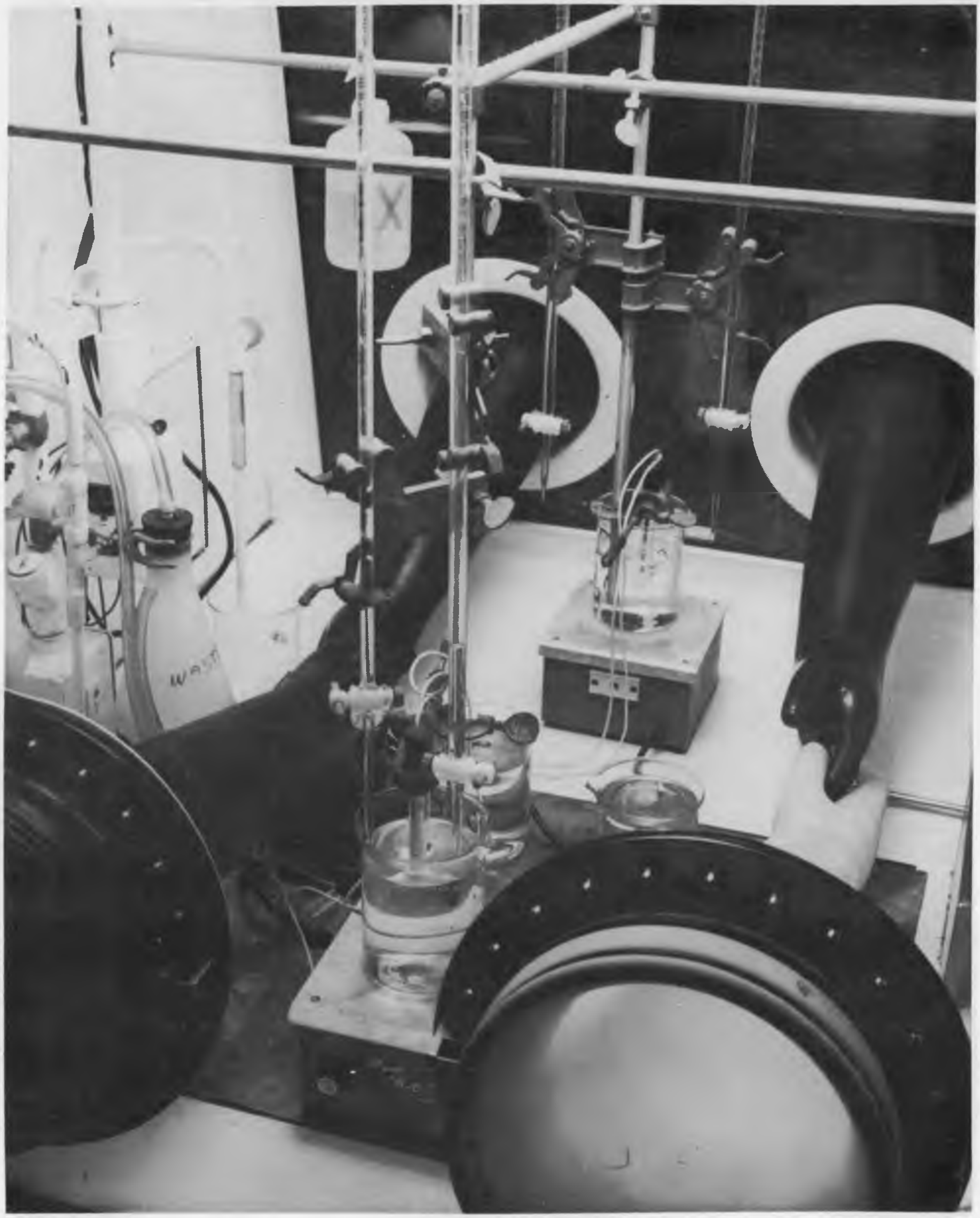

Figure 11. Titration Glove Box for Total Uranium Analyses (Operational Chemistry Laboratory)

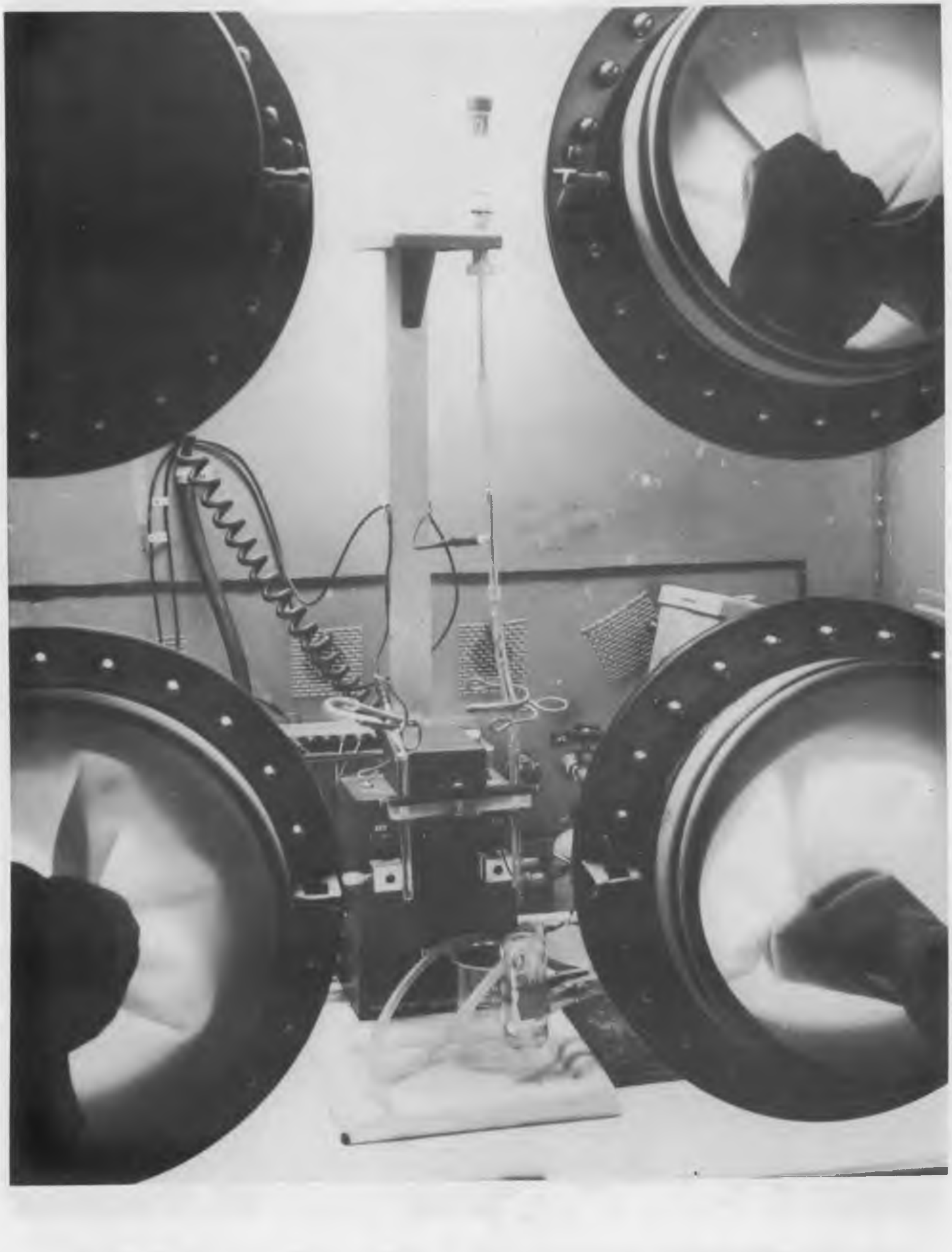

Figure 12. Dropping Mercury Electrode System for Polarographic Determination of Uranium VI in $^{233}UO_2$ and $^{233}UO_2$-$ThO_2$ (Operational Chemistry Laboratory)

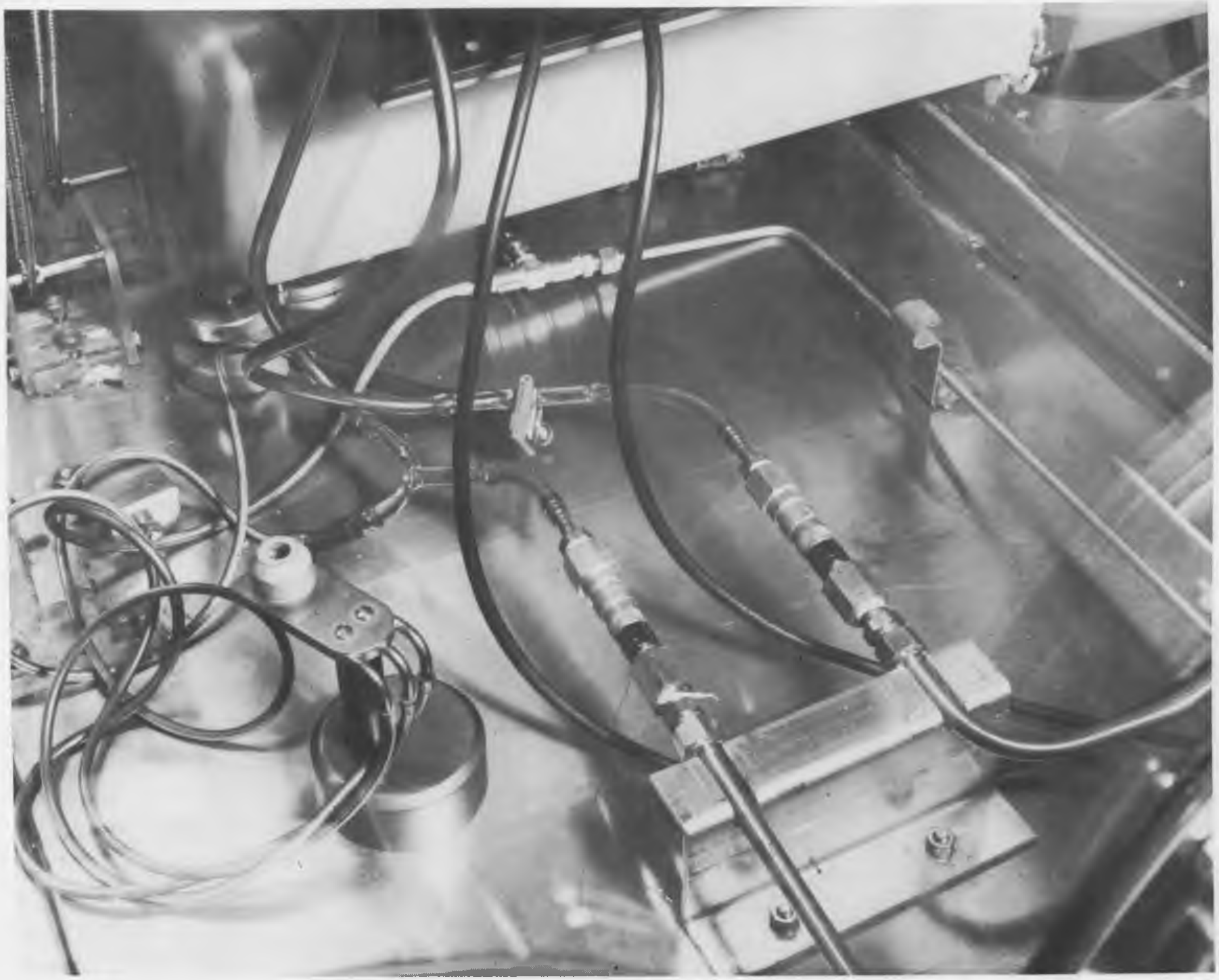

Figure 13. "Atmo-Jet" for Spectrographic Excitation of Rare Earth Oxides in a Controlled Atmosphere (Operational Chemistry Laboratory)

# APPENDIX A

## EMISSION SPECTROCHEMICAL PROCEDURES
(Analytical and Spectrochemical Analysis Laboratory)

# APPENDIX A

## EMISSION SPECTROCHEMICAL PROCEDURES
## (Analytical and Spectrochemical Analysis Laboratory)

## I. THE SPECTROCHEMICAL DETERMINATION OF ALUMINUM AND SILICON IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination of aluminum and silicon in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 25 to 500 ppm. This range can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with $BaF_2$: graphite, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curves.

### C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
   b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a resolution of 0.10 A. The plateholder will accommodate three 4-in. by 10-in. photographic plates.
2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining conditions listed in Section I.G of this Appendix.
3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.
4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.
5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.
6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.
7. **Mortar with Pestle**—Agate.

### D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section I.G of this Appendix.
2. **$ThO_2$**—High purity.
3. **Buffer Mixture**
   a. 1 part $BaF_2$—High purity.
   b. 1 part SP-1 graphite—High purity.
4. **$Al_2O_3$ and $SiO_2$**—High purity.
5. **Photographic Plates**—Eastman Kodak SA #1 or equivalent.
6. **Developer**—Eastman Kodak #D-19 or equivalent.
7. **Stop Bath**—1% acetic acid.
8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 80 mg of sample with 50 mg of the $BaF_2$: graphite in an agate mortar. Load 65 mg of this mixture into each of two 1/4-in.-diameter, 4-mm-deep, pedestal type electrodes. Repeat for the standards. Note that, due to the voluminous nature of the mixture of sample and buffer, it will be necessary to gently tap the top of the loading funnel in order to settle the electrode charge to a level below the top of the electrode. Also, before the samples are excited in the arc, each electrode charge should be center-vented by imbedding the pointed counter electrode into the sample contained in the electrode until it touches the bottom of the electrode crater, thereby creating a conical shaped void in the center of the electrode charge.

## G. Excitation and Exposure Parameters

### 1. Excitation Parameters

a. **D-c Arc**
- Current—28 amps.
- Applied voltage—220 volts.

b. **Electrode System**
- Upper (counter)—1/8-in.-diameter pointed; Met-Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.
- Lower (sample, anode)—1/4-in.-diameter pedestal type, 4-mm-deep crater, 0.03-in. wall thickness; Met Bay 1157, National Carbon SP-9024, Ultra Carbon 7010, or equivalent.
- Analytical gap—4 mm.

### 2. Exposure Conditions

Exposure conditions are presented in Table A-1.

**TABLE A-1. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF ALUMINUM AND SILICON**

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | **Wadsworth** | **Ebert Mark IV** |
| Slit width, $\mu$ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 2400 to 3000 (second order) | 2400 to 3000 (second order) |
| Wavelength setting | 5400 | 9.33° (5400), 0/72 tilt |
| Collimator mask, in. | 1/4 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | 1/4 by 5 7/8 |
| Pre-exposure time, sec | 3 | 3 |
| Exposure time, sec | 80 | 80 |
| Quartz filter at focal plane | None | None |
| Rotating sector percent transmission* | 15 | 6 |
| Arc stand lens | None | In |
| Exhaust draft (in. $H_2O$) (arc stand) | −0.06 to −0.08 | −0.06 to −0.08 |

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*Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## H. Photography and Processing

Use one calibrated Eastman Kodak SA #1 plate or equivalent on the right side of the camera for the Wadsworth spectrograph. When using the Ebert spectrograph, position the plate in the center of the camera. After exposure, process the plate in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the individual aluminum and silicon lines listed below as well as the transmission values for their adjacent backgrounds.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Aluminum | 2575.10 | 25 to 500 |
| Silicon | 2519.21 | 50 to 500 |

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of each element in each sample by referring its average corrected relative intensity to the appropriate standard curve.

## L. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix A, Section VI
2. Appendix E, Section V
3. Appendix E, Section VI
4. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of aluminum and silicon in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section I.

# II. THE SPECTROCHEMICAL DETERMINATION OF BORON IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of boron in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 0.25 to 5.0 ppm. This range can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

## B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with $AgCl$-$BaF_2$-$C$, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Hilger, large Littrow instrument or equivalent with quartz optics.
2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining conditions listed in Section II.G of this Appendix.
3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.
4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section II.G of this Appendix.

2. **$ThO_2$**—High purity.

3. **Carrier Mixture**
   a. 8 parts AgCl—High purity.
   b. 1 part $BaF_2$—High purity.
   c. 1 part C—High purity.

4. **Powdered Boron Metal**—Boron metal must be assayed for total boron before every standard preparation.

5. **Photographic Plates**—Eastman Kodak SA #1 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix. Suggested boron levels are 0.25, 0.50, 1.0, 2.5, and 5.0 ppm. It is essential that extensive hand grinding and blending (0.5 hour) accompany each dilution step. The powdered boron metal should be reduced to a particle size of 20 microns or less prior to distribution in the $ThO_2$ so that a statistically significant number of particles is ensured for each electrode charge.

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 135 mg of sample with 15 mg of $AgCl\text{-}BaF_2\text{-}C$ in an agate mortar. Load 75 mg of this mixture into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards.

## G. Excitation and Exposure Parameters

1. **Excitation Parameters**

   a. **D-c Arc**
      - Current—9 amps.
      - Applied voltage—220 volts.

   b. **Electrode System**
      - Upper (counter)—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.
      - Lower (sample, anode)—1/4-in.-diameter pedestal type, 7-mm-deep crater, 0.03-in. wall thickness; Met Bay S-3, National Carbon L-3718, Ultra Carbon 1998, or equivalent.
      - Analytical gap—4 mm.

2. **Exposure Conditions**

Exposure conditions are presented in Table A-2.

TABLE A-2. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF BORON

| | Hilger-Littrow Spectrograph |
|---|---|
| Slit width, $\mu$ | 15 |
| Slit height, mm | 1.5 |
| Spectral region, A | 2100 to 2650 |
| Wavelength setting | -- |
| Camera mask, mm | 3 |
| Collimator mask, in. | None |
| Exposure time, sec | 26 |

**TABLE A-2. (Cont)**

| | Hilger-Littrow Spectrograph |
|---|---|
| Rotating sector percent transmission* | 50 |
| Exterior lens | 1025 spherical, focal length 300 mm, located at the slit |
| Arc stand lens | None |
| Felt mask | None |
| Exhaust draft (in. $H_2O$) (arc stand) | None |

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*Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## H. Photography and Processing

Use one calibrated Eastman Kodak SA #1 plate or equivalent. After exposure, process the plate in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the boron line listed below as well as the transmission values for its adjacent background.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Boron | 2497.73 | 0.25 to 5 |

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of boron in each sample by referring its average corrected relative intensity to the standard curve.

## L. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix A, Section VI
2. Appendix E, Section V
3. Appendix E, Section VI
4. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of boron in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section II.

# III. THE SPECTROCHEMICAL DETERMINATION OF CALCIUM IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of calcium in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 20 to 1000 ppm. This range can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

## B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with $BaF_2$: graphite, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
   b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a resolution of 0.10 A. The plateholder will accommodate three 4-in. by 10-in. photographic plates.

2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining conditions listed in Section III.G of this Appendix.

3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.

4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section III.G of this Appendix.

2. **$ThO_2$**—High purity.

3. **Buffer Mixture**
   a. 1 part $BaF_2$—High purity.
   b. 1 part SP-1 graphite—High purity.

4. **$CaCO_3$**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #1 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 80 mg of sample with 20 mg of the $BaF_2$: graphite in an agate mortar. Load 50 mg of this mixture into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards.

## G. Excitation and Exposure Parameters

1. **Excitation Parameters**

   a. **D-c Arc** $\begin{cases} \text{Current—12 amps.} \\ \text{Applied voltage—220 volts.} \end{cases}$

**b. Electrode System**

- Upper (counter)—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.
- Lower (sample, anode)—1/4-in.-diameter pedestal type, 7-mm-deep crater, 0.03-in. wall thickness; Met Bay S-3, National Carbon L-3718, Ultra Carbon 1998, or equivalent.
- Analytical gap—4 mm.

### 2. Exposure Conditions

Exposure conditions are presented in Table A-3.

## H. Photography and Processing

Use two calibrated Eastman Kodak SA #1 plates or equivalent. When using the Ebert spectrograph, position one plate in the center and one on the left side of the camera. After exposure, process the plates in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the individual calcium lines listed below as well as the transmission values for their adjacent backgrounds.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Calcium | 3933.67 | 20 to 200 |
| Calcium | 3158.87 | 100 to 1000 |

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

### TABLE A-3. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF CALCIUM

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Slit width, $\mu$ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 3100 to 4300 (second order) | 3100 to 4300 (second order) |
| Wavelength setting | 7400 | 11.76° (6800), 1/20 tilt |
| Collimator mask, in. | 1/2 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | None |
| Pre-exposure time, sec | 3 | 3 |
| Exposure time, sec | 150 | 150 |
| Quartz filter at focal plane | 10% at Ca 3933.67 A | 10% at Ca 3933.67 A |
| Rotating sector percent transmission* | 5 | 5 |
| Arc stand lens | None | In |
| Exhaust draft (in. $H_2O$) (arc stand) | −0.06 to −0.08 | −0.06 to −0.08 |

---

*Filter settings may vary with passage of time, atmospheric conditions, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of calcium in each sample by referring its average corrected relative intensity to the standard curve.

## L. References

References to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix A, Section VI
2. Appendix E, Section V
3. Appendix E, Section VI
4. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of calcium in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section III.

# IV. THE SPECTROCHEMICAL DETERMINATION OF MOLYBDENUM IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of molybdenum in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 5 to 500 ppm. This range can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

## B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with $Ga_2O_3$, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
   b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a resolution of 0.10 A. The plateholder will accommodate three 4-in. by 10-in. photographic plates.

2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining conditions listed in Section IV.G of this Appendix.

3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.

4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.

7. **Mortar and Pestle**—Agate.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section IV.G of this Appendix.

2. **$ThO_2$**—High purity.

3. **$Ga_2O_3$**—High purity.
4. **$MoO_3$**—High purity.
5. **Photographic Plates**—Eastman Kodak SA #1 or equivalent.
6. **Developer**—Eastman Kodak #D-19 or equivalent.
7. **Stop Bath**—1% acetic acid.
8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 50 mg of sample with 50 mg of $Ga_2O_3$ in an agate mortar. Load 50 mg of this mixture into each of two 1/8-in.-diameter center-post electrodes. Repeat for the standards.

## G. Excitation and Exposure Parameters

### 1. Excitation Parameters

**a. D-c Arc**
- Current—8 amps.
- Applied voltage—220 volts.

**b. Electrode System**
- Upper (counter)—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.
- Lower (sample, anode)—1/8-in.-diameter cratered center post; Ultra Carbon 5985 or equivalent.
- Analytical gap—4 mm.

### 2. Exposure Conditions

Exposure conditions are presented in Table A-4.

**TABLE A-4. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF MOLYBDENUM**

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Slit width, μ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 2750 to 3400 (second order) | 2800 to 3400 (second order) |
| Wavelength setting | 6800 | 10.72° (6200), 1/0 tilt |
| Collimator mask, in. | 3/8 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | 1/4 by 5 7/8 |
| Pre-exposure time, sec | 3 | 3 |
| Exposure time, sec | 60 | 60 |
| Quartz filter at focal plane | None | None |
| Rotating sector percent transmission* | 100 | 100 |
| Arc stand lens | None | In |
| Exhaust draft (in. $H_2O$) (arc stand) | −0.06 to −0.08 | −0.06 to −0.08 |

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*Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## H. Photography and Processing

Use one calibrated Eastman Kodak SA #1 plate or equivalent on the right side of the camera for the Wadsworth spectrograph. When using the Ebert spectrograph, position the plate in the center of the camera. After exposure, process the plate in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the individual molybdenum lines listed below as well as the transmission values for their adjacent backgrounds.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Molybdenum | 3170.35 | 5 to 50 |
| Molybdenum | 3280.83 | 25 to 500 |

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of molybdenum in each sample by referring its average corrected relative intensity to the standard curve.

## L. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix A, Section VI
2. Appendix E, Section V
3. Appendix E, Section VI
4. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of molybdenum in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section IV.

# V. THE SPECTROCHEMICAL DETERMINATION OF MERCURY IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of mercury in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 1 to 10 ppm. This range can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

## B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with AgCl and loaded into sample graphite electrodes with a boiler cap placed on each electrode, and duplicate exposures are made utilizing a-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
   b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a resolution of 0.10 A. The plateholder will accommodate three 4 in. by 10-in. photographic plates.
2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console,

Model KE-1234 or equivalent, capable of obtaining conditions listed in Section V.G of this Appendix.

3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.

4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section V.G of this Appendix.

2. **$ThO_2$**—High purity.

3. **AgCl**—High purity.

4. **HgO**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

All standards are prepared on the basis of metal (Hg) in total oxide ($ThO_2$). Prepare a master synthetic standard by dry grinding oxide weights in accordance with Table A-5. Uranium dioxide is not included in the preparation of standards for this method because up to 10 w/o $UO_2$ has no influence on spectral response.

From the master standard (5000 ppm), make a series of successive dilutions in accordance with Table A-6.

### TABLE A-5. COMPOSITION OF MASTER SYNTHETIC MERCURY STANDARD

| Master Standard (5000 ppm) |
|---|
| 0.0540 gram HgO |
| 9.9460 grams $ThO_2$ |
| 10.0000 grams Total |

### TABLE A-6. MASTER STANDARD DILUTION IN SYNTHETIC MERCURY STANDARD PREPARATION

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 1 | 500 | 0.5000 gram of Master Standard<br>4.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 2 | 250 | 2.5000 grams of Standard #1<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 3 | 100 | 2.0000 grams of Standard #2<br>3.0000 grams of $ThO_2$<br>5.0000 grams Total |
| 4 | 50 | 2.5000 grams of Standard #3<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 5 | 25 | 2.5000 grams of Standard #4<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |

TABLE A-6. (Cont)

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 6 | 10 | 2.0000 grams of Standard #5<br>3.0000 grams of $ThO_2$<br>5.0000 grams Total |
| 7 | 5 | 2.5000 grams of Standard #6<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 8 | 2.5 | 2.5000 grams of Standard #7<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 9 | 1 | 2.0000 grams of Standard #8<br>3.0000 grams of $ThO_2$<br>5.0000 grams Total |

**NOTE**

*Uranium dioxide is not included in the preparation of standards for this method because up to 10 w/o $UO_2$ has no influence on spectral response.*

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 350 mg of sample with 50 mg of AgCl in an agate mortar. Load 200 mg of this mixture into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards. (If samples and/or standards appear moist, dry under a heat lamp for approximately 15 minutes.) Place a boiler cap on top of each electrode.

## G. Excitation and Exposure Parameters

### 1. Excitation Parameters

a. **A-c Arc**

Current—5 amps.

Applied voltage—2400 volts.

b. **Electrode System**

Upper (counter—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.

Lower (sample, anode)—1/4-in.-diameter pedestal type, 7-mm-deep crater, 0.03-in. wall thickness; Met Bay S-3, National Carbon L-3718, Ultra Carbon 1998, or equivalent.

Boiler caps—Met Bay BC-1, National Carbon L-3715, Ultra Carbon 300, or equivalent.

Analytical gap—4 mm.

2. Exposure Conditions

Exposure conditions are presented in Table A-7.

## H. Photography and Processing

Use one calibrated Eastman Kodak SA #3 plate or equivalent on the right side of the camera for the Wadsworth spectrograph. When using the Ebert spectrograph, position the plate in the center of the camera. After exposure, process the plate in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the mercury line listed below as well as the transmission values for its adjacent background.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Mercury | 2536.52 | 1 to 10 |

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate

TABLE A-7. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF MERCURY

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Slit width, $\mu$ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 2400 to 3000<br>(second order) | 2250 to 2850<br>(second order) |
| Wavelength setting | 6000 | 8.81° (5100),<br>0/62 tilt |
| Collimator mask, in. | 1/2 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | 1/2 by 5 7/8 |
| Pre-exposure time, sec | 2 | 2 |
| Exposure time, sec | 30 | 30 |
| Quartz filter at focal plane | None | None |
| Rotating sector percent transmission* | 100 | 100 |
| Arc stand lens | None | None |
| Exhaust draft (in. $H_2O$) (arc stand) | −0.06 to −0.08 | −0.06 to −0.08 |

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*Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of mercury in each sample by referring its average corrected relative intensity to the standard curve.

## L. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section V
2. Appendix E, Section VI
3. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of mercury in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section V.

# VI. THE SPECTROCHEMICAL DETERMINATION OF SELECTED IMPURITIES IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of the elements listed in Table A-8 in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration ranges listed in the table.

The ranges given in Table A-8 can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

TABLE A-8. TABULATION OF IMPURITIES THAT CAN BE SPECTROCHEMICALLY DETERMINED BY THE PROCEDURE OF APPENDIX A, SECTION VI

| Element | Concentration Range (ppm) |
|---|---|
| Chromium | 2.5 to 250 |
| Cobalt | 2.5 to 25 |
| Copper | 2.5 to 50 |
| Iron | 5 to 1000 |
| Magnesium | 2.5 to 100 |
| Manganese | 2.5 to 25 |
| Nickel | 2.5 to 50 |
| Titanium | 2.5 to 50 |
| Vanadium | 2.5 to 25 |

## B. Summary of Method

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground to a consistency capable of passing through a 200-mesh sieve prior to analysis. Portions of the samples are intimately mixed with AgCl, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curves.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
   b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a resolution of 0.10 A. The plateholder will accommodate three 4 in. by 10-in. photographic plates.

2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining conditions listed in Section VI.G of this Appendix.

3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.

4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

6. **Analytical Balances**—Mettler "Gram-Atic Balance" and Roller-Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section VI.G of this Appendix.

2. **$ThO_2$**—High purity.

3. **AgCl**—High purity.

4. **Oxides of Impurity Elements**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Synthetic Standards

All standards are prepared on the basis of metal in total oxide ($ThO_2$). Prepare a master synthetic standard by dry grinding oxide weights in accordance with Table A-9. Uranium dioxide is not included in the preparation of standards for this method because up to 10 w/o $UO_2$ has no influence on spectral response.

TABLE A-9. COMPOSITION OF MASTER SYNTHETIC IMPURITY STANDARDS (1 w/o Impurities)

| Impurity | Oxide Form | Conversion Factor | Oxide Added (grams) |
|---|---|---|---|
| Aluminum | $Al_2O_3$ | 1.8895 | 0.189 |
| Boron | Pure metal | 1.0526 (95%) | 0.010* |
| Calcium | $CaCO_3$ | 2.4970 | 0.250 |
| Chromium | $Cr_2O_3$ | 1.4616 | 0.146 |
| Cobalt | $Co_3O_4$ | 1.3620 | 0.136 |
| Copper | CuO | 1.2518 | 0.125 |
| Iron | $Fe_2O_3$ | 1.4297 | 0.143 |
| Magnesium | MgO | 1.6579 | 0.166 |
| Manganese | $Mn_3O_4$ | 1.3884 | 0.139 |
| Molybdenum | $MoO_3$ | 1.5003 | 0.150 |
| Nickel | NiO | 1.2726 | 0.127 |
| Silicon | $SiO_2$ | 2.1392 | 0.214 |
| Titanium | $TiO_2$ | 1.6681 | 0.167 |
| Vanadium | $V_2O_5$ | 1.7851 | 0.179 |
| | | Total impurities added | 2.141 |

**Master Standard (10,000 ppm)**

2.141 grams of impurity oxides
7.859 grams of $ThO_2$
10.000 grams Total

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*Concentration of boron is one-tenth that of other impurities in the standards.

From the master standard (10,000 ppm), make a series of successive dilutions in accordance with Table A-10.

## F. Sample and Charge Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Mix 140 mg of sample with 30 mg of AgCl in an agate mortar. Load 85 mg of this mixture into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards.

## G. Excitation and Exposure Parameters

### 1. Excitation Parameters

a. **D-c Arc**
- Current—12 amps.
- Applied voltage—220 volts.

**TABLE A-10. MASTER STANDARD DILUTION IN SYNTHETIC IMPURITY STANDARD PREPARATION**

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 1 | 1000 | 2.000 grams of Master Standard<br>18.000 grams of $ThO_2$<br>20.000 grams Total |
| 2 | 500 | 10.000 grams of Standard #1<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 3 | 250 | 10.000 grams of Standard #2<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 4 | 100 | 8.000 grams of Standard #3<br>12.000 grams of $ThO_2$<br>20.000 grams Total |
| 5 | 50 | 10.000 grams of Standard #4<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 6 | 25 | 10.000 grams of Standard #5<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 7 | 10 | 8.000 grams of Standard #6<br>12.000 grams of $ThO_2$<br>20.000 grams Total |
| 8 | 5 | 10.000 grams of Standard #7<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 9 | 2.5 | 10.000 grams of Standard #8<br>10.000 grams of $ThO_2$<br>20.000 grams Total |

**NOTE**

*Because of the expected impurity level of boron in the samples, the concentration is one-tenth that of the other impurities in the standards.*

**NOTE**

*Uranium dioxide is not included in the preparation of standards for this method because up to 10 w/o* $UO_2$ *has no influence on spectral response.*

**b. Electrode System**

Upper (counter)—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.

Lower (sample, anode)—1/4-in.-diameter pedestal type, 7-mm-deep crater, 0.03-in. wall thickness; Met Bay S-3, National Carbon L-3718, Ultra Carbon 1998, or equivalent.

Analytical gap—4 mm.

### 2. Exposure Conditions

Exposure conditions are presented in Table A-11.

## H. Photography and Processing

Use two calibrated Eastman Kodak SA #3 plates or equivalent. When using the Ebert spectrograph, place one plate in the center and one on the left side of the camera. After exposure, process the plates in accordance with the procedure described in Appendix E, Section VI.

## I. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values for the individual lines listed below as well as the transmission values for their adjacent backgrounds.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Chromium | 2835.63 | 2.5 to 100 |
| Chromium | 2843.25 | 5 to 250 |
| Chromium | 3021.56 | 5 to 250 |
| Cobalt | 3405.12 | 2.5 to 25 |
| Copper | 3247.54 | 2.5 to 50 |
| Iron | 2966.90 | 5 to 100 |
| Iron | 2635.80 | 100 to 1000 |
| Magnesium | 2776.69 | 2.5 to 100 |
| Manganese | 2801.06 | 2.5 to 25 |
| Nickel | 3101.55 | 2.5 to 50 |
| Titanium | 3371.45 | 2.5 to 50 |
| Vanadium | 3185.39 | 2.5 to 25 |

### TABLE A-11. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF SELECTED IMPURITIES

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Slit width, $\mu$ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 2500 to 3700<br>(second order) | 2525 to 3725<br>(second order) |
| Wavelength setting | 6250 | 9.76° (5650),<br>0/81 tilt |
| Collimator mask, in. | 1/2 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | 1 by 5 7/8 |
| Pre-exposure time, sec | 2 | 2 |
| Exposure time, sec | 60 | 60 |
| Quartz filter at focal plane | 10% at Cu<br>3247.54 A | 10% at Cu<br>3247.54 A |
| Rotating sector percent transmission* | 20 | 8 |
| Arc stand lens | None | In |
| Exhaust draft (in. $H_2O$) (arc stand) | −0.06 to −0.08 | −0.06 to −0.08 |

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*Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## J. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

## K. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot an analytical curve on log-log paper using the average corrected relative intensity of each standard versus its respective elemental concentration. Obtain the concentration of each element in each sample by referring its average corrected relative intensity to the appropriate standard curve.

## L. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section V
2. Appendix E, Section VI
3. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of selected impurities in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix B, Section VI.

# VII. THE SPECTROCHEMICAL DETERMINATION OF SELECTED RARE EARTHS IN $ThO_2$ USING A LANTHANUM OXIDE CARRIER-INTERNAL STANDARD

## A. Scope

This procedure describes the spectrochemical determination of the rare earths listed in Table A-12 in $ThO_2$ in the concentration ranges listed in the table.

The ranges given in Table A-12 can be expanded through selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $La_2O_3$.

**TABLE A-12. TABULATION OF RARE EARTH ELEMENTS THAT CAN BE SPECTROCHEMICALLY DETERMINED BY THE PROCEDURE OF APPENDIX A, SECTION VII**

| Element | Concentration Range (ppm) |
|---|---|
| Dysprosium | 0.25 to 8.00 |
| Europium | 0.07 to 4.00 |
| Gadolinium | 0.25 to 8.00 |
| Samarium | 0.25 to 8.00 |

## B. Summary of Method

The sample is dissolved in nitric acid with dilute hydrofluoric acid added as a catalyst and evaporated to dryness. After dissolution of the residue, the sample is passed through an anion exchange column that retains the thorium but allows the rare earths to pass. A fluoride precipitation using a lanthanum carrier separates the rare earths from the tramp elements. After ignition, the samples are intimately mixed with graphite and duplicate exposures are made in an argon-oxygen atmosphere utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities are obtained from the emulsion calibration curve, relative intensity ratios are calculated and a standard curve is prepared by plotting the relative intensity ratios of the standards versus concentration on log-log paper. The sample rare earth concentrations are then obtained by referring their relative intensity ratios to the standard curves.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:
    a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.
    b. 3.4-meter Jarrell-Ash Mark IV with a 15,000 lines per inch grating in an Ebert mounting or equivalent. The second order linear dispersion is 2.5 A/mm with a

resolution of 0.10 A. The plateholder will accommodate three 4-in. by 10-in. photographic plates.

2. **Excitation Source**—National Spectrographic Laboratories "Spec Power" console, Model KE-1234 or equivalent, capable of obtaining the conditions listed in Section VII.J of this Appendix.
3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 21-050, National Spectrographic Laboratories microphotometer, Model XM-102, or equivalent.
4. **Calculator**—Applied Research Laboratories Dunn Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.
5. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.
6. **Analytical Balances**—Mettler "Gram-Atic Balance," Federal Pacific Electric "Precision Balance," Model LG, Roller-Smith "Precision Balance," or equivalent.
7. **Muffle Furnace**—Hoskins or equivalent with quartz liner.
8. **Hot Plates**—Lindberg or equivalent.
9. **Suction Filter Apparatus**—Fabricated plastic Millipore or equivalent.
10. **Clinical Centrifuge**—International Equipment, Model CL or equivalent.
11. **Centrifuge Tubes**—50-ml plastic.
12. **Beakers**—150- and 400-ml Pyrex or equivalent and 250-ml platinum with lids.
13. **Graduated Cylinders**—100- and 250-ml Pyrex or equivalent and 25-ml polypropylene.
14. **Calibrated Pipettes**—Class A.
15. **Ion-Exchange Column**—1-in. inside diameter by 24 in. long.
16. **Crucibles**—20-ml platinum with lids.
17. **Mortar with Pestle**—Agate.
18. **Atmo-Jet**—Zeebac or equivalent.

## D. Reagents and Materials

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for standard preparations and dilution of all reagents.
2. **Nitric Acid (16N)**—Reagent grade.
3. **Nitric Acid (8N).**
4. **Nitric Acid (0.16N).**
5. **Hydrofluoric Acid (48%)**—Reagent grade.
6. **Hydrofluoric Acid (2.4%).**
7. **Hydrochloric Acid (12N)**—Reagent grade.
8. **Hydrochloric Acid (6N).**
9. **Hydrochloric Acid (3N).**
10. **Acetone.**
11. **Anion Exchange Resin**—Bio-Rad AG-1-X8, chloride form 200 to 400 mesh or equivalent.
12. **Filters**—0.22-micron pore size, Millipore Catalogue #GSWP 02500 or equivalent.
13. **Analytical Filter Pulp**—Schleicher and Schuell No. 289 or equivalent.
14. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section VII.J of this Appendix.
15. **80% Argon + 20% Oxygen Gas Mix**—Air Reduction Co. or equivalent.
16. **Lanthanum Oxide**—High purity.
17. **SP-2 Graphite**—National Carbon, Met Bay, or equivalent.
18. **Rare Earth Oxides**—High purity.
19. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.
20. **Developer**—Eastman Kodak #D-19 or equivalent.
21. **Stop Bath**—1% acetic acid.
22. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Preparation of Solutions

1. **Nitric Acid (8N)**—Dilute 500 ml of concentrated nitric acid to 1 liter with water.
2. **Nitric Acid (0.16N)**—Dilute 10 ml of concentrated nitric acid to 1 liter with water.
3. **Hydrofluoric Acid (2.4%)**—Dilute 50 ml of concentrated hydrofluoric acid to 1 liter with water.

4. **Hydrochloric Acid (6N)**—Dilute 500 ml of concentrated hydrochloric acid to 1 liter with water.
5. **Hydrochloric Acid (3N)**—Dilute 250 ml of concentrated hydrochloric acid to 1 liter with water.
6. **Lanthanum Oxide Internal Standard and Carrier Solution**—Weigh 2.500 g of $La_2O_3$ into a 250-ml beaker. Add 20 ml of 3N HCl, cover beaker, and heat gently to dissolve the oxide. After dissolution, transfer the solution to a 500-ml volumetric flask. Add 20 ml of concentrated hydrochloric acid to the flask and dilute to volume with water.

## F. Preparation of Rare Earth Stock Solutions and Master Standard Solution

Weigh the following quantities of rare earth oxides into 150-ml beakers:

$Dy_2O_3$—0.2869 g

$Eu_2O_3$—0.2895 g

$Gd_2O_3$—0.2882 g

$Sm_2O_3$—0.2899 g

Add 20 ml of 3N HCl to each of the beakers containing $Dy_2O_3$, $Eu_2O_3$, $Gd_2O_3$, and $Sm_2O_3$; cover and heat gently to dissolve.

Transfer each of the four solutions just prepared to separate 250-ml volumetric flasks. Add 7.5 ml of concentrated HCl to each flask in order to maintain an acid concentration of 5%. Dilute to volume with water. The resulting solutions will contain 1 mg/ml or 1000 μg/ml of each of the rare earths of interest.

Into separate 100-ml volumetric flasks, pipette 10.0 ml of each of the 1000 μg/ml rare earth solutions (Dy, Eu, Gd, and Sm). Add 3.5 ml of concentrated HCl to each flask and then dilute to volume with water. The resulting solutions will contain 100 μg/ml of each of the rare earths of interest.

Into a 500-ml volumetric flask, pipette 5.0 ml of the 100 μg/ml rare earth solutions of dysprosium, gadolinium, and samarium and 1.25 ml of the 100 μg/ml rare earth solution of europium. Add 25 ml of concentrated HCl and dilute to volume with water. The resulting solution will contain 1 μg/ml of dysprosium, gadolinium, and samarium and 0.25 μg/ml of europium. This solution will be used for standard preparation and will henceforth be designated as the master standard solution.

## G. Preparation of Synthetic Standards

To each of seven 400-ml beakers, add 40 ml of 8N $HNO_3$ plus a few drops of 2.4% HF and the master standard solution as shown in Table A-13.

**TABLE A-13. MASTER STANDARD ADDITION IN SYNTHETIC RARE EARTH STANDARD PREPARATION**

| Standard Number | Rare Earth Master Standard Solution (ml) | Nominal Standard Value (μg) | |
|---|---|---|---|
| | | Dy, Gd, Sm | Eu |
| 1 | 0 | 0 | 0 |
| 2 | 0.5 | 0.5 | 0.125 |
| 3 | 1 | 1 | 0.25 |
| 4 | 2 | 2 | 0.50 |
| 5 | 4 | 4 | 1 |
| 6 | 8 | 8 | 2 |
| 7 | 16 | 16 | 4 |

After the addition of the master standard solution to the beakers, proceed to the second paragraph of Section VII.H of this Appendix.

## H. Sample Preparation

Grind the sample to a consistency of approximately 200 mesh in a zirconium mortar or grinding mill. Weigh 2.000 g of sample and transfer to a 400-ml beaker. Dissolve the sample in 40 ml of 8N $HNO_3$ plus a few drops of 2.4% HF, heating to dissolution.

Evaporate the sample and standards (prepared in accordance with the procedure of Section VII.G of this Appendix) to dryness. Dissolve the residue in 25 ml of 8N $HNO_3$. Pass 100 ml of 8N $HNO_3$ through a 50-g conditioned column (see Section VII.O of this Appendix) of anion exchange resin, chloride form (200 to 400 mesh). Retain for scrapping. Add the sample and standards to the columns and rinse the beakers into the columns with two 10-ml portions of 8N $HNO_3$. Place a platinum beaker under each column and allow the solution to pass through at a rate of 0.5 ml/min. Elute the columns with two 75-ml portions of 8N $HNO_3$ into the platinum beakers. Add 2 ml (10 mg) of $La_2O_3$ internal standard solution, as a carrier, to each beaker.

Evaporate the sample and standards to dryness. Elute the thorium from the column with two 100-ml portions of 0.16N $HNO_3$ and retain for scrapping. Dissolve the sample residue in 25 ml of 6N HCl.

### NOTE

*Either a centrifuge or a Millipore filter apparatus may be employed for collecting the precipitate.*

If a centrifuge is chosen, add a small pinch of paper pulp to each beaker and stir to disperse the pulp. Do not add paper pulp if Millipore filter apparatus is chosen. Add 10 ml of concentrated HF to the beakers, cover the beakers with their lids, and place in a water bath maintained at 180° F (82° C). Digest for 15 to 20 minutes. Remove the beakers from the water bath and allow to stand for at least 8 hours to ensure complete rare earth and carrier precipitation. Collect the precipitate. If a centrifuge is used, centrifuge the solution using plastic centrifuge tubes and wash twice using 2.4% HF. Line a 20-ml platinum crucible with Millipore filters moistened with acetone. Transfer the precipitate to the crucible using deionized water. Use the minimum volume of water necessary to transfer quantitatively. Place the platinum crucible on a hot plate and take to dryness, being careful to avoid splattering of the sample. If a Millipore filter apparatus is used, filter onto a 0.22-micron Millipore filter using the Millipore suction filter apparatus. Wash twice using 2.4% HF. Dissolve the Millipore filter with approximately 1 ml of acetone in a 20-ml platinum crucible and dry on a hot plate. After drying, cover and ignite at 1000° C for at least 1 hour. Remove the platinum crucible containing the oxidized residue from the muffle furnace and allow to cool to room temperature in a desiccator.

## I. Charge Preparation

Weigh the oxidized residue obtained (10 mg ±25%) and add sufficient graphite to prepare a 20-mg charge. Mix the residue and graphite using an agate mortar and pestle to ensure a homogeneous mixture. Split the graphite-residue mixture by weighing into two equal portions. Press into two 3/16-in.-deep crater electrodes (see Section VII.J.1 of this Appendix). If the oxidized residue weight exceeds 12.5 mg, indicating thorium or tramp element pickup, redissolve the oxide and repeat the separation and precipitation steps or reanalyze a complete new sampling of the original oxide sample. Burn electrodes immediately after preparation.

## J. Excitation and Exposure Parameters

### 1. Excitation Parameters

| | |
|---|---|
| **a. D-c Arc** | Current—15 amps.<br>Applied voltage—220 volts. |
| **b. Electrode System** | Upper (counter)—1/8-in.-diameter pointed; Met Bay C-1, National Carbon L-4036, Ultra Carbon 1992, or equivalent.<br>Lower (sample, anode)—1/8-in.-diameter, 1/16-in.-crater diameter, 3/16-in.-deep; Met Bay 1155, National Carbon L-3777, Ultra Carbon 5000, or equivalent.<br>Analytical Gap—4 mm. |

### 2. Exposure Conditions

Exposure conditions are presented in Table A-14.

**TABLE A-14. EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF SELECTED RARE EARTH ELEMENTS**

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Slit width, $\mu$ | 30 | 20 |
| Slit height, mm | 1.5 | 1.5 |
| Spectral region, A | 3200 to 4500 (second order) | 2600 to 4400 (second order) |
| Wavelength setting | 7650 | 12.03° (6950), 1/25 tilt |
| Collimator mask, in. | 1/2 by 5 1/4 | None |
| Grating mask, in. | 2 by 2 1/2 | 1 by 5 7/8 |
| Pre-exposure time, sec | 2 | 2 |
| Exposure time, sec | Burn to completion (80 to 90)* | Burn to completion (80 to 90)* |

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*Cut off power as soon as sample is consumed (evidenced by sharp change in burn characteristic) to avoid harmful background buildups.

**TABLE A-14.** (Cont)

| | Jarrell-Ash Spectrographs | |
|---|---|---|
| | Wadsworth | Ebert Mark IV |
| Quartz filter at arc stand | Corning #7740 | Corning #7740 |
| Rotating sector percent transmission** | 50 | 100 |
| Gas flow to Atmo-Jet (80% argon + 20% oxygen) | 7 liters/min,<br>15 $ft^3$/hr | 7 liters/min,<br>15 $ft^3$/hr |
| Arc stand lens | None | None |
| Exhaust draft setting (in. $H_2O$) (arc stand) | 0.00 | 0.00 |

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**Filter settings may vary with passage of time, atmospheric changes, etc. Percent transmission values used should be those which produce spectral line intensities from 5 to 90 percent for all standards.

## K. Photography and Processing

Use two calibrated Eastman Kodak SA #3 photographic plates or equivalent. When using the Ebert spectrograph, position one plate in the center and one on the left side of the camera. After exposure, process the plates in accordance with the procedure described in Appendix E, Section VI.

## L. Photometry

Utilizing the microphotometry procedure described in Appendix E, Section VII, record the transmission values of the individual spectral lines listed below as well as the transmission values for their adjacent backgrounds.

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Dysprosium | 3407.80 | 0.25 to 8.00 |
| Europium | 3907.11 | 0.07 to 4.00 |
| Gadolinium | 3350.48 | 0.25 to 8.00 |
| Samarium | 3670.82 | 0.25 to 8.00 |
| Lanthanum (internal standard) | 3277.83 | -- |

## M. Emulsion Calibration

Prepare the emulsion calibration curve from a step-sectored spectrogram according to the procedure of Appendix E, Section V.

## N. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then divide the corrected relative intensity for each of the rare earth lines of interest (Dy, Eu, Gd, and Sm) by the corrected relative intensity of the lanthanum internal standard line. Plot the average corrected relative intensity ratio for each standard versus its respective elemental concentration on log-log paper. Obtain the sample impurity concentrations for the rare earths by referring their average relative intensity ratios to the appropriate standard curve. Convert micrograms to parts per million by dividing micrograms of elements found from the standard curve by the original sample weight expressed in grams.

## O. Preparation and Conditioning of Ion-Exchange Columns

Place approximately 50 g of resin into a 1000-ml beaker, add 600 ml of deionized water, and stir the contents. Let the resin settle for 5 to 10 minutes and decant the cloudy supernatant liquid containing the fines. Repeat the washing and decanting process until the supernatant liquid becomes clear.

Prepare a 250-ml, 1-in. by 24-in. column to receive the resin. Add approximately 150 ml of 0.16N $HNO_3$ to the column. Insert a small glass wool plug in the bottom of the column using a long glass rod. Squeeze out any air entrapped in the glass wool plug using the glass rod. With the glass rod resting on the glass wool plug to hold it in place, pour a slurry of the washed resin into the column and open the stopcock to allow the resin to settle on the wool plug. When approximately 0.5 in. of the resin has settled on the wool plug, remove the glass rod and close the stopcock. Continue adding the resin slurry and releasing the excess solution in the column until the resin height is 4.5 in.

### CAUTION

*At no time permit the solution level in the column to fall below the upper level of the resin bed. If this occurs, air will be introduced into the resin bed, making the resin column useless.*

Add 0.16N $HNO_3$ to nearly fill the column. Let the resin settle to form a level surface; then insert a glass wool plug into the column. Use a glass rod to hold the plug firmly in place. Open the stopcock and allow the solution level in the column to fall just below the upper glass wool plug; then add 100 ml of 8N $HNO_3$ to the column. When the acid level falls just below the upper glass wool plug, add 50 ml of 0.16N $HNO_3$. Let the 0.16N $HNO_3$ level fall just below the upper glass wool plug; then add an additional 400 ml of 0.16N $HNO_3$ in 50-ml portions. After adding the last 50 ml of 0.16N $HNO_3$, close the stopcock and store the column until ready for use.

## P. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section V
2. Appendix E, Section VI
3. Appendix E, Section VII.

The Operational Chemistry Laboratory procedure for the spectrochemical determination of selected rare earths in $ThO_2$ is given in Appendix B, Section VII.

# APPENDIX B

# EMISSION SPECTROCHEMICAL PROCEDURES
(Operational Chemistry Laboratory)

# APPENDIX B

## EMISSION SPECTROCHEMICAL PROCEDURES
(Operational Chemistry Laboratory)

## I. THE SPECTROCHEMICAL DETERMINATION OF ALUMINUM, MAGNESIUM, AND SILICON IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination of aluminum, magnesium, and silicon in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 10 to 500 ppm. This range can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are intimately mixed with $BaF_2$:graphite, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample concentrations of aluminum, magnesium, and silicon are then obtained by referring their relative intensities to the standard curves.

### C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *A* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.
2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.
3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.
4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.
5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.
6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.
7. **Mortar with Pestle**—Agate.

### D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1097, 1157, or equivalent (see Table B-1).
2. **$ThO_2$**—High purity.
3. **Buffer Mixture**
   a. 1 part $BaF_2$—High purity.
   b. 1 part SP-1 graphite—High purity.
4. **$Al_2O_3$, MgO, and $SiO_2$**—High purity.
5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.
6. **Developer**—Eastman Kodak #D-19 or equivalent.
7. **Stop Bath**—1% acetic acid.
8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.
9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

### E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 60 mg of sample and 40 mg of the 1:1 $BaF_2$:C mixture, transfer to an agate mortar, and mix thoroughly. Weigh 50 mg of the mixture and load into each of two 1/4-in.-diameter, 4-mm-deep, pedestal type electrodes. Repeat for the standards.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-1. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-1 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper. Obtain the sample impurity concentrations for aluminum, magnesium, and silicon by referring their average corrected relative intensities to the appropriate standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix B, Section VI
2. Appendix E, Section I
3. Appendix E, Section II
4. Appendix E, Section III
5. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of aluminum and silicon in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section I, while the procedure for the determination of magnesium is given in Appendix A, Section VI.

TABLE B-1. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF ALUMINUM, MAGNESIUM, AND SILICON

| | |
|---|---|
| **Excitation:** | *D-c arc |
| **Current:** | *AP-8 (~20 amps) |
| **Exposure Time:** | *Preburn—0 sec |
| | *Exposure—60 sec |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent |
| | Lower—Met Bay 1097, Met Bay 1157, or equivalent |
| | Gap distance—4 mm |
| **Slit Width:** | *20 $\mu$ |
| **Slit Height:** | *1.5 mm |

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

**TABLE B-1.** (Cont)

| | | |
|---|---|---|
| **Spectral Regions:** | *4800 to 5700 A | Not used |
| **Gratings:** | *A* | *B* |
| **Separation:** | None | |
| **Plate Rack:** | *1.5 mm | |
| **Filter:** | *50% illuminator | |
| | *25% slit | |
| | *6% stand | |
| | *10% at Mg 2795.53 A and Mg 2802.70 A focal planes | |
| **Atmosphere:** | Air | |
| **Plate:** | SA #3 or equivalent | |
| **Charge/Electrode:** | 50 mg | |
| **Sample/Electrode:** | 30 mg | |
| **Carrier/Electrode:** | 20 mg | |
| **Carrier:** | $BaF_2$-graphite (1:1) | |
| **Spectral Lines:** | Al—2575.10 A, 2660.39 A | |
| | Mg—2795.53 A, 2802.70 A | |
| | Si—2519.21 A, 2524.12 A | |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

## II. THE SPECTROCHEMICAL DETERMINATION OF BORON IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination of boron in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 0.25 to 5.0 ppm. This range can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are then intimately mixed with AgCl-$BaF_2$-graphite, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample concentrations of boron are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.
2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.
3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.
4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.
5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.
6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.
7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1097, S-3, or equivalent (see Table B-2).
2. **$ThO_2$**—High purity.
3. **Carrier Mixture**
   a. 8 parts AgCl—High purity.
   b. 1 part $BaF_2$—High purity.
   c. 1 part C—High purity.
4. **Boron Metal**—High purity.
5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.
6. **Developer**—Eastman Kodak #D-19 or equivalent.
7. **Stop Bath**—1% acetic acid.
8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.
9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 170 mg of sample and 30 mg of the AgCl-$BaF_2$-C mixture, transfer to an agate mortar, and mix thoroughly. Weigh 100 mg of the mixture and load into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-2. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-2 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper.

## TABLE B-2. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF BORON

| | | |
|---|---|---|
| **Excitation:** | *D-c arc | |
| **Current:** | *AP-4 (~9 amps) | |
| **Exposure Time:** | *Preburn—0 sec<br>*Exposure—30 sec | |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent<br>Lower—Met Bay 1097, Met Bay S-3, or equivalent<br>Gap distance—4 mm | |
| **Slit Width:** | *20 μ | |
| **Slit Height:** | *1.5 mm | |
| **Spectral Regions:** | *4600 to 5500 A | Not used |
| **Gratings:** | *A* | *B* |
| **Separation:** | None | |
| **Plate Rack:** | *1.5 mm | |
| **Filter:** | *100% illuminator<br>*15% slit | |
| **Atmosphere:** | Air | |
| **Plate:** | SA #3 or equivalent | |
| **Charge/Electrode:** | 100 mg | |
| **Sample/Electrode:** | 85 mg | |
| **Carrier/Electrode:** | 15 mg | |
| **Carrier:** | AgCl-BaF$_2$-C (8:1:1) | |
| **Spectral Lines:** | B—2496.78 A, 2497.73 A | |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

Obtain the sample impurity concentrations for boron by referring their average corrected relative intensities to the standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix B, Section VI
2. Appendix E, Section I
3. Appendix E, Section II
4. Appendix E, Section III
5. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of boron in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section II.

# III. THE SPECTROCHEMICAL DETERMINATION OF CALCIUM IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

## A. Scope

This procedure describes the spectrochemical determination of calcium in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 10 to 500 ppm. This range can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

## B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are intimately mixed with $BaF_2$:graphite, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectal lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample concentrations of calcium are then obtained by referring their relative intensities to the standard curve.

## C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.

2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.

3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.

4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.

5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.

6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1097, 1157, or equivalent (see Table B-3).

2. **$ThO_2$**—High purity.

3. **Buffer Mixture**
   a. 1 part $BaF_2$—High purity.
   b. 1 part C—High purity.

4. **$CaCO_3$**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 60 mg of sample and 40 mg of the $BaF_2$-C mixture, transfer to an agate mortar, and mix thoroughly. Weigh 50 mg of the mixture and load into each of two 1/4-in.-diameter, 4-mm-deep, pedestal type electrodes. Repeat for the standards.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-3. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-1 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper. Obtain the sample impurity concentrations for calcium by referring their average corrected relative intensities to the standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix B, Section VI
2. Appendix E, Section I
3. Appendix E, Section II
4. Appendix E, Section III
5. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of calcium in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section III.

### TABLE B-3. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF CALCIUM

| | | |
|---|---|---|
| **Excitation:** | *D-c arc | |
| **Current:** | *AP-7 (~16 amps) | |
| **Exposure Time:** | *Preburn—0 sec | |
| | *Exposure—105 sec | |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent | |
| | Lower—Met Bay 1097, Met Bay 1157, or equivalent | |
| | Gap distance—4 mm | |
| **Slit Width:** | *20 $\mu$ | |
| **Slit Height:** | *1.5 mm | |
| **Spectral Regions:** | *7600 to 8500 A | Not used |
| **Gratings:** | *B* | *A* |

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

TABLE B-3. (Cont)

| | |
|---|---|
| **Separation:** | None |
| **Plate Rack:** | *1.5 mm |
| **Filter:** | *12% illuminator |
| | *6% and 6% slit |
| | *6% stand |
| **Atmosphere:** | Air |
| **Plate:** | SA #3 or equivalent |
| **Charge/Electrode:** | 50 mg |
| **Sample/Electrode:** | 30 mg |
| **Carrier/Electrode:** | 20 mg |
| **Carrier:** | $BaF_2$-graphite (1:1) |
| **Spectral Lines:** | Ca—3933.67 A, 3968.47 A |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

## IV. THE SPECTROCHEMICAL DETERMINATION OF MOLYBDENUM IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination of molybdenum in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 2.5 to 250 ppm. This range can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are intimately mixed with $Ga_2O_3$, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample concentrations of molybdenum are then obtained by referring their relative intensities to the standard curve.

### C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order,

while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.

2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.

3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.

4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.

5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.

6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1153, or equivalent (see Table B-4).

2. **$ThO_2$**—High purity.

3. **$Ga_2O_3$**—High purity.

4. **$MoO_3$**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Preparation of Synthetic Standards

Prepare dry ground standards in accordance with Section VI.E of this Appendix.

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 60 mg of sample and 40 mg of $Ga_2O_3$, transfer to an agate mortar, and mix thoroughly. Weigh 50 mg of the mixture and press into each of two center-post electrodes. Repeat for the standards.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-4. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-4 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper. Obtain the sample impurity concentrations for molybdenum by referring their average corrected relative intensities to the standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix B, Section VI
2. Appendix E, Section I
3. Appendix E, Section II
4. Appendix E, Section III
5. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of molybdenum in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section IV.

## TABLE B-4. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF MOLYBDENUM

| | | |
|---|---|---|
| **Excitation:** | *D-c arc | |
| **Current:** | *AP-4 (∼9 amps) | |
| **Exposure Time:** | *Preburn—3 sec | |
| | *Exposure—60 sec | |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent | |
| | Lower—Met Bay 1153 or equivalent | |
| | Gap distance—4 mm | |
| **Slit Width:** | *20 μ | |
| **Slit Height:** | *1.5 mm | |
| **Spectral Regions:** | *6000 to 6900 A | Not used |
| **Gratings:** | *B* | *A* |
| **Separation:** | None | |
| **Plate Rack:** | *1.5 mm | |
| **Filter:** | *50% illuminator | |
| | *6% slit | |
| **Atmosphere:** | Air | |
| **Plate:** | SA #3 or equivalent | |
| **Charge/Electrode:** | 50 mg | |
| **Sample/Electrode:** | 30 mg | |
| **Carrier/Electrode:** | 20 mg | |
| **Carrier:** | $Ga_2O_3$ | |
| **Spectral Lines:** | Mo—3132.59 A, 3170.35 A, 3208.83 A | |

### NOTE

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

## V. THE SPECTROCHEMICAL DETERMINATION OF MERCURY IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination of mercury in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ in the concentration range of 0.5 to 10 ppm. This range can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are intimately mixed with AgCl and loaded into sample graphite electrodes with a boiler cap placed on each electrode, and duplicate exposures are made utilizing a-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample concentrations of mercury are then obtained by referring their relative intensities to the standard curve.

### C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.

2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.

3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.

4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.

5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.

6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.

7. **Mortar with Pestle**—Agate.

### D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1097, S-3, BC-1, or equivalent (see Table B-7).

2. **$ThO_2$**—High purity.

3. **AgCl**—High purity.

4. **HgO**—High purity.

5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.

6. **Developer**—Eastman Kodak #D-19 or equivalent.

7. **Stop Bath**—1% acetic acid.

8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

### E. Preparation of Synthetic Standards

Standards are prepared on the basis of metal (Hg) in total oxide ($ThO_2$). Prepare a master synthetic standard by dry grinding oxide weights in accordance with Table B-5. Uranium dioxide is not included in the preparation of these standards because up to 10 w/o $UO_2$ has no influence on spectral response.

From the master standard (5000 ppm), make a series of successive dilutions in accordance with Table B-6.

TABLE B-5. COMPOSITION OF MASTER SYNTHETIC MERCURY STANDARD

| Master Standard (5000 ppm) |
|---|
| 0.0540 gram HgO |
| 9.9460 grams $ThO_2$ |
| 10.0000 grams Total |

## TABLE B-6. MASTER STANDARD DILUTION IN SYNTHETIC MERCURY STANDARD PREPARATION

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 1 | 500 | 0.5000 gram of Master Standard<br>4.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 2 | 250 | 2.5000 grams of Standard #1<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 3 | 100 | 2.0000 grams of Standard #2<br>3.0000 grams of $ThO_2$<br>5.0000 grams Total |
| 4 | 50 | 2.5000 grams of Standard #3<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 5 | 25 | 2.5000 grams of Standard #4<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 6 | 8.3 | 2.0000 grams of Standard #5<br>4.0000 grams of $ThO_2$<br>6.0000 grams Total |
| 7 | 4.2 | 2.5000 grams of Standard #6<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 8 | 2.1 | 2.5000 grams of Standard #7<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 9 | 1.0 | 2.5000 grams of Standard #8<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |
| 10 | 0.5 | 2.5000 grams of Standard #9<br>2.5000 grams of $ThO_2$<br>5.0000 grams Total |

**NOTE**

*Uranium dioxide is not included in the preparation of these standards because up to 10 w/o* $UO_2$ *has no influence on spectral response.*

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 350 mg of sample and 50 mg of AgCl, transfer to an agate mortar, and mix thoroughly. Weigh 200 mg of the mixture and load into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards. Place a boiler cap on each of the electrodes.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-7. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-7 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper. Obtain the sample impurity concentrations for mercury by referring their average corrected relative intensities to the standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section I
2. Appendix E, Section II
3. Appendix E, Section III
4. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of mercury in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section V.

TABLE B-7. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF MERCURY

| | | |
|---|---|---|
| **Excitation:** | *A-c arc | |
| **Current:** | *AP-3 (2 breaks/cycle ~5 amps) | |
| **Exposure Time:** | *Preburn—0 sec | |
| | *Exposure—30 sec | |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent | |
| | Lower—Met Bay 1097, Met Bay S-3, Met Bay BC-1, or equivalent | |
| | Gap distance—4 mm | |
| **Slit Width:** | *20 $\mu$ | |
| **Slit Height:** | *1.5 mm | |
| **Spectral Regions:** | *4800 to 5700 A | Not used |
| **Gratings:** | *A* | *B* |
| **Separation:** | None | |

---

*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

**TABLE B-7.** (Cont)

| | |
|---|---|
| **Plate Rack:** | *1.5 mm |
| **Filter:** | *100% illuminator<br>*35% slit |
| **Atmosphere:** | Air |
| **Plate:** | SA #3 or equivalent |
| **Charge/Electrode:** | 200 mg |
| **Sample/Electrode:** | 175 mg |
| **Carrier/Electrode:** | 25 mg |
| **Carrier:** | AgCl |
| **Spectral Lines:** | Hg—2536.52 A |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

## VI. THE SPECTROCHEMICAL DETERMINATION OF SELECTED IMPURITIES IN $ThO_2$ AND $UO_2$-$ThO_2$ UP TO 10 w/o $UO_2$

### A. Scope

This procedure describes the spectrochemical determination in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ of the elements listed in Table B-8 in the concentration ranges listed in the table.

The ranges given in Table B-8 can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $ThO_2$.

### B. Summary of Method

Samples submitted as powders are analyzed as received. Samples submitted as pellets are crushed in a zirconium mortar and ground to a consistency of approximately 200 mesh. Portions of the samples are intimately mixed with AgCl, and duplicate exposures are made utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained

**TABLE B-8. TABULATION OF IMPURITIES THAT CAN BE SPECTROCHEMICALLY DETERMINED BY THE PROCEDURE OF APPENDIX B, SECTION VI**

| Element | Concentration Range (ppm) |
|---|---|
| Chromium | 2.5 to 250 |
| Cobalt | 2.5 to 50 |
| Copper | 2.5 to 50 |
| Iron | 5 to 500 |
| Manganese | 2.5 to 25 |
| Nickel | 2.5 to 250 |
| Titanium | 2.5 to 50 |
| Vanadium | 2.5 to 50 |

from the emulsion calibration curve, a standard curve is prepared by plotting the relative intensities of the standards versus concentration on log-log paper. The sample impurity concentrations are then obtained by referring their relative intensities to the standard curves.

## C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.
2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.
3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.
4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.
5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.
6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.
7. **Mortar with Pestle**—Agate.

## D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, 1097, S-3, or equivalent (see Table B-11).
2. **$ThO_2$**—High purity.
3. **AgCl**—High purity.
4. **Oxides of Impurity Elements**—High purity.
5. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.
6. **Developer**—Eastman Kodak #D-19 or equivalent.
7. **Stop Bath**—1% acetic acid.
8. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.
9. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Preparation of Synthetic Standards

Standards are prepared on the basis of metal in total oxide ($ThO_2$). Prepare a master synthetic standard by dry grinding oxide weights in accordance with Table B-9. Uranium dioxide is not included in the preparation of standards for this method because up to 10 w/o $UO_2$ has no influence on spectral response.

From the master standard (10,000 ppm), make a series of successive dilutions in accordance with Table B-10.

**TABLE B-9. COMPOSITION OF MASTER SYNTHETIC IMPURITY STANDARDS**

**(1 w/o Impurities)**

| Impurity | Oxide Form | Conversion Factor | Oxide Added (grams) |
|---|---|---|---|
| Aluminum | $Al_2O_3$ | 1.8895 | 0.189 |
| Boron | As metal | -- | 0.010* |
| Calcium | $CaCO_3$ | 2.4970 | 0.250 |
| Chromium | $Cr_2O_3$ | 1.4616 | 0.146 |
| Cobalt | $Co_3O_4$ | 1.3620 | 0.136 |
| Copper | CuO | 1.2518 | 0.125 |
| Iron | $Fe_2O_3$ | 1.4297 | 0.143 |

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*Concentration of boron is one-tenth that of other impurities in the standards.

## TABLE B-9. (Cont)

| Impurity | Oxide Form | Conversion Factor | Oxide Added (grams) |
|---|---|---|---|
| Magnesium | $MgO$ | 1.6581 | 0.166 |
| Manganese | $Mn_3O_4$ | 1.3883 | 0.139 |
| Molybdenum | $MoO_3$ | 1.5003 | 0.150 |
| Nickel | $NiO$ | 1.2725 | 0.127 |
| Silicon | $SiO_2$ | 2.1393 | 0.214 |
| Titanium | $TiO_2$ | 1.6680 | 0.167 |
| Vanadium | $V_2O_5$ | 1.7852 | 0.179 |
| | | Total impurities added | 2.141 |

**Master Standard (10,000 ppm)**

2.141 grams of impurity oxides
7.859 grams of $ThO_2$
10.000 grams Total

## TABLE B-10. MASTER STANDARD DILUTION IN SYNTHETIC IMPURITY STANDARD PREPARATION

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 1 | 1000 | 2.000 grams of Master Standard<br>18.000 grams of $ThO_2$<br>20.000 grams Total |
| 2 | 500 | 10.000 grams of Standard #1<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 3 | 250 | 10.000 grams of Standard #2<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 4 | 100 | 8.000 grams of Standard #3<br>12.000 grams of $ThO_2$<br>20.000 grams Total |
| 5 | 50 | 10.000 grams of Standard #4<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 6 | 25 | 10.000 grams of Standard #5<br>10.000 grams of $ThO_2$<br>20.000 grams Total |

**TABLE B-10. (Cont)**

| Standard Number | Concentration (ppm) | Material Weights |
|---|---|---|
| 7 | 10 | 8.000 grams of Standard #6<br>12.000 grams of $ThO_2$<br>20.000 grams Total |
| 8 | 5 | 10.000 grams of Standard #7<br>10.000 grams of $ThO_2$<br>20.000 grams Total |
| 9 | 2.5 | 10.000 grams of Standard #8<br>10.000 grams of $ThO_2$<br>20.000 grams Total |

**NOTE**

*Because of the expected impurity level of boron in the samples, the concentration is one-tenth that of the other impurities in the standards.*

**NOTE**

*Uranium dioxide is not included in the preparation of standards because up to 10 w/o $UO_2$ has no influence on spectral response.*

## F. Procedure

### 1. Sample and Charge Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 180 mg of sample and 30 mg of AgCl, transfer to an agate mortar, and mix thoroughly. Weigh 105 mg of the mixture and load into each of two 1/4-in.-diameter, 7-mm-deep, pedestal type electrodes. Repeat for the standards.

### 2. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-11. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 3. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-12 as well as the transmission values for their adjacent backgrounds.

## G. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then average the differences thus obtained for each set of duplicate exposures. Plot the average corrected relative intensity of each standard versus its elemental concentration on log-log paper. Obtain the sample concentrations for the selected impurities by referring their average corrected relative intensities to the appropriate standard curve.

## H. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section I
2. Appendix E, Section II
3. Appendix E, Section III
4. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of selected impurities in $ThO_2$ and $UO_2$-$ThO_2$ up to 10 w/o $UO_2$ is given in Appendix A, Section VI.

## TABLE B-11. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF SELECTED IMPURITIES

| | |
|---|---|
| **Excitation:** | *D-c arc |
| **Current:** | *AP-5 (~11 amps) |
| **Exposure Time:** | *Preburn—0 sec |
| | *Exposure—60 sec |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent |
| | Lower—Met Bay 1097, Met Bay S-3, or equivalent |
| | Gap distance—4 mm |
| **Slit Width:** | *20 $\mu$ |
| **Slit Height:** | *1.5 mm |
| **Spectral Regions:** | *6000 to 6900 A     5500 to 6400 A |
| **Gratings:** | *A*     *B* |
| **Separation:** | *38 mm |
| **Plate Rack:** | *1.5 mm |
| **Filter:** | *12% *A*, *6% *B* illuminator |
| | *15% slit |
| | *10% at Cu 3247.54 A and Cu 3273.96 A focal planes |
| **Atmosphere:** | Air |
| **Plate:** | SA #3 or equivalent |
| **Charge/Electrode:** | 105 mg |
| **Sample/Electrode:** | 90 mg |
| **Carrier/Electrode:** | 15 mg |
| **Carrier:** | AgCl |
| **Spectral Lines:** | See Table B-12 |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

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*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

### TABLE B-12. TABULATION OF SPECTRAL LINES TO BE USED IN PHOTOMETRY PROCEDURE FOR SELECTED IMPURITIES

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Chromium | 3021.56 | 2.5 to 250 |
| Cobalt | 3412.34 | 2.5 to 50 |
| Cobalt | 3412.63 | 2.5 to 50 |
| Copper | 3247.54 | 2.5 to 50 |
| Copper | 3273.96 | 2.5 to 50 |
| Iron | 2966.90 | 5 to 500 |
| Iron | 2994.46 | 5 to 500 |
| Manganese | 2801.06 | 2.5 to 25 |
| Nickel | 3101.55 | 2.5 to 250 |
| Nickel | 3101.88 | 2.5 to 250 |
| Nickel | 3012.00 | 2.5 to 250 |
| Titanium | 3075.22 | 2.5 to 25 |
| Titanium | 3088.03 | 2.5 to 50 |
| Titanium | 3186.45 | 2.5 to 50 |
| Vanadium | 3102.30 | 2.5 to 50 |
| Vanadium | 3118.38 | 2.5 to 50 |

# VII. THE SPECTROCHEMICAL DETERMINATION OF SELECTED RARE EARTHS IN $ThO_2$ USING A LANTHANUM OXIDE CARRIER-INTERNAL STANDARD

## A. Scope

This procedure describes the spectrochemical determination of the rare earths listed in Table B-13 in $ThO_2$ in the concentration ranges listed in the table.

The ranges given in Table B-13 can be expanded through the selection of alternate spectral lines, percent transmission modifications, and/or sample dilutions with pure $La_2O_3$.

## B. Summary of Method

The sample is dissolved in a nitric-hydrofluoric acid mixture and evaporated to dryness. After redissolving in nitric acid, the sample is passed through an anion exchange column that retains the thorium but allows the rare earths to pass. A fluoride precipitation using lanthanum as a carrier separates the rare earths from the tramp elements. After ignition, the samples are intimately mixed with graphite and duplicate exposures are made in an argon-oxygen atmosphere utilizing d-c arc excitation. The emission spectra produced are recorded photographically along with a set of standards, and the percent transmission values of resultant spectral lines of interest are recorded from a microphotometer. After the relative intensities for both standards and samples are obtained from the emulsion calibration curve, intensity ratios are calculated and a standard curve is prepared by plotting relative intensity ratios of the standards versus concentration on log-log paper. The sample rare earth concentrations are then obtained by referring their relative intensity ratios to the standard curves.

## C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.

2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.

3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.

4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board, Hewlett-Packard 9100B calculator, or equivalent.

5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.

### TABLE B-13. TABULATION OF RARE EARTH ELEMENTS THAT CAN BE SPECTROCHEMICALLY DETERMINED BY THE PROCEDURE OF APPENDIX B, SECTION VII

| Element | Concentration Range (ppm) |
|---|---|
| Dysprosium | 0.12 to 4.00 |
| Europium | 0.03 to 1.00 |
| Gadolinium | 0.12 to 4.00 |
| Samarium | 0.12 to 4.00 |

6. **Analytical Balances**—Mettler H10 and Roller Smith "Precision Balance" or equivalent.
7. **Muffle Furnace**—Lindberg Hevi-Duty or equivalent.
8. **Hot Plates**—Corning PC-100 or equivalent.
9. **Suction Filter Apparatus**—Fabricated plastic Millipore or equivalent.
10. **Beakers**—150- and 400-ml Pyrex or equivalent and 250-ml platinum with lids.
11. **Graduated Cylinders**—100- and 250-ml and 1-liter Pyrex or equivalent and 25-ml polypropylene.
12. **Calibrated Pipettes**—Class A.
13. **Ion-Exchange Column**—1-in. inside diameter by 24 in. long.
14. **Crucibles**—30-ml platinum with lids.
15. **Mortar with Pestle**—Agate.
16. **Atmo-Jet**—Zeebac or equivalent.

## D. Reagents and Materials

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for standard preparations and dilution of all reagents.
2. **Nitric Acid** (**16N**)—Reagent grade.
3. **Nitric Acid** (**8N**)—Dilute 500 ml of concentrated nitric acid to 1 liter with water.
4. **Nitric Acid** (**0.16N**)—Dilute 10 ml of concentrated nitric acid to 1 liter with water.
5. **Hydrofluoric Acid** (**29.4N**)—Reagent grade.
6. **Hydrofluoric Acid** (**2.94N**)—Dilute 10 ml of concentrated hydrofluoric acid to 100 ml with water.
7. **Hydrofluoric Acid** (**1.47N**)—Dilute 5 ml of concentrated hydrofluoric acid to 100 ml with water.
8. **Hydrochloric Acid** (**12N**)—Reagent grade.
9. **Hydrochloric Acid** (**6N**)—Dilute 500 ml of concentrated hydrochloric acid to 1 liter with water.
10. **Hydrochloric Acid** (**3N**)—Dilute 250 ml of concentrated hydrochloric acid to 1 liter with water.
11. **Nitric Acid** (**13M**)-**Hydrofluoric Acid** (**0.05M**) **Solution**—Add 155 ml of water and 828 ml of concentrated nitric acid to a 1-liter polyethylene bottle. Cool and add 17 ml of 2.94N hydrofluoric acid.
12. **Acetone.**
13. **Anion Exchange Resin**—Bio-Rad AG-1-X8, chloride form, 200 to 400 mesh or equivalent.
14. **Filters**—0.22-micron pore size, Millipore Catalogue #GSWP 02500 or equivalent.
15. **Electrodes**—Met Bay C-1, 1155, or equivalent (see Table B-15).
16. **$ThO_2$**—High purity.
17. **80% Argon + 20% Oxygen Gas Mix**—Air Reduction Co. or equivalent.
18. **Lanthanum Oxide**—High purity.
19. **Graphite**—Met Bay MP-200 or equivalent.
20. **Rare Earth Oxides**—High purity.
21. **Photographic Plates**—Eastman Kodak SA #3 or equivalent.
22. **Developer**—Eastman Kodak #D-19 or equivalent.
23. **Stop Bath**—1% acetic acid.
24. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.
25. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Preparation of Lanthanum Oxide Internal Standard and Carrier Solution

Weigh 2.500 g of $La_2O_3$ into a 250-ml beaker. Add 20 ml of 3N HCl, cover beaker, and heat gently to dissolve the oxide. After dissolution, transfer the solution to a 500-ml volumetric flask. Add 20 ml of concentrated HCl to the flask and dilute to volume with water.

## F. Preparation of Rare Earth Stock Solutions and Master Standard Solution

Weigh the following quantities of rare earth oxides into 150-ml beakers:

$Dy_2O_3$—0.2869 g

$Eu_2O_3$—0.3619 g

$Gd_2O_3$—0.2882 g

$Sm_2O_3$—0.2899 g

Add 20 ml of 3N HCl to each of the beakers. Cover and heat gently to dissolve.

Transfer each of the four solutions just prepared to separate 250-ml volumetric flasks. Add 8 ml of concentrated HCl to each flask and dilute to volume with water. The resulting solutions will contain 1 mg/ml of dysprosium, gadolinium, and samarium and 1.25 mg/ml of europium.

Pipette 10.0 ml from each of these rare earth solutions into separate 100-ml volumetric flasks. Add 4 ml of concentrated HCl to each flask and dilute to volume with water. The resulting solutions will contain 100 $\mu$g/ml of dysprosium, gadolinium, and samarium and 125 $\mu$g/ml of europium.

Pipette 5.0 ml of the 100 $\mu$g/ml solutions containing dysorosium, gadolinium, and samarium and 1 ml of the 125 $\mu$g/ml solution containing europium into a 500-ml volumetric flask. Add 25 ml of concentrated HCl and dilute to volume with water. The resulting solution will contain 1 $\mu$g/ml of dysprosium, gadolinium, and samarium and 0.25 $\mu$g/ml of europium. This solution is used for standard preparation and will henceforth be designated as the master standard solution.

## G. Preparation of Synthetic Standards

Pipette 2.0 ml (5 mg/ml) of the lanthanum internal standard solution into each of five 250-ml platinum beakers. Pipette the master standard into the beakers as shown in Table B-14.

After the addition of the internal standard and master standard solutions, evaporate the solution to dryness. Continue as in Section VII.H.1 of this Appendix, starting with the dissolution of the samples, control, and standard residues in 25 ml of 6N HCl.

### TABLE B-14. MASTER STANDARD ADDITION IN SYNTHETIC RARE EARTH STANDARD PREPARATION

| Standard Number | Rare Earth Master Standard Solution (ml) | Nominal Standard Value ($\mu$g) | |
|---|---|---|---|
| | | Dy, Gd, Sm | Eu |
| 1 | 0.25 | 0.25 | 0.063 |
| 2 | 0.5 | 0.5 | 0.125 |
| 3 | 1.0 | 1 | 0.25 |
| 4 | 2.0 | 2 | 0.50 |
| 5 | 4.0 | 4 | 1 |
| 6 | 8.0 | 8 | 2 |

## H. Procedure

### 1. Sample Preparation

Grind the sample in accordance with the appropriate procedure as described in Appendix E, Section I. Weigh 2.000 g of sample into a 400-ml Pyrex beaker or equivalent. Make a duplicate weighing of one of the samples or weigh pure $ThO_2$ into a separate beaker to be used as a control. Dissolve each sample and control in 25 ml of 13M $HNO_3$-0.05M HF solution.

Pipette 1.0 ml of the master standard solution into the control. Evaporate the samples and the control to dryness and dissolve the residue in 25 ml of 8N $HNO_3$.

Pass 100 ml of 8N $HNO_3$ in 25-ml portions through a conditioned column (see Section VII.J of this Appendix) containing anion exchange resin, chloride form (200 to 400 mesh). Retain the eluant for solution salvage.

Transfer the sample or control to the column and rinse the beaker using two 10-ml portions of 8N $HNO_3$. Place a 250-ml platinum beaker under the column and open the stopcock to allow the solution to pass through the column at a rate of 2 to 3 drops/5 sec (approximately 1.5 to 2.5 ml/min). Rinse the column with six 25-ml portions of 8N $HNO_3$, allowing each addition to drain to the top of the resin column before the next portion is added.

Evaporate the samples and control to near dryness. Pipette 2.0 ml (5 mg/ml) of the $La_2O_3$ internal standard solution to each beaker and evaporate to dryness.

Dissolve the samples, the control, and the standard residues in approximately 25 ml of 6N HCl, warming the solution if necessary. Add approximately 10 ml of concentrated HF to each beaker. Swirl the solution, cover, and place in a water bath maintained at 80 to 85°C. Digest for 15 to 20 minutes. Remove the beakers from the water bath and allow to cool to room temperature.

The precipitate is collected on a 0.22-micron Millipore filter. Wash the beaker twice using 1.47N HF and transfer to the Millipore filter. Transfer the dry Millipore filter to a 30-ml platinum crucible. Dissolve the filter with approximately 1 ml of acetone and dry on a hot plate. After drying, cover and ignite at 1000°C for at least 1 hour. Place the crucible in a desiccator and allow to cool to room temperature. Proceed with Sections VII.H.2 and VII.H.3 of this Appendix immediately after cooling to minimize moisture and $CO_2$ pickup.

Elute the thorium by passing 250 ml of 0.16N $HNO_3$ in 25-ml portions through the column at a rate of 2.5 to 6 ml/min. Retain the eluant thorium for solution salvage. The column may be stored using deionized water or 0.16N $HNO_3$.

### 2. Charge Preparation

Weigh the oxidized residue obtained (10 mg ±25%) and add sufficient graphite to prepare a 20-mg charge. Mix the residue and graphite intimately using an agate mortar and pestle. Weigh 10 mg of the mixture and press into each of two 3/16-in.-deep crater electrodes (see Section VII.H.3 of this Appendix). Repeat for the standards. If the oxidized residue weight exceeds 12.5 mg, indicating thorium or tramp element pickup, reanalyze a new sampling of the original oxide.

### 3. Excitation and Exposure Parameters

Arc the samples and standards according to the conditions listed in Table B-15. Along with the samples, shoot a calibration curve consisting of at least five different standards in duplicate exposures.

### 4. Photographic Processing and Photometry

Process the plate in accordance with the procedure described in Appendix E, Section III. Utilizing the microphotometry procedure described in Appendix E, Section IV, record the transmission values for the lines listed in Table B-16 as well as the transmission values for their adjacent backgrounds.

### TABLE B-15. EXCITATION AND EXPOSURE CONDITIONS OF SAMPLE ELECTRODES FOR SPECTROCHEMICAL DETERMINATION OF SELECTED RARE EARTH ELEMENTS

| | | |
|---|---|---|
| **Excitation:** | *D-c arc | |
| **Current:** | *AP-5 (~11 amps) | |
| **Exposure Time:** | *Preburn—2 sec | |
| | *Exposure—80 to 90 sec | |

**NOTE**

*Cut off power as soon as the sample is consumed.*

| | | |
|---|---|---|
| **Electrodes:** | Upper—Met Bay C-1 or equivalent | |
| | Lower—Met Bay 1155 or equivalent | |
| | Gap distance—4 mm | |
| **Slit Width:** | *20 $\mu$ | |
| **Slit Height:** | *1.5 mm | |
| **Spectral Regions:** | *7200 to 8100 A | *6500 to 7400 A |
| **Gratings:** | *A* | *B* |
| **Separation:** | *38 mm | |
| **Plate Rack:** | *1.5 mm | |
| **Filter:** | *25% *A*, *6% *B* illuminator | |
| | *100% slit | |

---

*These parameters are instrument settings and should remain constant throughout sample and standard analyses.

**TABLE B-15. (Cont)**

| | |
|---|---|
| **Atmosphere:** | 80% argon + 20% oxygen |
| **Gas Flow to Atmo-Jet:** | 20 ft$^3$/hr |
| **Plate:** | SA #3 or equivalent |
| **Charge/Electrode:** | 10 mg ±25% |
| **Sample/Electrode:** | 5 mg ±25% |
| **Carrier/Electrode:** | 5 mg ±25% |
| **Carrier:** | Graphite |
| **Spectral Lines:** | See Table B-16 |

**NOTE**

*These parameters are subject to environmental conditions (variations in room temperature and relative humidity) and instrument component aging. Any change in sensitivity due to the above can be compensated for by selection of alternate spectral lines and/or optical filters.*

**TABLE B-16. TABULATION OF SPECTRAL LINES TO BE USED IN PHOTOMETRY PROCEDURE FOR SELECTED RARE EARTHS**

| Element | Wavelength (A) | Concentration Range (ppm) |
|---|---|---|
| Dysprosium | 3407.80 | 0.12 to 4.00 |
| Dysprosium | 3445.58 | 0.12 to 4.00 |
| Europium | 3907.11 | 0.03 to 1.00 |
| Gadolinium | 3350.48 | 0.12 to 4.00 |
| Gadolinium | 3439.99 | 0.12 to 4.00 |
| Samarium | 3670.82 | 0.12 to 4.00 |
| Lanthanum (internal standard) | 3277.83 | -- |
| Lanthanum (internal standard) | 3256.60 | -- |

## I. Calculations

Obtain the relative intensities for the spectral lines of interest and their adjacent backgrounds for all samples and standards by referring their individual percent transmission values to the emulsion calibration curve. The calibration curve is drawn from two-step data according to the procedure of Appendix E, Section II. Subtract the relative intensity of the background from the relative intensity of the respective spectral line and then divide the corrected relative intensity for each of the rare earth lines of interest (Dy, Eu, Gd, and Sm) by the corrected relative intensity of the lanthanum internal standard line. Plot the average corrected relative intensity ratio for each standard versus its elemental concentration on log-log paper. Obtain the sample impurity concentrations for the rare earths by referring their average corrected relative intensity ratios to the appropriate standard curve. Convert micrograms to parts per million by dividing micrograms of elements found from the standard curve by the original sample weight expressed in grams.

## J. Preparation and Conditioning of Ion-Exchange Columns

Place approximately 200 g of resin into a 600-ml breaker. Add approximately 300 ml of deionized water and stir the contents.

Prepare a 250-ml, 1-in. by 24-in. column to receive the resin. Add approximately 100 ml of deionized water to the column. Insert a small glass wool plug in the bottom of the column using a long glass rod. Squeeze out any air entrapped in the glass wool plug using the glass rod. Pour the well-mixed slurry of resin into the column, stirring with the glass rod to ensure level packing. Open the stopcock to allow the resin to settle onto the wool plug. When approximately 0.5 in. of the resin has settled onto the wool plug, remove the glass rod and close the stopcock. Continue adding the well-mixed resin slurry to the column until the resin height is approximately 4.5 in.

### CAUTION

> *At no time permit the water level in the column to fall below the upper level of the resin bed. If this occurs, air will be introduced into the resin bed, making the resin column useless.*

Rinse the column with approximately 1 liter of deionized water. Let the resin settle in the column to form a level surface. Insert a glass wool plug into the column and hold the plug firmly in place with a glass rod. Open the stopcock and allow the water level to fall just below the upper glass wool plug.

Pass 100 ml of 8N $HNO_3$ through the column in 25-ml portions. When the final acid level falls just below the upper glass wool plug, add 50 ml of deionized water. Let the water level fall just below the upper glass wool plug. Pass an additional 400 ml of deionized water through the column in 50-ml portions. After addition of the last 50 ml portion, close the stopcock and store the column until ready for use.

## K. References

Reference to procedures in the following appendix sections is required for complete execution of this procedure:

1. Appendix E, Section I
2. Appendix E, Section II
3. Appendix E, Section III
4. Appendix E, Section IV.

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrochemical determination of selected rare earths in $ThO_2$ is given in Appendix A, Section VII.

# APPENDIX C

## WET CHEMICAL PROCEDURES
(Analytical and Spectrochemical Analysis Laboratory)

# APPENDIX C

## WET CHEMICAL PROCEDURES
## (Analytical and Spectrochemical Analysis Laboratory)

## I. THE SPECTROPHOTOMETRIC DETERMINATION OF NITROGEN IN $ThO_2$ AND $UO_2$-$ThO_2$

### A. Scope

This procedure describes the determination of nitrogen in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 10 to 40 ppm on a 0.5-g sample basis using a 10-cm light path for photometric measurement. This range can be extended by altering sample sizes or by using shorter path length absorption cells and larger nitrogen aliquots for calibration curves.

### B. Summary of Method

The sample is dissolved by refluxing in a sulfuric-phosphoric acid mixture. The resulting solution is made basic by the addition of a strong sodium hydroxide solution, and nitrogen is separated as ammonia by steam distillation. Ammonia is determined spectrophotometrically in the distillate with Nessler reagent.

### C. Apparatus

1. **Condenser**—Reflux air-cooled condenser equipped with a 24/40 ground glass joint without the drip spout or reflux water-cooled Graham condenser or equivalent equipped with a 24/40 ground glass joint.

2. **Steam Distillation Apparatus (see Figure C-1)**—The standard unit employs an Aminco #4-1842 or equivalent heating assembly equipped with a Teflon plug, an

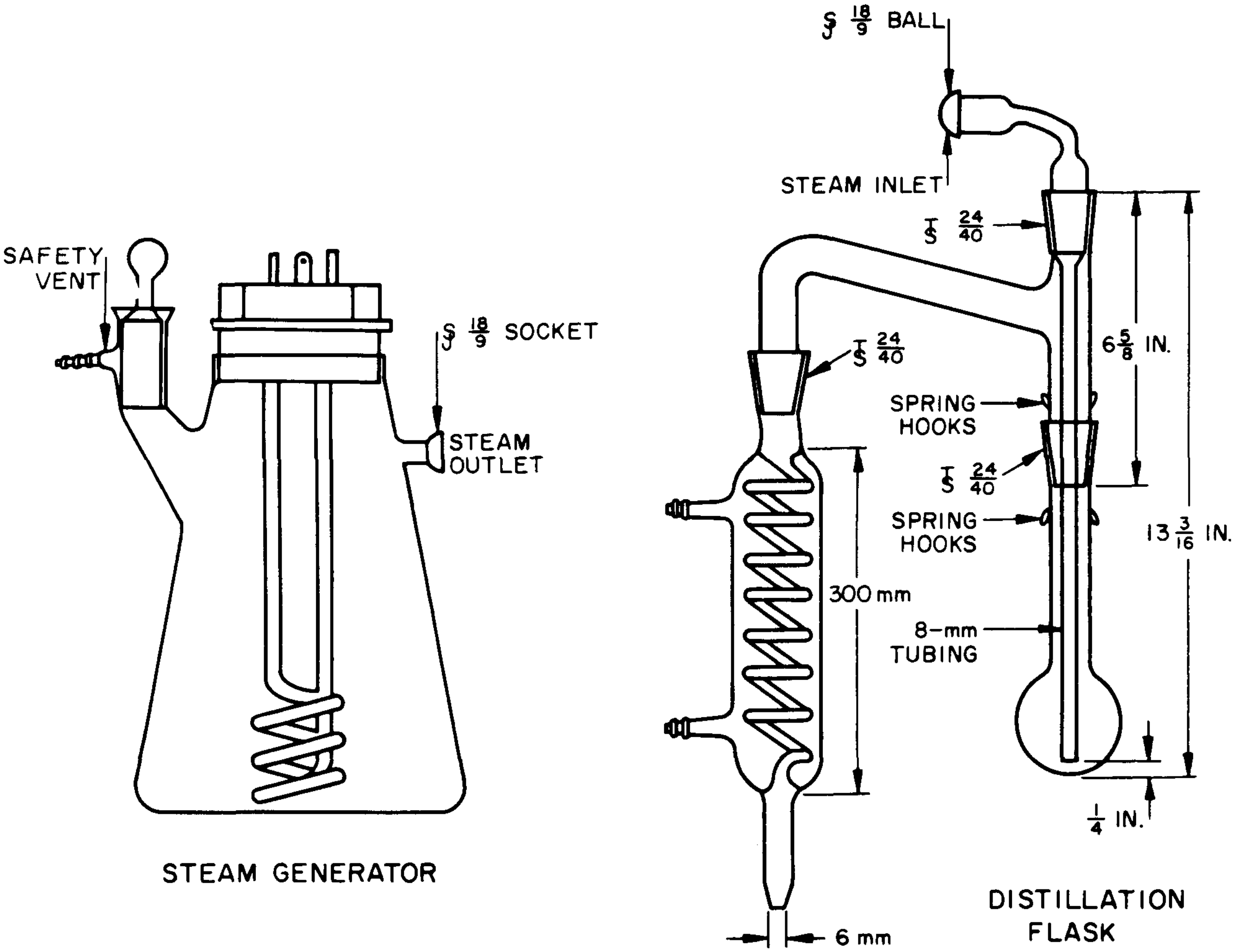


Figure C-1. Steam Distillation Apparatus for Nitrogen Determination in $ThO_2$ and $UO_2$-$ThO_2$

Aminco #5104 or equivalent 2-liter generating flask, and a 300-ml distillation flask. The generating flask and steam inlet to the distillation unit are modified so that the connection between them is made with glass tubing wrapped in asbestos and glass ball-and-socket joints.

3. **Vycor Erlenmeyer Flask**—125 ml, equipped with a 24/40 standard taper ground glass joint.

4. **Spectrophotometer**—Beckman Model DU-2 or equivalent, equipped with 2- and 10-cm absorption cells.

5. **Volumetric Flask**—50 ml.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare water that is free of ammonia by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.

2. **Standard Ammonia Solution (10 $\mu$g nitrogen/ml)**—Dissolve 3.819 g of ammonium chloride in water and dilute to 1 liter in a volumetric flask. Dilute 10.0 ml of this solution to 1 liter in a volumetric flask.

3. **Standard Ammonia Solution (2 $\mu$g nitrogen/ml)**—Dilute 20.0 ml of the 10 $\mu$g/ml standard ammonia solution (Item 2) to 100 ml in a volumetric flask.

4. **Sulfuric Acid (18M)**—Reagent grade.

5. **Phosphoric Acid (85%)**—Reagent grade, low nitrogen content.

6. **Sodium Hydroxide (37.5%)**—Dissolve 600 g of sodium hydroxide in 1 liter of water.

7. **Nessler Reagent**—Commercially prepared reagent for urea, ammonia nitrogen, or non-protein nitrogen such as Fisher SO-N-16 or equivalent may be used if accurate quantitative data are obtainable at the 5 $\mu$g nitrogen/50 ml level. As an alternative, dissolve 50 g of potassium iodide in a minimum volume of cold water (approximately 35 ml). Add a saturated solution of mercuric chloride slowly, until the first slight precipitate of red mercuric iodide persists, and then add 400 ml of a clarified 9N solution of alkali (potassium or sodium hydroxide). Dilute the solution to 1 liter with water and allow to clarify. Remove the clear supernatant liquid for use. This reagent does not deteriorate and can be stored indefinitely.

8. **Potassium Hydroxide (9N)**—Dissolve 505 g of potassium hydroxide in 400 ml of water and cool to room temperature. Transfer the clear solution only to a 1-liter volumetric flask and dilute to volume.

Prepare all solutions in an ammonia-free atmosphere and store in tightly stoppered bottles. Boil all rubber stoppers for 30 minutes in a 10% sodium hydroxide solution and then rinse with water.

## E. Procedure

### 1. Calibration Curve

*a. 0 to 20 $\mu$g Nitrogen*—Pipette 0 (blank), 2.0, 4.0, 6.0, 8.0, and 10.0 ml (0, 4, 8, 12, 16, and 20 $\mu$g of nitrogen) of the 2 $\mu$g/ml standard ammonia solution (Item 3 of Section I.D of this Appendix) into separate 50-ml volumetric flasks containing 25 to 30 ml of water. Add 1 ml of Nessler reagent to the flask by blowing it directly into the solution without splashing. Dilute to volume, stopper, and shake well. Let stand at least 20 minutes. Transfer the solution to a 10-cm absorption cell. Adjust the spectrophotometer to the initial setting using a light band centered at 420 m$\mu$ with the blue sensitive phototube. While maintaining this adjustment, take photometric readings of the calibration solutions using deionized water in the reference cell. Correct for the blank and plot absorbance versus micrograms of nitrogen in 50 ml of solution.

*b. 0 to 100 $\mu$g Nitrogen*—Pipette 0 (blank), 2.0, 4.0, 6.0, 8.0, and 10.0 ml (0, 20, 40, 60, 80, and 100 $\mu$g of nitrogen) of the 10 $\mu$g/ml standard ammonia solution (Item 2 of Section I.D of this Appendix) into separate 50-ml volumetric flasks containing 25 to 30 ml of water. Add 1 ml of Nessler reagent to the flask by blowing it directly into the solution without splashing. Dilute to volume, stopper, and shake well. Let stand at least 20 minutes. Transfer the solution to a 2-cm absorption cell and continue as in Section I.E.1.a of this Appendix.

### 2. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Weigh a 0.5-g sample to ±0.1 mg and transfer into a 125-ml Vycor Erlenmeyer flask equipped with a 24/40 ground glass joint. Pipette 10.0 ml of $H_3PO_4$ into the flask and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate. Heat gently until slight fumes of $SO_3$ appear. Add 1 drop of $H_2SO_4$ to the ground glass joint as a lubricant and attach the air-cooled condenser. (Condensers are not required for powder samples.) Heat strongly until the sample dissolves.

**NOTE**

> *It is crucial for the heat to be controlled so that fumes do not escape from the outlet end of the air condenser.*

The controls, blanks, and pellet or powder samples should be heated under the same conditions and for the same length of time for any given set of samples. Allow the dissolved samples to cool and then rinse each condenser down with 20 ml of water. In the case of powder samples that were dissolved without the use of air condensers, rinse each flask down with 20 ml of water. Transfer each solution to a 200- or 300-ml distillation flask. Rinse each dissolution flask three times, using no more that 15 ml of water for the total rinses. Mix well and cool.

While the samples are cooling, fill the steam generating flask of the distillation apparatus with deionized water. Apply heat and pass steam through the distillation flask and into the condenser at a rate yielding approximately 50 ml of distillate in 10 minutes. Collect 50-ml portions of distillate until the analysis described in Section I.E.1.a of this Appendix shows the apparatus to be free of ammonia. Add 25 to 30 ml of water to the distilling flask containing the sample. Mix well. Immediately, add slowly 50 ml of 37.5% NaOH solution down the sidewall of the flask so as to form two layers. Connect the flask to the distillation apparatus and distill into a 50-ml volumetric flask, collecting approximately 40 ml of distillate. Add 1 ml of Nessler reagent to the flask by blowing it directly into the solution without splashing, dilute to volume, and continue as in Section I.E.1.a of this Appendix, reading each sample against the deionized water reference solution.

### 3. Blanks

Two reagent blanks are run with each set of samples. Pipette 10.0 ml of $H_3PO_4$ and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate to each of two Erlenmeyer flasks. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section I.E.2 of this Appendix. Use an average of the two blanks for the sample blank.

### 4. Control Standards

To prepare the control standards, pipette 3.0 and 6.0 ml the 2 $\mu g/ml$ standard ammonia solution (Item 3 of Section I.D of this Appendix) into two separate Erlenmeyer flasks. Pipette 10.0 ml of $H_3PO_4$ and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate to each flask. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section I.E.2 of this Appendix, and use the data obtained to calculate the recovery.

If greater than 20 $\mu g$ of nitrogen is found in the sample, repeat the analysis using the procedure of Section I.E.1.b of this Appendix for color measurement. Two reagent blanks along with 20-$\mu g$-nitrogen and 80-$\mu g$-nitrogen controls are run with each set of samples when this condition occurs.

## F. Calculations

Correct for the average blank, determine the micrograms of nitrogen from the calibration curve, and calculate the nitrogen content of the samples as follows:

$$\text{ppm Nitrogen} = \frac{A}{B}$$

where:

A = nitrogen present, $\mu g$

B = weight of sample, g.

## G. References

The determination of nitrogen by ammonia gas-detecting electrode is given in Section II of this Appendix.

The Operational Chemistry Laboratory procedure for the spectrophotometric determination of nitrogen in $ThO_2$ and $UO_2$-$ThO_2$ is given in Appendix D, Section II.

# II. THE DETERMINATION OF NITROGEN IN $ThO_2$ AND $UO_2$-$ThO_2$ BY AMMONIA GAS-DETECTING ELECTRODE

## A. Scope

This procedure describes the determination of nitrogen in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 10 to 100 ppm on a 0.5-g sample basis. For related samples of higher concentration, this range can be extended to 1000 ppm since electrode response is Nernstian to this level and beyond.

## B. Summary of Method

The sample is dissolved by refluxing in a sulfuric-phosphoric acid mixture. The resulting solution is made basic by the addition of a strong sodium hydroxide solution, and nitrogen is separated as ammonia by steam distillation. After adjusting the distillate to at least a pH of 12, the nitrogen concentration is measured by the ammonia gas-detecting electrode.

## C. Apparatus

1. **Condenser**—Reflux air-cooled condenser equipped with a 24/40 ground glass joint without the drip spout or reflux water-cooled Graham condenser or equivalent equipped with a 24/40 ground glass joint.

2. **Steam Distillation Apparatus** (see Figure C-2)—The standard unit employs an Aminco #4-1842 or equivalent heating assembly equipped with a Teflon plug, an Aminco #5104 or equivalent 2-liter generating flask, and a 300-ml distillation flask. The generating flask and steam inlet to the distillation unit are modified so that the connection between them is made with glass tubing wrapped in asbestos and glass ball-and-socket joints.

3. **Vycor Erlenmeyer Flask**—125 ml, equipped with a 24/40 standard taper ground glass joint.

4. **Electrode**—Orion ammonia gas-detecting electrode Model 95-10 or equivalent.

5. **Electrode Holder**—Orion Model 92-00-01 or equivalent. (Electrode must be held at a 20° angle with respect to the vertical to prevent air bubble entrapment underneath it.)

6. **Expanded Scale pH Meter**—Equipped with a range of at least ±300 mV and a precision of at least ±1 mV.

7. **Powerstat Variable Transformer**—10-amp capacity.

8. **Magnetic Stirrer and Stirring Bar.**

9. **Tripour Polypropylene Beakers**—100 ml, graduated to ±1.5% accuracy (Fisher Scientific #2-513-50A or equivalent).

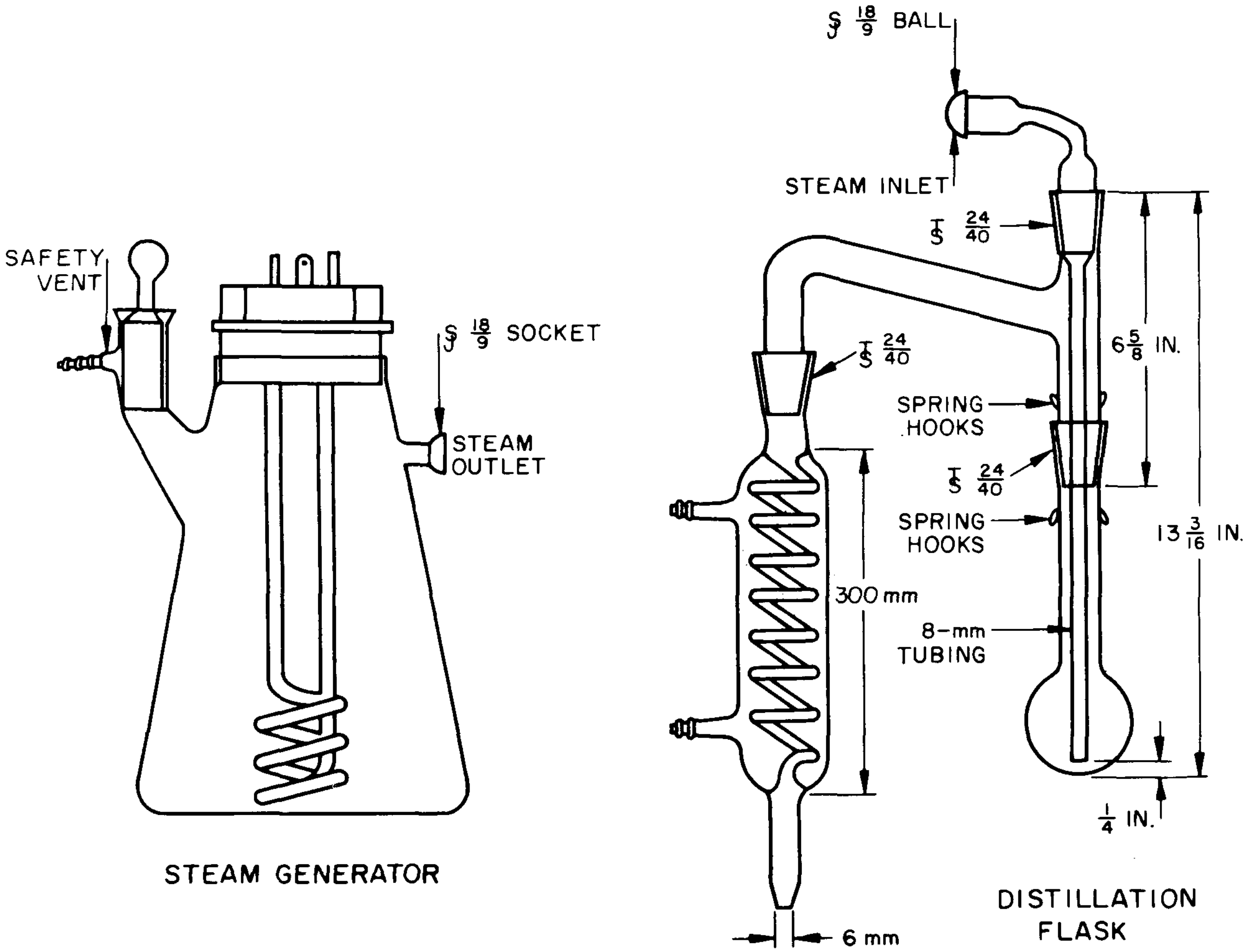


**Figure C-2. Steam Distillation Apparatus for Nitrogen Determination in $ThO_2$ and $UO_2$-$ThO_2$**

10. **Polyethylene Sheets**—Circular, 4-in.-diameter with a 5/8-in.-diameter hole cut in their center to function as beaker covers during EMF measurements.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare water that is free of ammonia by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.

2. **Standard Ammonia Solution (10 $\mu$g nitrogen/ml)**—Dissolve 3.819 g of ammonium chloride in water and dilute to 1 liter in a volumetric flask. Dilute 10.0 ml of this solution to 1 liter in a volumetric flask.

3. **Ammonium Chloride Solution (0.1M)**—Dissolve 2.68 g of ammonium chloride in water and dilute to 500 ml in a volumetric flask. Use this solution for storing the electrode when not in use.

4. **Sulfuric Acid (18M)**—Reagent grade.

5. **Phosphoric Acid (85%)**—Reagent grade, low nitrogen content.

6. **Sodium Hydroxide (37.5%)**—Dissolve 600 g of sodium hydroxide in 1 liter of water.

7. **Sodium Hydroxide (5M)**—Dissolve 100 g of sodium hydroxide in water and cool to room temperature. Transfer the solution to a 500-ml volumetric flask and dilute to volume.

Prepare all solutions in an ammonia-free atmosphere and store in tightly stoppered bottles. Boil all rubber stoppers for 30 minutes in a 10% sodium hydroxide solution and then rinse with water.

## E. Procedure

### 1. Calibration Curve (0 to 100 $\mu$g nitrogen)

Pipette 0 (blank), 0.5, 1.0, 2.0, 5.0, and 8.0 ml (0, 5, 10, 20, 50, and 80 $\mu$g of nitrogen) of the 10 $\mu$g/ml standard ammonia solution (Item 2 of Section II.D of this Appendix) into separate rinsed polypropylene beakers containing 30 to 35 ml of water. Add 1 ml of 5M NaOH and dilute to 50 ml. Rinse the electrode carefully with water and dry by gently blotting with soft, absorbent tissue.

**CAUTION**

*Do not rub electrode membrane.*

Insert the electrode into the solution, cover the beaker, stir at a moderate speed so as not to form a vortex, and read the EMF after 3 minutes. Ammonia gas is lost to the air from the solutions, so between standardizations, keep the beakers containing solutions covered. Do not add NaOH to the solutions until they are ready to be measured.

Plot the millivolt readings for each standard on the linear axis and the nitrogen concentration on the logarithmic axis of two-cycle semilog graph paper. Prepare a calibration curve whenever new reagents are used, a new membrane is placed in the electrode, or if there is a major change of room temperature. Check at least one calibration point with each set of samples to mark any slight day-to-day curve shifting and to ensure curve validity. Where minor shifting is detected the curves will be parallel with each other when made under comparable conditions. In cases of major curve shifting, drift, or poor response, the membrane should be changed. Membrane failure may be apparent on visual inspection as dark spots or discoloration. (A membrane will last from 1 week to several months depending upon usage.)

### 2. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Weigh a 0.5-g sample to ±0.1 mg and transfer into a 125-ml Vycor Erlenmeyer flask equipped with a 24/40 ground glass joint. Pipette 10.0 ml of $H_3PO_4$ into the flask and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate. Heat gently until slight fumes of $SO_3$ appear. Add 1 drop of $H_2SO_4$ to the ground glass joint as a lubricant and attach the air-cooled condenser. (Condensers are not required for powder samples.) Heat strongly until the sample dissolves.

**NOTE**

*It is crucial for the heat to be controlled so that fumes do not escape from the outlet end of the air condenser.*

The controls, blanks, and pellet or powder samples should be heated under the same conditions and for the same length of time for any given set of samples. Allow the dissolved samples to cool and then rinse each condenser down with 20 ml of water. In the case of powder samples that were dissolved without the use of air condensers, rinse each flask down with 20 ml of water. Transfer each solution to a 200- or 300-ml distillation flask. Rinse each dissolution flask three times, using no more than 15 ml of water for the total rinses. Mix well and cool.

While the samples are cooling, fill the steam generating flask of the distillation apparatus with deionized water. Apply heat and pass steam through the distillation flask and into the condenser at a rate yielding approximately 50 ml of distillate in 10 minutes. Collect 50-ml portions of the distillate until the analysis described in Section II.E.1 of this Appendix shows the apparatus to be free of ammonia. Pretreat the still before running samples. Pipette 10 $\mu g$ nitrogen into a round-bottom flask and dilute to approximately 50 ml. Add 20 ml of 37.5% NaOH solution down the sidewall of the flask. Distill the solution until 50 ml of condensate are collected. This may be discarded. Add 15 to 20 ml of water to the distilling flask containing the sample. Mix well. Immediately, add slowly 50 ml of 37.5% NaOH solution down the sidewall of the flask so as to form two layers. Connect the flask to the distillation apparatus and distill 40 to 45 ml into a rinsed polypropylene beaker. Treat the distillate as described in Section II.E.1 of this Appendix, starting with the addition of the 5M NaOH.

### 3. Blanks

Two reagent blanks are run with each set of samples. Pipette 10.0 ml of $H_3PO_4$ and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate to each of two Erlenmeyer flasks. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section II.E.2 of this Appendix. Use an average of the two blanks for the sample blank.

### 4. Control Standards

To prepare the control standards, pipette 0.5 and 7.0 ml of the 10 $\mu g$/ml standard ammonia solution (Item 2 of Section II.D of this Appendix) into two separate Erlenmeyer flasks. Pipette 10.0 ml of $H_3PO_4$ and then add 4 ml of $H_2SO_4$ measured with a 10-ml graduate to each flask. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section II.E.2 of this Appendix.

## F. Calculations

Determine the micrograms of nitrogen present in the blanks by comparing the average millivolt reading with the calibration curve. Determine the micrograms of nitrogen present in the samples from the calibration curve and correct for the average blank. Calculate the nitrogen content of the samples as follows:

$$\text{ppm Nitrogen} = \frac{A}{B}$$

where:

A = nitrogen present, $\mu g$

B = weight of sample, g.

## G. References

The spectrophotometric determination of nitrogen is given in Section I of this Appendix.

# III. THE FLUORIMETRIC DETERMINATION OF URANIUM IN $ThO_2$

## A. Scope

This procedure describes the determination of uranium in $ThO_2$ in the concentration range of 1 to 40 ppm on a 0.5-g sample basis. This range can be extended by changing the size of the aliquot used for the final uranium determination.

## B. Summary of Method

The sample is dissolved in a mixture of hydrofluoric and nitric acids. Acid-deficient aluminum nitrate solution containing tetra-n-propylammonium hydroxide is added. Uranium is then extracted as tetra-n-propylammonium uranyltrinitrate with methyl isobutyl ketone. An aliquot of the organic phase is evaporated on a pellet of sodium-lithium fluoride in a small platinum dish, and the mixture is fused into a button. The characteristic uranium fluorescence emitted by the button under ultraviolet light is measured with a fluorimeter.

## C. Apparatus

**NOTE**

*All apparatus should be kept separate and used only for trace uranium analysis. Pipettes and other glassware should be cleaned by soaking for 1 hour in hot 8N* $HNO_3$.

1. Galvanek-Morrison Fluorimeter—Jarrell-Ash or equivalent.

2. **Platinum Dishes**—Stamped from 0.015- by 0.75-in. discs using Jarrell-Ash platinum dish stamping die or equivalent.

**NOTE**

*The platinum dishes are reshaped as needed, using the dish-forming tool. For cleaning purposes, the dishes are arranged so that no stacking results and are then immersed in warm concentrated* $HNO_3$ *and left standing overnight. The dishes are then rinsed in tap water, then in deionized water, and finally in acetone and are dried. The platinum dishes and fluoride discs should be handled only with forceps to prevent the introduction of fluorescent impurities.*

3. **Shaker**—Burrell wrist-action or equivalent.
4. **Centrifuge.**
5. **Burner and Support**—Fisher burner and support or equivalent for the platinum dishes.
6. **Specimen Bottles**—35 ml with polyethylene caps.
7. **Heat Lamp.**
8. **Pipettes**—250 and 500 microliter.
9. **Polyethylene Bottles**—4 oz.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.
2. **Standard Uranium Solution (100 $\mu$g uranium/ml)**—Dissolve 0.1179 g of $U_3O_8$ in 5 ml of concentrated nitric acid. Transfer to a 1-liter volumetric flask and dilute to volume with water.
3. **Standard Uranium Solution (10 $\mu$g uranium/ml)**—Dilute 10.0 ml of the 100 $\mu$g/ml standard uranium solution (Item 2) to 100 ml with water in a volumetric flask.
4. **Nitric Acid (1.6N)**—Dilute 100 ml of concentrated nitric acid to 1 liter with water.
5. **Hydrofluoric Acid (1%)**—Dilute 2 ml of concentrated hydrofluoric acid to 100 ml with water. Store in a polyethylene bottle.
6. **Nitric Acid (13N)-Hydrofluoric Acid (0.04N) Solution**—Add 810 ml of concentrated nitric acid to a 1-liter polyethylene bottle containing 190 ml of water. Pipette 1.4 ml of concentrated hydrofluoric acid into the bottle.
7. **Tetra-n-propylammonium Hydroxide**—10% in water.
8. **Aluminum Nitrate Solution (2.8M)**—Transfer 1050 g of aluminum nitrate nonahydrate to a 2-liter beaker. Add water to a volume of 800 ml and warm on a hot plate. After dissolution, add 80 ml of ammonium hydroxide. Stir to dissolve the precipitate, cool to room temperature, and add 10 ml of 10% tetra-n-propylammonium hydroxide solution. Stir to dissolve the precipitate, transfer to a 1-liter volumetric flask, and dilute to volume with water. If the blanks are high and erratic, the aluminum nitrate may be discarded or a preliminary extraction with methyl isobutyl ketone is recommended to remove the uranium. Tetra-n-propylammonium hydroxide must be added again if this purifying extraction is done.
9. **Fusion Mixture (98% sodium fluoride-2% lithium fluoride)**—Thoroughly blend 9 g of lithium fluoride and 454 g of sodium fluoride. Essentially uranium free lots of sodium fluoride and lithium fluoride must be selected for the fusion mixture.
10. **Methyl Isobutyl Ketone.**
11. **Thorium Dioxide**—High purity.

## E. Procedure

1. **Calibration Curve (0 to 20 $\mu$g uranium)**

Pipette 0 (blank), 0.2, 0.5, 1.0, and 2.0 ml (0, 2, 5, 10, and 20 $\mu$g of uranium) of the 10 $\mu$g/ml standard uranium solution (Item 3 of Section III.D of this Appendix) into separate 50-ml Vycor crucibles, each containing 0.500 g of $ThO_2$ powder. Heat the crucibles on a hot plate until all of the liquid has evaporated.

Add 10 ml of 13N $HNO_3$-0.04N HF solution to each crucible. Cover each crucible with a flat Vycor lid such that a slight opening is left for the slow evaporation of acid. Heat the solutions to a very gentle boil on a hot plate. Continue to heat the solutions, with frequent, gentle swirling, until dissolution is complete. If dissolution is not complete before all of the acid solution evaporates, add an additional 10 ml of 13N $HNO_3$-0.04N HF solution, repeating the procedure of this paragraph until dissolution is complete.

After dissolution is complete, remove the solutions from the hot plate and allow them to cool for approximately 5 minutes. Remove each lid, rinsing any condensation into the crucible with a minimum volume of water (approximately 1 ml). Place the crucibles on a hot plate and evaporate the solutions to near dryness. Do not bake. Cool to room temperature.

Wash down the walls of each crucible with 5 ml of 1.6N nitric acid. Swirl the solutions to completely dissolve the salts. Gentle heating may be used. If a white precipitate forms during this step, heat gently on a hot plate until dissolution is complete. Transfer the solutions to 4-oz polyethylene bottles. Rinse each crucible twice with water, using no more than 5 ml of total wash solution. Add 25 ml of aluminum nitrate solution. Pipette 10.0 ml of methyl isobutyl ketone, cap tightly, and shake for 3 minutes using a mechanical shaker. Transfer a portion of the combined phases to a specimen bottle, cap, and centrifuge for 3 minutes.

Place pellets containing approximately 0.4 g of fusion mixture into platinum dishes.

### NOTE

*The fusion mixture can be measured readily using a 2-ml hypodermic syringe in which the end face has been cut parallel with the milliliter graduations.*

Pipette duplicate 0.25-ml aliquots of the methyl isobutyl ketone phase onto the pellets. Dry under a heat lamp. Fuse the pellets. The fusion technique will depend upon the type of fusion apparatus used.

### NOTE

*Calibrate the burner so that reproducible conditions can be obtained for fusing the pellets. The temperature should be such that complete fusion of the pellet takes place during the second minute (approximately 900 °C). The total time for fusion should be 4 minutes.*

Allow the dish to cool (approximately 15 minutes) and read the fluorescence of the fused button. Correct the average of the readings for the blank. Construct a calibration curve by plotting corrected meter readings (microamperes) versus concentration (micrograms) per 0.25-ml aliquot.

### 2. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Weigh a 0.5-g sample to ± 1 mg and transfer into a 50-ml Vycor crucible. Continue as in Section III.E.1 of this Appendix, starting with the addition of 13N $HNO_3$-0.04N HF solution.

## F. Calculations

Determine the micrograms of uranium present in the blank by comparing the average milliampere reading with the calibration curve. Determine the micrograms of uranium present in the samples from the calibration curve and correct for the blank. Calculate the uranium content of the samples as follows:

$$\text{ppm Uranium} = \frac{V_1 \times A}{V_2 \times B}$$

where:

$V_1$ = total volume of methyl isobutyl ketone extract, ml

$V_2$ = aliquot volume of methyl isobutyl ketone, ml

$A$ = uranium present, $\mu$g/0.25 ml

$B$ = weight of sample, g.

## G. References

The Operational Chemistry Laboratory procedure for the fluorimetric determination of uranium in $ThO_2$ is given in Appendix D, Section III.

## IV. THE DETERMINATION OF THORIUM IN $ThO_2$ BY THE OXALATE PRECIPITATION-GRAVIMETRIC METHOD

## A. Scope

This procedure describes the determination of thorium in $ThO_2$ using a 0.5-g sample. Interfering elements are those that are precipitated as an oxalate or hydrolyzed in the dilute acid solution from which the thorium is precipitated as the oxalate. Yttrium, scandium, lanthanum, the lanthanide rare earths, niobium, and tantalum are known to interfere. Sulfate ion, if present, prevents quantitative precipitation of thorium oxalate and therefore must be removed. Metals such as uranium, zirconium, and the alkaline earths do not interfere.

## B. Summary of Method

The sample is dissolved by fusion with sodium pyrosulfate, and thorium is precipitated as a hydrous oxide with ammonia. The precipitate is dissolved in hydrochloric acid, and thorium is reprecipitated as the oxalate from this solution. The precipitate is filtered, ignited to the oxide, and weighed.

## C. Apparatus

1. **Muffle Furnace**—Equipped with exhaust duct.
2. **Platinum Crucibles**—20 to 50 ml with lids.
3. **Vycor Crucibles**—50 ml with flat lids.
4. **Burner and Support.**
5. **Filter Paper**—Whatman #40 or equivalent, 11 or 12.5 cm.
6. **Filter Tablet or Pulp**—Whatman or equivalent.
7. **Black Ribbon Paper**—Schleicher and Schuell #589 or equivalent, 11 or 12.5 cm.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.
2. **Sodium Pyrosulfate or Sodium Bisulfate**—When using sodium bisulfate, heat over a low flame to remove water before weighing.
3. **Sulfuric Acid (18M)**—Reagent grade.
4. **Ammonium Hydroxide (37.5M)**—Reagent grade.
5. **Hydrochloric Acid (6N)**—Add 500 ml of concentrated hydrochloric acid to 500 ml of water and dilute to 1 liter in a volumetric flask.
6. **Hydrochloric Acid Wash Solution (0.12N)**—Dilute 20 ml of 6N hydrochloric acid to 1 liter in a volumetric flask. Transfer to a 1-liter wash bottle.
7. **Oxalic Acid Reagent Solution (0.555M)**—Dissolve 70 g of $H_2C_2O_4 \cdot 2H_2O$ in 750 ml of water and dilute to 1 liter in a volumetric flask. Transfer to a 1-liter wash bottle.
8. **Oxalic Acid Wash Solution (0.1M)**—Dissolve 12.6 g of $H_2C_2O_4 \cdot 2H_2O$ in 500 ml of water. Add 40 ml of 6N hydrochloric acid and dilute to 1 liter with water in a volumetric flask. Transfer to a 1-liter wash bottle.
9. **Ammonium Chloride Wash Solution (0.375M)**—Dissolve 20 g of ammonium chloride in 500 ml of water and dilute to 1 liter in a volumetric flask. Transfer to a 1-liter wash bottle.
10. **Methyl Red Indicator Solution**—Dissolve 0.25 g of methyl red in 150 ml of ethanol and dilute to 250 ml with water in a volumetric flask.
11. **Thorium Dioxide**—High purity, ignited.

## E. Procedure

### 1. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Weigh a 0.5-g sample to ±0.1 mg and transfer into a Vycor crucible. Add 3 g of sodium pyrosulfate or sodium bisulfate and cover the crucible. Heat over a burner to a clear melt. If the sample does not fuse after 15 minutes, cool, add 4 to 6 drops of concentrated sulfuric acid, and reheat over the burner. Cool. If necessary, repeat the sulfuric acid additions and heatings to complete fusion of the sample.

Place the crucible and crucible lid in a 400-ml beaker. Add 100 ml of water and 20 ml of 6N hydrochloric acid. Cover with a watch glass. Heat at approximately 80°C until the melt breaks and can be removed from the crucible and crucible lid. With a stirring rod, remove the crucible and crucible lid, rinsing with water. Warm the beaker to clear the solution and cool.

Add one-half of a large Whatman filter tablet or filter pulp or equivalent and stir. Add 10 ml of concentrated ammonium hydroxide, 5 drops of methyl red indicator, and stir. If necessary, stir in concentrated ammonium hydroxide dropwise until the solution is just alkaline. Stir in 6N hydrochloric acid dropwise until the solution is just acidic; then add 4 ml of 6N hydrochloric acid in excess. Add the appropriate amount of water to adjust the total volume to 200 ml.

Heat in a water bath to approximately 80 to 85°C. Stir in concentrated ammonium hydroxide dropwise until the solution is just alkaline; then add 10 drops of concentrated ammonium hydroxide in excess. Heat at 80 to 85°C for 10 minutes with occasional stirring. Remove from the water bath and allow the precipitate to settle.

While hot, filter through an 11- or 12.5-cm black ribbon paper. Test the filtrate with ammonium hydroxide and methyl red for completeness of precipitation. Wash the beaker, precipitate, and filter paper with approximately 50 ml of warm ammonium chloride wash solution.

Return the filter paper with precipitate to the original 400-ml beaker. Discard the filtrate. Add 16 ml of 6N hydrochloric acid and 24 ml of water, cover, and heat at approximately 80°C for 30 minutes. Stir to dissolve the precipitate and break up the filter paper. Add water to a total volume of 250 ml. Heat in a water bath to 80 to 85°C.

Slowly stir in 15 to 16 ml of 0.555M oxalic acid reagent solution. Stir well and allow to digest at 80 to 85°C for 2 hours or until the supernatant solution is clear. Add a few drops of the 0.555M oxalic acid reagent solution. The completeness of precipitation of the thorium oxalate is indicated by observation of no turbidity in the supernatant solution. Allow to stand overnight at room temperature.

Decant the supernatant solution through an 11- or 12.5-cm Whatman #40 filter paper or equivalent. Using the 0.1M oxalic acid wash solution, transfer the precipitate to the filter paper and police the beaker with a rubber policeman. The beaker precipitate and filter paper should be washed a total of not less than five times with the 0.1M oxalic acid wash solution, allowing each washing to drain. Wash the precipitate and filter paper twice with the 0.12N hydrochloric acid wash solution.

Transfer the filter paper with precipitate to a tared platinum crucible that has been preignited at 1000°C for 1 hour. Place in a cool, vented muffle furnace, heat to about 400°C with the door open, and hold until the paper has burned off. Take the furnace to 950°C with the door shut and ignite the sample for 1 hour. Remove the crucible and cool in a desiccator for 1/2 hour. Weigh as $ThO_2$ to ±0.1 mg.

### 2. Control Standards

To prepare the control standards, weigh a 0.5-g sample of high purity $ThO_2$ to ±0.1 mg and transfer into a Vycor crucible. Continue as in Section IV.E.1 of this Appendix, starting with the addition of 3 g of sodium pyrosulfate or sodium bisulfate.

## F. Calculations

Calculate the thorium content of the samples as follows:

$$\%\ \text{Thorium} = \frac{A \times 0.8788 \times 100}{B}$$

A = $ThO_2$ present, g

B = weight of sample, g.

## G. References

The Operational Chemistry Laboratory procedure for the determination of thorium in $ThO_2$ by the oxalate precipitation-gravimetric method is given in Appendix D, Section IV.

# V. THE CHROMATOGRAPHIC DETERMINATION OF CARBON IN $ThO_2$ AND $UO_2$-$ThO_2$

## A. Scope

This procedure describes the determination of carbon in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 10 to 800 ppm on a 0.5-g sample basis. This range can be extended to 4000 ppm by using sample weights as low as 0.1g, but sample segregation must be considered when such small samples are used.

## B. Summary of Method

The carbon analyzer utilizes the difference in thermal conductivity between helium and carbon dioxide to determine the carbon content of the sample. A crucible containing the sample and accelerators is burned in a purified oxygen stream using induction heating. The oxygen is purified by passage through a preburn catalyst furnace to convert any carbon monoxide to carbon dioxide and then through a series of absorption bulbs containing Ascarite, magnesium perchlorate, and sulfuric acid to remove carbon dioxide, water, and organic compounds. The oxygen then enters at the bottom of a vertically positioned furnace tube to react with the sample. Carbon in the sample is converted to carbon dioxide at a combustion temperature in excess of 1600°C. The exit gases pass through a sulfur and halogen trap containing manganese dioxide and silver wire, a catalyst furnace to convert any carbon monoxide to carbon dioxide, a moisture trap containing magnesium perchlorate, and finally into the chromatographic analyzer. The amount of carbon in the sample is determined by measuring the change in the thermal conductivity of the helium carrier gas as the carbon dioxide is eluted from the column. This measurement is made automatically and read directly as micrograms of carbon on a digital voltmeter (DVM).

## C. Apparatus

1. **Induction Furnace**—Leco No. 521-100 or equivalent.
2. **Low Carbon Analyzer**—Leco No. 589-600 or equivalent.
3. **Oxygen Purification Assembly**—Leco No. 516-100, 507-000, and 507-010 or equivalent.
4. **Induction Furnace Crucibles**—Leco No. 528-035 or equivalent.
5. **Combustion Tubes (quartz)**—Leco No. 550-120 or equivalent.
6. **High Temperature Tube or Muffle Furnace.**
7. **Leak-Check Seal Assembly**—Leco No. 589-911 or equivalent.
8. **Glass Wool**—Pyrex or equivalent.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Ascarite**—8 to 20 and 20 to 30 mesh.
2. **Magnesium Perchlorate**—Anhydrous.
3. **Sulfuric Acid (18M)**—Reagent grade.
4. **Manganese Dioxide**—Burrell Sulsorbent No. 25-433 or equivalent.
5. **Silver Wire.**
6. **Accelerator Iron**—Leco No. 501-317 or equivalent.
7. **Accelerator Tin**—Leco No. 501-76 or equivalent.
8. **Steel Samples**—National Bureau of Standards (NBS) samples with certified carbon content.

## E. Procedure

### 1. Preparation of Crucibles

Preburn crucibles at approximately 1350°C for 10 minutes in a tube furnace in a stream of purified oxygen maintained at a flow rate of 0.25 liter/min. When cool, weigh 1.0 g of accelerator iron into each crucible. Heat the crucibles in a muffle furnace at 800 to 900°C for at least 2 hours. Cool and store the crucibles in a closed container.

### 2. Instrument Preparation and Leak Check

Place a plug of fine glass wool loosely in the narrow portion of the furnace tube and install the tube in the induction furnace. Replace daily the magnesium perchlorate and glass wool in the drying tube located on the left side of the analyzer.

Connect the oxygen line to the 8-lb pressure bench outlet, turn on the preburn catalyst furnace, and fully open the bench outlet valve. Fully open the valve on the helium flowmeter on the analyzer and verify that the flow rate is at the value marked on the flowmeter.

Check the induction furnace for leaks before running samples by plugging the furnace exit tube with the leak-check seal assembly and allowing the system pressure to build to 8 lb with the oxygen flowing at 1.5 liters/min. Any leak will show up as bubbling in the sulfuric acid trap.

### 3. Balancing the Analyzer

To balance the analyzer, turn on the DVM by turning the OFF-NORM-REV switch to the REV position. Allow the DVM to warm up for 15 minutes. Turn the RANGE switch to the *1.000* position. Place the SELECT control of the DVM on the *0* position. Adjust the zero control until the DVM indicates *0.0000.* Place the SELECT control in the AMP BAL position. Adjust the BAL control until the DVM indicates *0.0000.* Place the SELECT control in the SYSTEM BAL position. Adjust the SYSTEM BAL control until the DVM indicates *0.0000.* This adjustment is quite sensitive, hence the control should be rotated slowly until approximate DVM zero indication is achieved. Activate the locking mechanism on this control. It is normal that there be a slight wandering about *0* due to variations in oven temperature as the oven heater cycles. When the balancing is completed, leave the DVM switch in the REV position, set the selector switch to OPERATE, and turn on the filament power to the induction furnace, letting it warm for 15 minutes.

### 4. General Operating Procedure

Place the crucible on the pedestal of the induction furnace and lock the sealing assembly. Purge the system for 30 seconds with oxygen at a flow rate of 1.5 liters/min.

Turn on the BLANK, CLAMP, and TIMER switches and start the analysis by turning the timer knob clockwise to the mechanical stop and releasing. The remainder of the analysis is automatic. The carbon content is read as micrograms of carbon on the DVM. Another sample can be loaded when the COLLECT light goes out; however, the READ light must be on and the trap temperature must be below 100°F before another analysis is begun.

### 5. Calibration

Condition the furnace tube by running two samples composed of 1 g of each accelerator in an unburned crucible followed by a 0.5-g sample of NBS Standard 8i, also containing the accelerators.

Using Table C-1, select the proper standards based on the expected range of the samples. Weigh three or four high point calibration standards into the preburned crucibles and add 1 g of accelerator tin to each standard.

TABLE C-1. CALIBRATION STANDARDS FOR CHROMATOGRAPHIC DETERMINATION OF CARBON

| Carbon Range ($\mu$g) | Low | High |
|---|---|---|
| 0 to 200 | Accelerators (0 $\mu$g carbon) | 0.25-g NBS Standard 8i (192 $\mu$g carbon) |
| 0 to 400 | Accelerators (0 $\mu$g carbon) | 0.5-g NBS Standard 8i (385 $\mu$g carbon) |

Run the low point calibration standard first, and as soon as the reading appears on the DVM, shut off the timer by pressing the TIMER switch. If the DVM reading is 0000 ±3 $\mu$g, turn on the timer as quickly as possible, allow the cycle to continue to completion, and proceed to the next paragraph. If the DVM reading is beyond the ±3 $\mu$g limits, reset the DVM in the direction of the actual value, moving it about one-half of the difference between the observed and the actual value by adjusting the BLANK control. Then run a second blank. Repeat until the blank is within the ±3 $\mu$g limits and then proceed to the next paragraph.

Run the high point calibration standard and again shut off the timer when the reading appears on the DVM. If the DVM reading is within ±5 percent of the actual value, turn on the timer as quickly as possible, let the cycle continue to completion, and run a control sample and blank as described in Section V.E.7 of this Appendix before starting sample analysis. If the reading is beyond the ±5-percent limits, reset the DVM as described for the low point calibration standard using the SLOPE control. Then run another high point, and if the reading is in the correct range, run a control sample and blank as described in Section V.E.7 of this Appendix before starting sample analysis. If the second standard is out of range, recheck the amplifier balance and recalibrate, starting with the low point.

### 6. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Weigh a 0.5-g sample to ±1 mg and transfer to a preburned crucible.

Place the crucible on the pedestal of the induction furnace and lock the sealing assembly. Purge the system for 30 seconds with oxygen at a flow rate of 1.5 liters/min and continue as in Section V.E.4 of this Appendix.

### 7. Control Standards

To prepare the control standards, run an NBS standard of appropriate weight to give a carbon content in the mid-point range of the calibration curve. Do not use samples larger than 1 g. If the control value is within ±5 percent of the NBS value, run a blank (low point calibration standard). If the blank is 0000 ±3 $\mu$g, start sample analysis. If the blank is out of range, repeat the blank, resetting the BLANK control if necessary, and then proceed to sample analysis.

If the control value is beyond the ±5-percent limits, run a second control, and if this control is in range, run a blank as described in the preceding paragraph.

If the second control is also out of range, run a blank, repeating and resetting the BLANK control if necessary.

## F. Calculations

Calculate the carbon content of the samples as follows:

$$\text{ppm Carbon} = \frac{A}{B}$$

where:

A = DVM carbon reading, $\mu$g

B = weight of sample, g.

### G. References

The Operational Chemistry Laboratory procedure for the chromatographic determination of carbon in $ThO_2$ and $UO_2$-$ThO_2$ is given in Appendix D, Section V.

## VI. THE PYROHYDROLYTIC DETERMINATION OF FLUORIDE IN $ThO_2$ AND $UO_2$-$ThO_2$ USING A SPECIFIC ION ELECTRODE

### A. Scope

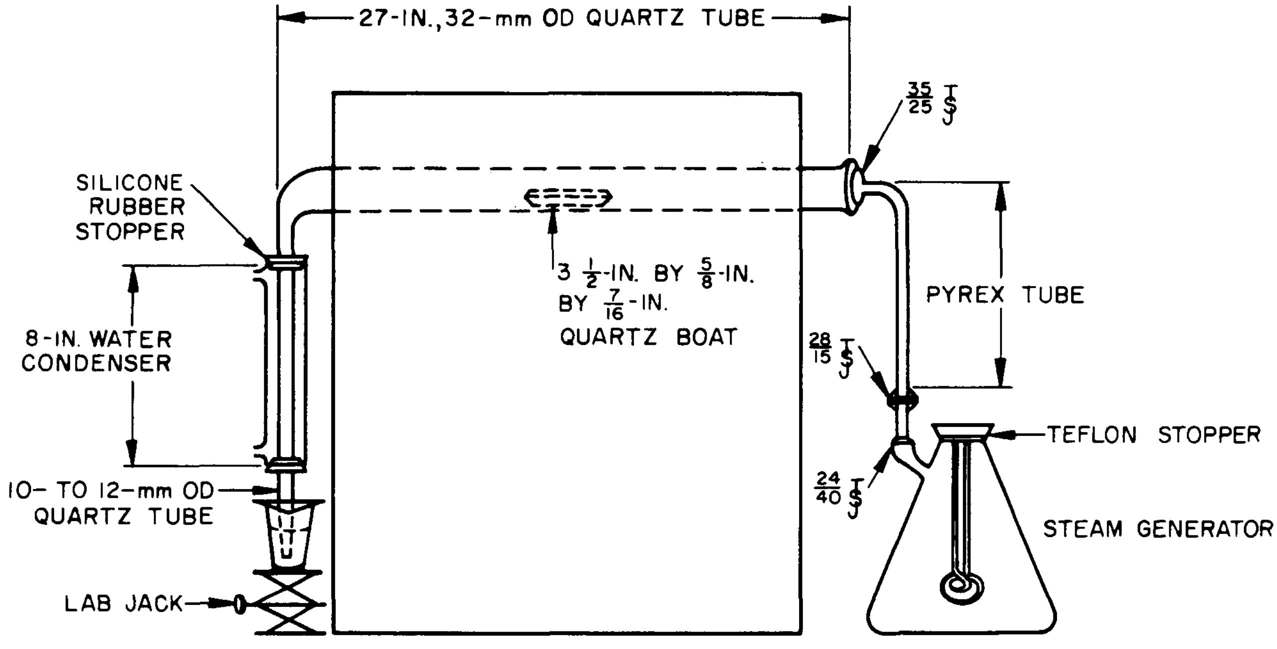
This procedure describes the determination of fluoride in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 2 to 50 ppm on a 1-g sample basis. For related samples of higher concentration, this range can be extended to 1000 ppm since electrode response is Nernstian to this level and beyond.

### B. Summary of Method

Fluoride is separated from the sample as hydrofluoric acid by pyrohydrolysis with steam in a quartz tube at approximately 1050°C. Hydrofluoric acid is absorbed in water and is determined by measuring its concentration with a fluoride specific ion electrode.

### C. Apparatus

1. **Pyrohydrolysis Apparatus**—See Figure C-3.
2. **Quartz Combustion Boats**—3 in. long.
3. **Polypropylene Volumetric Flasks**—250 ml and 1 liter for preparation of fluoride solutions.
4. **Fluoride Ion Electrode**—Orion Model 94-09 or equivalent.
5. **Reference Electrode**—Orion Model 90-01 or equivalent.
6. **Expanded Scale pH Meter**—Equipped with a range of at least ±300 mV and a precision of at least ±1 mV.
7. **Powerstat Variable Transformer**—10-amp capacity.



BURRELL MODEL # H-2-9 FURNACE
(CONTROL AT 1050 ±25 °C)

NOTE
ALWAYS USE DEIONIZED WATER
IN THE STEAM GENERATOR

Figure C-3. Pyrohydrolysis Apparatus for Fluoride Determination in $ThO_2$ and $UO_2$-$ThO_2$

8. **Magnetic Stirrer and Stirring Bar.**

9. **Tripour Polypropylene Beakers**—50 ml, graduated to ±1.5% accuracy (Fisher Scientific #2-593-50A or equivalent).

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.

2. **Standard Fluoride Solution (100 μg fluoride/ml)**—Dissolve 0.221 g of sodium fluoride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 1 liter in a polypropylene volumetric flask.

3. **Standard Fluoride Solution (10 μg fluoride/ml)**—Dilute 25.0 ml of the 100 μg/ml standard fluoride solution (Item 2) to 250 ml in a polypropylene volumetric flask.

4. **Total Ionic Strength Adjustment Buffer (TISAB)**—Orion No. 94-09-09 or equivalent.

## E. Procedure

### 1. Calibration Curve (0 to 50 μg fluoride)

Pipette 0 (blank), 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 ml (0, 2, 5, 10, 20, 30, and 50 μg of fluoride) of the 10 μg/ml standard fluoride solution (Item 3 of Section VI.D of this Appendix) into seven 50-ml polypropylene beakers. Add 10 ml of TISAB solution to each beaker and dilute to 50 ml with water. Insert the fluoride ion electrode and reference electrode pair into the solution. Stir each solution vigorously with a magnetic stirrer and read the EMF of the electrode system after 10 minutes. Plot the millivolt readings on the linear axis and the fluoride ion concentration in micrograms per 50 ml of solution on the logarithmic axis of two-cycle semilog graph paper. After each measurement, rinse the electrodes carefully with water and dry them by gently patting with soft, absorbent tissue.

**CAUTION**

*Do not rub fluoride ion electrode membrane.*

Prepare a calibration curve whenever new reagents are used. It is not necessary to obtain a calibration curve for each set of samples; however, at least one calibration point should be run with each set to mark any minor curve shifting and to ensure the validity of the calibration curve.

### 2. Blanking the Pyrohydrolysis Apparatus

Insert a quartz boat in the pyrohydrolysis tube at approximately 1050°C and adjust the steam flow to produce 30 ml of distillate in 20 minutes.

**NOTE**

*It has been experimentally determined that 30 ml of distillate can be collected in 20 minutes with a setting of approximately 73 on a powerstat connected to the heating elements of the steam generator.*

Blank the apparatus in this manner for 1 hour. Collect 30-ml portions of distillate and continue as in Section VI.E.1 of this Appendix, starting with the addition of the TISAB solution. Continue this process until 30 ml of distillate give a constant millivolt reading within ±10 mV of the reagent blank, which is determined in accordance with Section VI.E.1 of this Appendix.

### 3. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Transfer approximately 1.0 g of the sample, weighed to the nearest mg, to a blanked quartz boat. Place a 50-ml polypropylene beaker containing 6 to 8 ml of deionized water such that the condenser tip is below the water surface. Insert the boat quickly in the hot zone of the combustion tube, connect the steam line, and collect close to but under 40 ml of distillate. Treat the distillate in the same manner as in Section VI.E.1 of this Appendix, starting with the addition of the TISAB solution. Store the electrodes in a water solution containing 1 ppm fluoride.

### 4. Control Standards

To prepare the control standard, pipette 0.1 ml of the 100 μg/ml standard fluoride solution (Item 2 of Section VI.D of this Appendix) into a previously pyrohydrolyzed sample in a quartz boat. Dry the control in a vacuum desiccator or for 1 hour in an oven at approximately 100°C. Treat the control as a sample, analyzing it as described in Section VI.E.3 of this Appendix, and use the data obtained to calculate the recovery.

## F. Calculations

Convert millivolt readings to micrograms of fluoride by means of the calibration curve. Calculate the fluoride content of the samples as follows:

$$\text{ppm Fluoride} = \frac{A}{B}$$

where:

A = fluoride present, $\mu g$

B = weight of sample, g.

## G. References

Other pyrohydrolytic analysis procedures for chloride and/or fluoride ion determination are given in Sections VII and VIII of this Appendix.

The Operational Chemistry Laboratory pyrohyrolytic analysis procedures for chloride and fluoride ion determination are given in Appendix D, Sections VI and VII.

# VII. THE PYROHYDROLYTIC DETERMINATION OF CHLORIDE IN $ThO_2$ AND $UO_2$-$ThO_2$ USING A SPECTROPHOTOMETER

## A. Scope

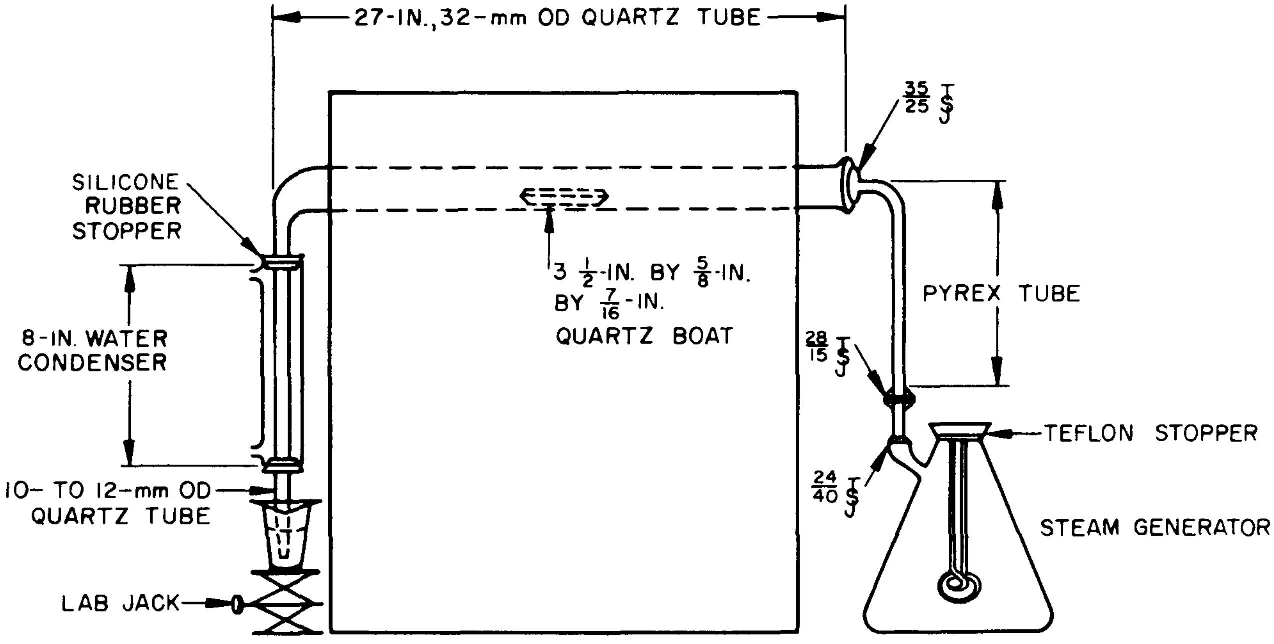
This procedure describes the determination of chloride in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 3 to 25 ppm on a 3-g sample basis using a 10-cm light path for photometric measurement. This range can be extended by using dilution techniques, altering sample sizes, or using shorter path length absorption cells and larger chloride aliquots for calibration curves.

## B. Summary of Method

Chloride is separated from the sample as hydrochloric acid by pyrohydrolysis with steam in a quartz tube at approximately 1050°C. The chloride reacts with mercuric thiocyanate, releasing thiocyanate ions which in turn react with ferric ions to produce the red ferric thiocyanate complex. The intensity of the color measured at 470 m$\mu$ is proportional to the chloride content.

## C. Apparatus

1. **Pyrohydrolysis Apparatus**—See Figure C-4.



NOTE
ALWAYS USE DEIONIZED WATER
IN THE STEAM GENERATOR

**Figure C-4. Pyrohydrolysis Apparatus for Chloride Determination in $ThO_2$ and $UO_2$-$ThO_2$**

2. **Quartz Combustion Boats**—3 in. long.

3. **Spectrophotometer**—Beckman Model DU-2 or equivalent equipped with 5- and 10-cm cells.

4. **Powerstat Variable Transformer**—10-amp capacity.

5. **Magnetic Stirrer and Stirring Bar.**

6. **Volumetric Flask**—50 ml.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.

2. **Standard Chloride Solution (100 $\mu$g chloride/ml)**—Dissolve 0.1648 g of sodium chloride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 1 liter in a volumetric flask.

3. **Standard Chloride Solution (10 $\mu$g chloride/ml)**—Dilute 10.0 ml of the 100 $\mu$g/ml standard chloride solution (Item 2) to 100 ml in a volumetric flask.

4. **Standard Chloride Solution (5 $\mu$g chloride/ ml)**—Dilute 5.0 ml of the 100 $\mu$g/ml standard chloride solution (Item 2) to 100 ml in a volumetric flask.

5. **Nitric Acid (6N)**—Dilute 190 ml of concentrated nitric acid to 500 ml with water.

6. **Ferric Ammonium Sulfate Solution**—Dissolve 49.85 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 300 ml of 6N nitric acid and dilute to 500 ml in a volumetric flask. Allow the solution to stand 24 hours before use and store in a brown bottle.

7. **Mercuric Thiocyanate Solution**—Add 7.5 g of mercuric thiocyanate to 500 ml of methyl alcohol and stir for 1 hour with a magnetic stirrer. Filter the solution through Whatman No. 41 or 41H filter paper or equivalent. If the filtrate is not clear, allow the solution to stand 24 hours before use.

## E. Procedure

### 1. Calibration Curve

*a. 0 to 75 $\mu$g Chloride*—Pipette 0 (blank), 1.0, 3.0, 5.0, 10.0, and 15.0 ml (0, 5, 15, 25, 50, and 75 $\mu$g of chloride) of the 5 $\mu$g/ml standard chloride solution (Item 4 of Section VII.D of this Appendix) to separate 50-ml volumetric flasks and dilute with water to approximately 40 ml. Add 2.0 ml of the ferric ammonium sulfate solution, rinse down the necks of the flasks, and mix by swirling the flasks. Add 2.0 ml of the mercuric thiocyanate solution and mix again by swirling. Care should be taken not to agitate the mercuric thiocyanate solution or to transfer undissolved mercuric thiocyanate to the volumetric flask. Dilute to volume with water, mix well, and allow to stand for 15 minutes. Read the absorbance at 470 m$\mu$ in 10-cm cells using deionized water in the reference cell. Correct for the blank and plot absorbance versus micrograms of chloride in 50 ml. Prepare a new calibration curve whenever new reagents are used.

*b. 0 to 100 $\mu$g Chloride*—Pipette 0 (blank), 2.0, 4.0, 6.0, 8.0, and 10.0 ml (0, 20, 40, 60, 80, and 100 $\mu$g of chloride) of the 10 $\mu$g/ml standard chloride solution (Item 3 of Section VII.D of this Appendix) to separate 50-ml volumetric flasks and dilute with water to approximately 40 ml. Add 2.0 ml of the ferric ammonium sulfate solution, rinse down the neck of the flasks, and mix by swirling the flasks. Add 2.0 ml of the mercuric thiocyanate solution and mix again by swirling. Care should be taken not to agitate the mercuric thiocyanate solution or to transfer undissolved mercuric thiocyanate to the volumetric flasks. Dilute to volume with water, mix well, and allow to stand for 15 minutes. Read the absorbance at 470 m$\mu$ in 5-cm cells using deionized water in the reference cell. Correct for the blank and plot absorbance versus micrograms of chloride in 50 ml. Prepare a new calibration curve whenever new reagents are used.

### 2. Blanking the Pyrohydrolysis Apparatus

Insert a quartz boat in the pyrohydrolysis tube at approximately 1050°C and adjust the steam flow to produce 30 ml of distillate in 20 minutes.

#### NOTE

*It has been experimentally determined that 30 ml of distillate can be collected in 20 minutes with a setting of approximately 73 on a powerstat connected to the heating elements of the steam generator.*

Blank the apparatus in this manner for 1 hour. Collect 30-ml portions of distillate, transfer to 50-ml volumetric flasks, and dilute to approximately 40 ml. Continue as in Section VII.E.1.a of this Appendix, starting with the addition of the ferric ammonium sulfate. Continue this process until 30 ml of distillate gives an absorbance reading within 0.005 to 0.01 of the reagent blank, which is determined in accordance with Section VII.E.1.a of this Appendix.

### 3. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Transfer approximately 3.0 g of the sample, weighed to the nearest mg, to a blanked quartz boat, quickly place the boat in the hot zone of the combustion tube, connect the steam line, and collect approximately 30 ml of distillate. Transfer the distillate to a 50-ml volumetric flask, dilute to approximately 40 ml, and continue as in Section VII.E.1.a of this Appendix, starting with the addition of the ferric ammonium sulfate.

### 4. Control Standards

To prepare the control standard, pipette 1.0 ml of the 10 $\mu$g/ml standard chloride solution (Item 3 of Section VII.D of this Appendix) into a previously pyrohydrolyzed sample in a quartz boat. Dry the control in a vacuum desiccator or for 1 hour in an oven at approximately 100°C. Treat the control as a sample, analyzing it as described in Section VIII.E.3 of this Appendix, and use the data obtained to calculate the recovery.

## F. Calculations

Correct for the blank, determine the micrograms of chloride from the calibration curve, and calculate the chloride content of the samples as follows:

$$\text{ppm Chloride} = \frac{A}{B}$$

where:

A = chloride present, $\mu$g

B = weight of sample, g.

## G. References

Other pyrohydrolytic analysis procedures for chloride and/or fluoride ion determination are given in Sections VI and VIII of this Appendix.

The Operational Chemistry Laboratory pyrohydrolytic analysis procedures for chloride and fluoride ion determination are given in Appendix D, Sections VI and VII.

# VIII. THE PYROHYDROLYTIC DETERMINATION OF CHLORIDE AND FLUORIDE IN $ThO_2$ AND $UO_2$-$ThO_2$ USING SPECIFIC ION ELECTRODES

## A. Scope

This procedure describes the determination of chloride and fluoride in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 5 to 50 ppm on a 3-g sample basis. For related samples of higher concentration, this range can be extended to 1000 ppm since electrode response is Nernstian to this level and beyond.

## B. Summary of Method

Chloride and fluoride are separated from the sample as hydrochloric acid and hydrofluoric acid by pyrohydrolysis with steam in a quartz tube at approximately 1050°C. The acids and steam are condensed into glacial acetic acid. In this medium, chloride concentration can be directly determined by measuring the EMF between a chloride specific ion electrode and a double junction reference electrode. After buffering the solution to a pH of 4.5 with sodium acetate solution, the fluoride concentration can be measured by a fluoride specific ion electrode and the same reference electrode as used for the chloride determination.

## C. Apparatus

1. **Pyrohydrolysis Apparatus**—See Figure C-5.
2. **Quartz Combustion Boats**—3 in. long.
3. **Polypropylene Volumetric Flasks**—500 ml for preparation of fluoride solutions.
4. **Fluoride Ion Electrode**—Orion Model 94-09 or equivalent.
5. **Chloride Ion Electrode**—Orion Model 94-17 or equivalent.
6. **Double Junction Reference Electrode**—Orion Model 90-02 or equivalent.
7. **Expanded Scale pH Meter**—Equipped with a range of at least ±300 mV and a precision of at least ±1 mV.

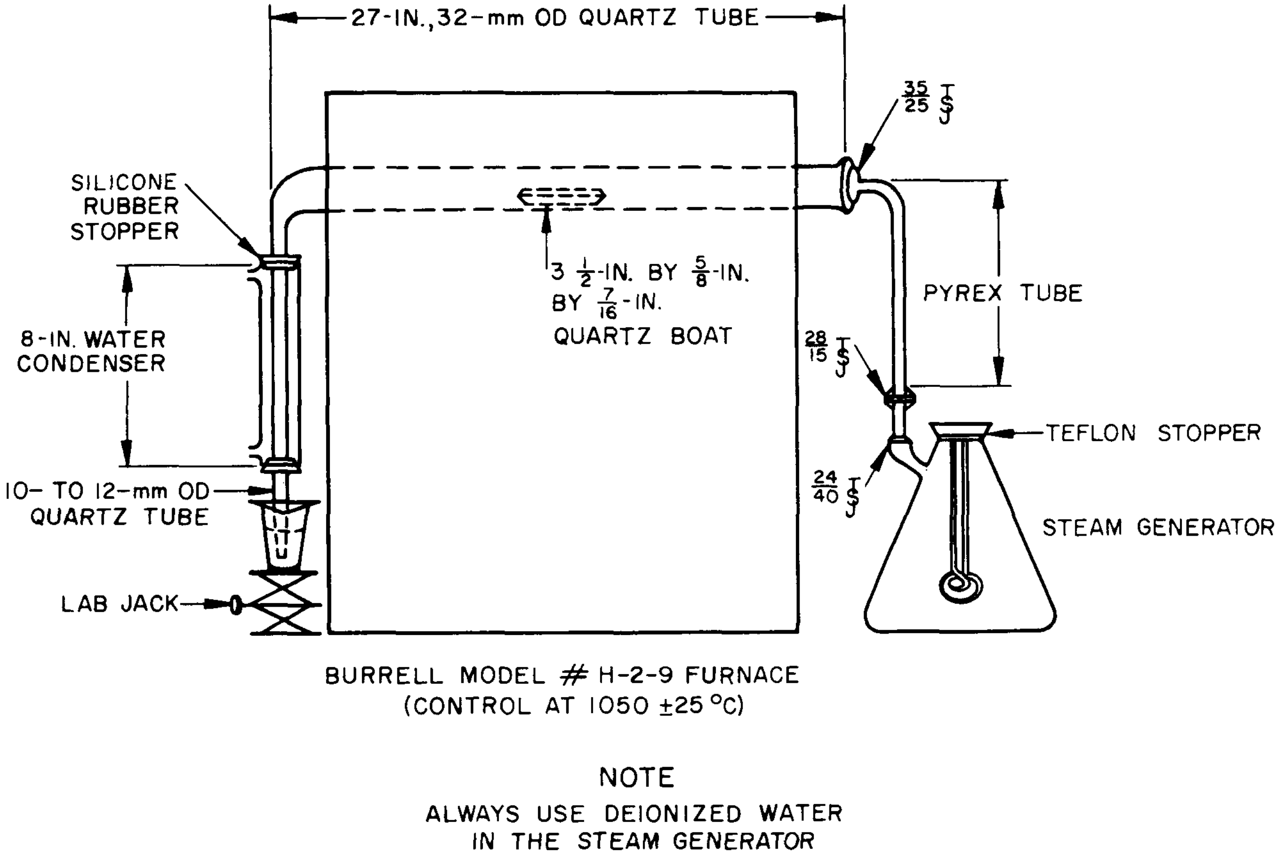


**Figure C-5. Pyrohydrolysis Apparatus for Chloride-Fluoride Determination in $ThO_2$ and $UO_2$-$ThO_2$**

8. **Powerstat Variable Transformer**—10-amp capacity.

9. **Magnetic Stirrer and Stirring Bar.**

10. **Tripour Polypropylene Beakers**—250 ml, graduated to ±1.5% accuracy (Fisher Scientific #2-593-50A or equivalent).

11. **Polyethylene Sheets**—Circular, 4-in.-diameter. One has a 1/2-in.-diameter hole cut in its center to function as a beaker cover during distillate collection and the other has three 1/2-in.-diameter holes cut in the same arrangement as the electrodes to function as a beaker cover during measurements.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.

2. **Standard Chloride Solution** (1000 $\mu g$ **chloride/ml**)—Dissolve 0.824 g of sodium chloride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 500 ml in a volumetric flask.

3. **Standard Fluoride Solution** (1000 $\mu g$ **fluoride/ml**)—Dissolve 1.105 g of sodium fluoride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 500 ml in a polypropylene volumetric flask.

4. **Standard Chloride-Fluoride Solution** (10 $\mu g$ **chloride/ml-10** $\mu g$ **fluoride/ml**)—Dilute 5.0 ml of the 1000 $\mu g$/ml standard chloride solution (Item 2) and 5.0 ml of the 1000 $\mu g$/ml standard fluoride solution (Item 3) to 500 ml in a polypropylene volumetric flask.

5. **Glacial Acetic Acid**—Reagent grade.

6. **Sodium Acetate Buffer Solution**—Dissolve 666 g of $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to 2 liters in a volumetric flask.

## E. Procedure

### 1. Calibration Curve (0 to 30 μg chloride and fluoride)

Pipette 0 (blank), 0.5, 1.0, 2.0, and 3.0 ml (0, 5, 10, 20, and 30 μg of chloride and fluoride) of the 10 μg/ml standard chloride-fluoride solution (Item 4 of Section VIII.D of this Appendix) into separate rinsed polypropylene beakers. Dilute to 30 ml with water and add 50 ml of glacial acetic acid. Rinse the electrodes carefully with water and dry them by gently patting with soft, absorbent tissue.

**CAUTION**

*Do not rub chloride or fluoride ion electrode membrane.*

Insert the chloride and fluoride ion electrode and the double junction reference electrode into the solution and cover the beaker. Stir at a moderate speed with a magnetic stirrer, and read the EMF between the chloride ion electrode and the double-junction reference electrode after 5 minutes. Dilute the sample to 200 ml with sodium acetate buffer solution. Read the EMF between the fluoride ion electrode and the double junction reference electrode in the same manner as with the chloride ion electrode. Plot the millivolt readings for each electrode on the linear axis and the chloride and fluoride concentration in micrograms on the logarithmic axis of two-cycle semilog graph paper. Prepare a calibration curve whenever new reagents are used. It is not necessary to obtain a calibration curve for each set of samples; however, at least one calibration point should be run with each set to mark any minor curve shifting and to ensure validity of the calibration curve.

### 2. Blanking the Pyrohydrolysis Apparatus

Insert a quartz boat in the pyrohydrolysis tube at approximately 1050°C and adjust the steam flow to produce 30 ml of distillate in 20 minutes.

**NOTE**

*It has been experimentally determined that 30 ml of distillate can be collected in 20 minutes with a setting of approximately 73 on a powerstat connected to the heating elements of the steam generator.*

Blank the apparatus in this manner for 1 hour. Collect 30-ml portions of distillate in 50 ml of glacial acetic acid contained in a new polypropylene beaker that has been rinsed with water. Cover the beaker during distillate collection and at all other times to decrease the amount of acid evaporation. Ensure the tube outlet is submerged in the acid. Analyze as in Section VIII.E.1 of this Appendix, starting with the rinsing of the electrodes. Continue this process until 30 ml of distillate gives a constant millivolt reading within ±10 mV of the reagent blank for both chloride and fluoride, which is determined in accordance with Section VIII.E.1 of this Appendix.

### 3. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Transfer approximately 3.0 g of the sample, weighed to the nearest mg, to a blanked quartz boat, quickly place the boat in the hot zone of the combustion tube, connect the steam line, and collect 30 ml of distillate into 50 ml of glacial acetic acid in a new rinsed polypropylene beaker. For the duration of the distillation, immerse the condenser tip in the acid and cover the beaker. Having collected the exact volume, remove the beaker without rinsing the condenser tip into it. Measure the EMF of the chloride and fluoride ion electrodes as described in Section VIII.E.1 of this Appendix.

Between sample analyses, store the electrodes in deionized water. Over longer periods of time store them in approximately 80 ml of water spiked with 30 μg of chloride and 20 μg of fluoride. Change the outer filling solution of the reference electrode (10% $KNO_3$) each day before use and the inner filling solution on a weekly basis.

### 4. Control Standards

To prepare the control standard, pipette 0.5 ml of the 10 μg/ml standard chloride-fluoride solution (Item 4 of Section VIII.D of this Appendix) into a previously pyrohydrolyzed sample in a quartz boat. Dry the control in a vacuum desiccator or for 1 hour in an oven at approximately 100°C. Treat the control as a sample, analyzing it as described in Section VIII.E.3 of this Appendix, and use the data obtained to calculate the recovery.

### F. Calculations

Convert millivolt readings to micrograms of fluoride and chloride by means of the calibration curve. Calculate the chloride or fluoride content of the samples as follows:

$$\text{ppm Chloride or Fluoride} = \frac{A}{B}$$

where:

A = chloride or fluoride present, $\mu g$

B = weight of sample, g.

### G. References

Other pyrohydrolytic analysis procedures for chloride and/or fluoride ion determination are given in Sections VI and VII of this Appendix.

The Operational Chemistry Laboratory pyrohydrolytic analysis procedures for chloride and fluoride ion determination are given in Appendix D, Sections VI and VII.

## IX. THE POLAROGRAPHIC DETERMINATION OF URANIUM VI IN $UO_2$ AND $UO_2$-$ThO_2$

### A. Scope

This procedure describes the determination of $U^{+6}$ in $UO_2$ and $UO_2$-$ThO_2$. The lower limit of detection is 1% $U^{+6}$ in 1.5 w/o $UO_2$-$ThO_2$ based on the weight of uranium present. The detection limit will vary with the uranium content of the sample. The $U^{+6}$ content is used to calculate the O/U ratio of $UO_2$ and $UO_2$-$ThO_2$.

### B. Summary of Method

The sample is dissolved in a hot solution of concentrated sulfuric and phosphoric acids under an argon atmosphere. The $U^{+6}$ content is determined polarographically with a dropping mercury electrode.

### C. Apparatus

1. **Recording Polarograph.**
2. **Dropping Mercury Electrode Assembly.**
3. **Polarograph Cell**—Designed for use with a mercury pool reference electrode.

### D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Prepare by passing distilled water through a mixed-bed ion-exchange column. Use this water for sample dilutions and in the preparation of all reagents.
2. **Standard Uranium Solution (2 mg $U^{+6}$/ml)**—Dissolve 2.358 g of National Bureau of Standards 950a $U_3O_8$ in 10 ml of 8M nitric acid. Fume to dryness several times with 5-ml portions of 9M sulfuric acid. Dilute to 1 liter with 4N sulfuric acid in a volumetric flask.
3. **Standard Uranium Solution (100 $\mu g$ $U^{+6}$/ml)**—Dilute 10.0 ml of the 2 mg/ml standard uranium solution (Item 2) to 200 ml with 1N sulfuric acid in a volumetric flask.
4. **Sulfuric Acid (4N)**—Dilute 56 ml of concentrated sulfuric acid to 500 ml with water.
5. **Sulfuric Acid (9M)**—Dilute 500 ml of concentrated sulfuric acid to 1 liter with water.
6. **Sulfuric Acid (1N)**—Dilute 14 ml of concentrated sulfuric acid to 500 ml with water.
7. **Nitric Acid (8M)**—Dilute 500 ml of concentrated nitric acid to 1 liter with water.
8. **Phosphoric-Sulfuric Acid Solution (2:1)**—Prepare a solution containing two parts concentrated phosphoric acid to one part concentrated sulfuric acid and deaerate with argon for 1 hour. Maintain a small stream of argon through the mixture at all times.
9. **Triton X-100 Solution (0.2%)**—Shake 0.2 g of the commercial product with 100 ml of water until a clear solution results.
10. **Thorium Dioxide**—High purity, ignited.
11. **Uranium Dioxide**—High purity, stored under argon.
12. **Argon**—High purity.
13. **Mercury**—High purity.

## E. Procedure

### 1. Calibration Curve (0 to 1000 $\mu g$ $U^{+6}$)

Based on the sample weight and the known percent $ThO_2$ and $UO_2$ in the samples, weigh the appropriate amounts of the $ThO_2$ and $UO_2$ (Items 10 and 11 of Section IX.D of this Appendix) to ±0.2 mg and transfer into four 50-ml volumetric flasks. Pipette 0 (blank), 2.0, 6.0, and 10.0 ml (0, 200, 600, and 1000 $\mu g$ of $U^{+6}$) of the 100 $\mu g$/ml standard uranium solution (Item 3 of Section IX.D of this Appendix) into successive flasks. Flush the flasks with argon at a flow rate of approximately 10 $ft^3$/hr for 2 to 3 minutes and then add 15 ml of the deaerated phosphoric-sulfuric acid solution to these synthetic standard samples. Place the flasks on a hot plate and heat at 240 to 250°F, maintaining an argon flow of approximately 1 $ft^3$/hr into the flasks until the samples are dissolved. When the samples have dissolved, remove the flasks from the hot plate and stopper immediately. When cool, dilute nearly to volume with water while swirling and keeping the flasks in a cold water bath maintained at approximately 25°C. Bring the flasks to room temperature, dilute to volume, and mix. Transfer 10 ml of each solution individually to the polarograph cell, add 2 drops of Triton-X-100 solution, and deaerate for 6 to 7 minutes. Record the polarogram from −0.15 to −0.6V versus a mercury pool reference electrode using the current sensitivity that gives the maximum wave height at −0.6V. Measure the wave height at −0.55V, correct for the residual current obtained on the standard blank solution at −0.55V, and calculate the diffusion current constant ($I_s$) as follows for each standard:

$$I_s = \frac{i_d}{c}$$

where:

$i_d$ = corrected diffusion current of the standard, microamps

c = concentration of the standard, mg/50 ml.

### 2. Sample Preparation and Analysis

Samples submitted in the powdered oxide form are analyzed as received. Samples submitted as pellets are ground in a zirconium mortar or grinding mill to a consistency capable of passing through a 200-mesh sieve prior to analysis. Select the appropriate sample weight according to Table C-2 and transfer the sample to a dry 50-ml volumetric flask. Add 15 ml of the deaerated acid mixture, dissolve the samples, and record the polarograms as in Section IX.E.1 of this Appendix after flushing the flasks with argon at a flow rate of approximately 10 $ft^3$/hr for 2 to 3 minutes before heating. As a blank for the samples, place a flask containing only the acid mixture on the hot plate along with the samples.

**TABLE C-2. SAMPLE WEIGHTS FOR POLAROGRAPHIC DETERMINATION OF URANIUM VI**

| % $UO_2$ | Sample Weight |
|---|---|
| 1.5 to 3 | 0.5 g ±0.001 |
| 3 to 6 | 0.3 g ±0.001 |

## F. Calculations

Correct the sample diffusion current for the residual current obtained on the sample blank, and calculate the $U^{+6}$ content as follows:

$$\% U^{+6} = \frac{i'_d \times 100}{\overline{I_s} \times W}$$

where:

$i'_d$ = corrected diffusion current of the sample, microamps

$\overline{I_s}$ = average specific diffusion current constant for the three standards, microamps/mg

W = weight of uranium in the sample, mg.

## G. References

The Operational Chemistry Laboratory procedure for the polarographic determination of $U^{+6}$ in $UO_2$ and $UO_2$-$ThO_2$ is given in Appendix D, Section VIII.

# APPENDIX D

## WET CHEMICAL PROCEDURES
(Operational Chemistry Laboratory)

# APPENDIX D

## WET CHEMICAL PROCEDURES
(Operational Chemistry Laboratory)

## I. THE DETERMINATION OF TOTAL URANIUM IN $UO_2$ AND $UO_2$-$ThO_2$ BY THE DAVIES-GRAY REDUCTION CERIC TITRATION METHOD

### A. Scope

This procedure describes the determination of total uranium in $UO_2$ powder and $UO_2$-$ThO_2$ powder or pellets in the concentration range of 1.2 to 6 w/o uranium. Sample size varies with the concentration of uranium.

### B. Summary of Method

$UO_2$ powder is dissolved in either a nitric-hydrofluoric or a phosphoric-sulfuric acid solution.

$UO_2$-$ThO_2$ pellets are dissolved in a nitric-hydrofluoric acid solution, while the $UO_2$-$ThO_2$ powder is dissolved in a phosphoric-sulfuric acid solution.

If the sample is dissolved using the nitric-hydrofluoric acid solution, a mixture of phosphoric-sulfuric acid is added. The solution is heated to strong fumes of sulfur trioxide, which remove the nitric and hydrofluoric acids. Samples dissolved in the phosphoric-sulfuric acid solution are taken to strong fumes of sulfur trioxide to remove excess water in the mixed acid. Water is added to the cooled sample to hydrolyze any meta or pyrophosphates, and the uranium is reduced to the tetravalent state using the Davies-Gray reduction method (Reference D-1). Upon sample dilution, the ferric sulfate oxidizes the tetravalent uranium to the hexavalent state with a corresponding formation of ferrous iron. The ferrous iron is stoichiometrically oxidized to ferric iron by adding standard ceric to a potential of 800 to 820 mV (Calomel reference-platinum indicator electrode system). Ferrous ammonium sulfate is used for the back-titration, and 5,6-dimethylorthophenanthroline ferrous sulfate is used as an indicator to verify the end point potential.

### C. Apparatus

1. **Semimicro Balance**—Mettler H20 or equivalent.
2. **Research pH Meter**—Corning Model 112 or equivalent.
3. **Electrode System**—Calomel reference-platinum indicator.
4. **Hot Plate**—Corning PC 100 or equivalent.
5. **Burettes**—Class *A*, serialized, 10, 25, and 50 ml.
6. **Pipettes**—Class *A*, serialized, 25 ml.
7. **Volumetric Flasks**—Class *A*, serialized, 2 liter.
8. **Polyethylene Carboy**—20 liter.

### D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.
2. **Standard Ceric Solution** (0.2N)—Add 600 g of $Ce(HSO_4)_4$ (G. F. Smith or equivalent) to a 6-liter Florence flask. Add 4.5 liters of water. While stirring on a magnetic hot plate, add slowly 750 ml of concentrated sulfuric acid. Continue stirring until all the ceric is in solution. Cool to room temperature. Filter the solution through a vacuum filter using Whatman #41 filter paper or equivalent. Transfer three of these filtered solutions to a 20-liter polyethylene carboy and dilute to 17.5 liters. After the exact normality of this solution is determined (see Item 5.a), label the bottle with the exact normality and the number of milliliters of ceric solution required to prepare the 0.020N and 0.040N standard ceric solutions.
3. **Standard Ceric Solution** (0.020N)—Transfer the calculated amount of 0.2N ceric solution (approximately 3.5 liters, see Item 2) to a 20-liter polyethylene carboy. Add 4 liters of water and 50 ml of concentrated sulfuric acid. Dilute to 17.5 liters with water.
4. **Standard Ceric Solution** (0.040N)—Transfer the calculated amount of 0.2N ceric solution (approximately 1.7 liters, see Item 2) to a 20-liter polyethylene carboy. Add 4 liters of water and 280 ml of concentrated sulfuric acid. Dilute to 17.5 liters with water.
5. **Primary Standard Arsenious Acid Solution** (0.035N)—National Bureau of Standards (NBS) Standard Sample 83C arsenious

oxide is recommended. Dry at 105°C for 1 hour, cool, and store in a desiccator when not in use. Dissolve 3.5 g of arsenious oxide (weighed to ±0.0001 g) in 80 ml of warm 10% potassium hydroxide. When solution is complete, add 9M sulfuric acid dropwise until pH paper indicates the solution is acidic. Cool to room temperature. Transfer the standard to a 2-liter volumetric flask. Rinse the beaker at least 10 times with water. Equilibrate the flask in a constant temperature bath regulated at 25°C and dilute to volume.

a. **Standardization of Ceric with Arsenious Oxide**—Pipette 25.00 ml of 0.035N arsenious acid solution to each of three 150-ml beakers. Add 6 ml of 9M sulfuric acid, 1 drop of ferroin indicator, and 4 drops of osmium tetroxide immediately before the titration. Titrate with 0.020N, 0.040N, or 0.2N ceric solution to the disappearance of the orange color (0.05 to 0.20 ml in excess). Back-titrate with ferrous ammonium sulfate solution to the first appearance of an orange color. Determine a blank by titrating 25 ml of water containing 6 ml of 9M sulfuric acid, 1 drop of ferroin indicator, and 4 drops of osmium tetroxide. Titration values for triplicate aliquots should have a maximum range of 0.03 ml. If the range exceeds 0.03 ml, a fourth aliquot must be taken for the standardization.

6. **Standard Uranium Solution** (0.0121**N**) (**36 mg uranium/25 ml**)—Transfer the contents of NBS 950a uranium oxide ($U_3O_8$) to a 250-ml platinum beaker. Ignite at 900°C for 1 hour and cool to room temperature. Transfer the oxide to a weighing bottle and store in a desiccator. Weigh approximately 3.40 g of oxide to ±0.0001 g, transfer to a 400-ml beaker, and add 10 ml of water and 10 ml of concentrated nitric acid. Cover the beaker with a watch glass and heat gently to start the reaction. If the reaction becomes too vigorous, set the beaker aside to cool. Reheat as necessary to completely dissolve the sample. When the sample is completely dissolved, cool to room temperature. Rinse the watch glass and beaker walls three times with water. Add 25 ml of 9M sulfuric acid and swirl the solution. Heat to dense fumes of sulfur trioxide, cover the beaker, and continue heating the solution at least 5 minutes. Remove the sample from the hot plate and cool to room temperature. Wash down the walls of the beaker and the watch glass with a small volume of water. Swirl to dissolve the salt, and transfer the solution to a 2-liter volumetric flask. Rinse the beaker 10 times with water. Equilibrate the flask at 25°C and dilute to volume. A 25.00-ml aliquot of this solution gives approximately a 14-ml titration with 0.020N ceric solution.

7. **Standard Uranium Solution** (0.0185**N**) (**55 mg uranium/25 ml**)—This standard is prepared in an identical manner to the 0.0121N standard uranium solution (Item 6) except that 5.19 g of the oxide (±0.0001 g) is transferred to the 400-ml beaker.

a. *Standardization of Ceric with Uranium Oxide*—Pipette 25.00 ml of the uranium solution to a 600-ml beaker. Evaporate the solution to dryness, cool to room temperature, and add 15 ml of water to the beaker. Swirl the beaker to dissolve the salt and place the beaker on a magnetic stirrer. Pipette 5.0 ml of 1.5M sulfamic acid directly into the solution in the beaker. Stir approximately 15 seconds. Add 40 ml of concentrated phosphoric acid, rinsing down the walls of the beaker during the addition. Stir approximately 15 seconds. Pipette 5.0 ml of 1M ferrous sulfate directly into the solution. Stir approximately 30 seconds. Pipette 5.0 ml of the nitric acid-sulfamic acid-ammonium molybdate solution to the beaker, rinsing down the beaker walls during the addition. Stir the solution until the brown color disappears (1.5 to 3.5 minutes). Stir an additional 1 minute and let stand approximately 7 minutes. Add 30 ml of 9M sulfuric acid, stir approximately 15 seconds, and add 400 ml of 1M sulfuric acid in 100-ml portions. Stir approximately 15 seconds after each addition and an additional 1 minute after the final addition. Add 3 drops of 5,6-dimethylorthophenanthroline ferrous sulfate indicator. Stir approximately 30 seconds. Rinse a 50-ml burette several times with ceric solution that has reached equilibrium in a water bath regulated at 25°C. Fill the burette with ceric solution just prior to the titration to minimize any temperature change of the titrant.

Using a Calomel reference-platinum indicator electrode system, titrate with ceric to a potential of 800 to 820 mV, making certain the potential is maintained within these limits for 15 to 30 seconds. Back-titrate with ferrous ammonium sulfate to a potential of 700 to 720 mV or to the first visual change of the indicator from blue to tan. Determine a blank by adding 15 ml of water to a 600-ml beaker. Treat the blank in the same manner as a uranium sample, beginning with the addition of 5.0 ml of 1.5M sulfamic acid.

The uranium content of each uranium standard must be verified by total uranium determinations. Triplicate aliquots plus a blank must be run prior to using a new uranium standard for control samples. Titration values for triplicate aliquots should have a maximum range of 0.03 ml.

Agreement between the two methods of standardization of the ceric solution (arsenious oxide and uranium oxide) should be within ±1.5 parts per thousand.

8. **Primary Standard Uranium Oxide (NBS 950a)**—Ignite 25 g of the oxide at 900°C for 1 hour in a platinum beaker. Cool in a desiccator. Transfer the oxide to a weighing bottle and store in a desiccator when not in use.

9. **Phosphoric Acid** (85%)—Reagent grade.

10. **Phosphoric-Sulfuric Acid Solution**—Add 1.5 liters of concentrated phosphoric acid to 500 ml of concentrated sulfuric acid in a 2-liter reagent bottle.

11. **Sulfuric Acid (9M)**—Add 1.5 liters of concentrated sulfuric acid to 1.5 liters of water in a 4-liter beaker.

12. **Sulfuric Acid (1M)**—Add 960 ml of concentrated sulfuric acid to 12 liters of water in a 20-liter polyethylene carboy. Dilute to 16 liters.

13. **Hydrofluoric Acid** (**2.94N**)—Dilute 10 ml of concentrated hydrofluoric acid to 100 ml in a polyethylene bottle.

14. **Nitric Acid (13N)-Hydrofluoric Acid (0.05N) Solution**—Add 1656 ml of concentrated nitric acid to 310 ml of water in a 2-liter polyethylene bottle. Add 34 ml of 2.94N hydrofluoric acid.

15. **Sulfamic Acid (1.5M)**—Dissolve 72.8 g of sulfamic acid in 425 ml of water. Transfer the solution to a 500-ml volumetric flask. Rinse the beaker two or three times and dilute to volume.

16. **Nitric Acid (8M)-Sulfamic Acid (0.15M)-Ammonium Molybdate (0.4%) Solution**—Weigh 4.0 g of ammonium molybdate tetrahydrate into a 2-liter beaker. Add 400 ml of water, stir until completely dissolved, and add 500 ml of concentrated nitric acid. Transfer the solution to a 1-liter volumetric flask. Add 100 ml of 1.5M sulfamic acid and dilute to volume. Transfer to a polyethylene bottle for storage.

17. **Ferrous Sulfate (1M)**—Dissolve 139 g of ferrous sulfate heptahydrate in 400 ml of water and 50 ml of phosphoric-sulfuric acid solution. Transfer the solution to a 500-ml volumetric flask and dilute to volume. Store in a 500-ml reagent bottle. This reagent must be prepared fresh biweekly.

18. **Ferrous Ammonium Sulfate Solution (0.020N)**—Dissolve 123 g of ferrous ammonium sulfate hexahydrate in 1.2 liters of 1.8M sulfuric acid in a 3-liter beaker. When solution is complete, transfer to a 20-liter polyethylene carboy and dilute to 16 liters with water. To determine the ratio $Ce^{+4}/Fe^{+2}$, add 75 ml of 1M sulfuric acid and 1 drop of ferroin indicator to a 250-ml beaker. Using a 10-ml burette, add 8.0 ml of 0.020N, 4.0 ml of 0.040N, or 2.0 ml of 0.2N ceric solution. Using a 10-ml burette, titrate with ferrous ammonium sulfate solution to the first appearance of the orange color. The $Ce^{+4}/Fe^{+2}$ ratio is equal to the milliliters of ceric solution used divided by the milliliters of ferrous ammonium sulfate solution used.

19. **5,6-Dimethylorthophenanthroline Ferrous Sulfate Indicator (0.008M)**—Dissolve 1.54 g of 5,6-dimethylorthophenanthroline in 100 ml of ferrous ammonium sulfate solution. Dilute to 250 ml in a volumetric flask with water.

20. **Ferroin Indicator** (**0.020M**)—Dissolve 1.5 g of orthophenanthroline monohydrate in 100 ml of ferrous ammonium sulfate solution.

21. **Osmium Tetroxide Catalyst (0.01M)**—Mark with a sharp file a 0.25-g vial of osmium tetroxide. Place the vial in a 500-ml reagent bottle. Prepare 0.05M sulfuric acid by diluting 5 ml of 1M sulfuric acid to 100 ml. Add just enough 0.05M sulfuric acid to the reagent bottle so that the vial does not float. Strike the vial with a solid glass rod to break it. Add the remainder of the 0.05M sulfuric acid. Stopper the reagent bottle and let stand overnight for complete solution of the osmium tetroxide. Shake well before using.

22. **Thorium Dioxide**—High purity, ignited.

## E. Procedure

### 1. Sample Preparation and Dissolution

Grind the sample using the appropriate procedure as described in Appendix E, Section I.

*a. $UO_2$ Powder or $UO_2$-$ThO_2$ Pellets*—See Table D-1 for the appropriate sample size. Weigh the $UO_2$ to ±0.0001 g and the $UO_2$-$ThO_2$ to ±0.00001 g and transfer to a 600-ml beaker. Add 30 ml of the 13N nitric acid-0.05N hydrofluoric

## TABLE D-1. SAMPLE IDENTIFICATION AND SIZE AND QUANTITY OF URANIUM STANDARD REQUIRED FOR CONTROL ADDITIONS

| Pellet Type Designation | Pellet Type | %U | %$UO_2$ | Sample Size (g) | Uranium Standard (mg/25-ml aliquot) |
|---|---|---|---|---|---|
| 1 | Low seed | 4.29 | 4.88 | 1.3 | 55 |
| 2 | High seed | 5.17 | 5.88 | 1.1 | 55 |
| 3 | Low standard blanket | 1.21 | 1.36 | 3.0 | 36 |
| 4 | Medium standard blanket | 1.66 | 1.89 | 3.3 | 55 |
| 5 | High standard blanket | 2.00 | 2.27 | 2.7 | 55 |
| 6 | Low power flattening blanket | 1.65 | 1.87 | 3.3 | 55 |
| 7 | Medium power flattening blanket | 2.00 | 2.29 | 2.7 | 55 |
| 8 | High power flattening blanket | 2.73 | 3.10 | 2.0 | 55 |
| None | --- | 88 | 100 | 0.125 | 55 |

acid solution, rinsing down the beaker walls during the addition. Cover with a watch glass and heat the sample to a temperature just below boiling. At this temperature the sample dissolves rapidly. Continue heating at this temperature until the sample is in solution (0.1 to 1.5 hours). Cool 5 to 10 minutes and rinse the beaker walls and watch glass four times with water.

Evaporate the solution to a moist paste. Do not take to dryness as the dried salt may spatter, with possible loss of sample. Cool and then rinse the beaker walls three times with water (approximately 15 ml). Swirl the solution to dissolve the salts. Add 20 ml of the phosphoric-sulfuric acid solution, rinsing down the walls of the beaker during the addition. Swirl the acid solution. Heat the solution gently until light fumes of sulfur trioxide are evolved, cover with a watch glass, and heat to strong fumes of sulfur trioxide. Fume 5 minutes. Remove the watch glass for a few seconds several times during the fuming operation to allow the nitric and hydrofluoric acid to be carried away by the sulfur trioxide fumes. Cool to room temperature and let stand 5 to 30 minutes. Add 15 ml of water directly to the solution. Swirl well and cool to room temperature.

*b. $UO_2$ Powder or $UO_2$-$ThO_2$ Powder*—See Table D-1 for the appropriate sample size. Weigh the sample to ±0.00001 g and transfer to a 600-ml beaker. Add 20 ml of the phosphoric-sulfuric acid solution, rinsing down the walls of the beaker during the addition. Swirl to distribute the powder throughout the acid solution. Heat the solution gently until light fumes of sulfur trioxide are evolved. If the sample has not completely dissolved, cover the beaker with a watch glass and continue heating until the sample is in solution (5 to 15 minutes). Cool to room temperature and let stand 5 to 30 minutes. Add 15 ml of water directly to the solution. Swirl well and cool to room temperature.

### 2. Reduction and Titration of Sample

Place the beaker on a magnetic stirrer. Pipette 5.0 ml of 1.5M sulfamic acid directly into the solution. Stir approximately 15 seconds. Add 25 ml of concentrated phosphoric acid, rinsing down the walls of the beaker during the addition. Stir approximately 15 seconds. Pipette 5.0 ml of 1M ferrous sulfate directly into the solution. Stir approximately 30 seconds. Pipette 5.0 ml of the nitric acid-sulfamic acid-ammonium molybdate solution to the beaker, rinsing down the beaker walls during the addition. Stir the solution until the brown color disappears (1.5 to 3.5 minutes). Stir an additional 1 minute and let stand approximately 7 minutes. Add 30 ml of 9M sulfuric acid, stir approximately 30 seconds, and add 400 ml of 1M sulfuric acid in 100-ml portions. Stir approximately 15 seconds after each addition and for an additional 1 minute after the final addition. Add 3 drops of 5,6-dimethylorthophenanthroline ferrous sulfate indicator. Stir approximately 30 seconds. Rinse a 25-ml burette several times with ceric solution that has reached equilibrium in a water bath regulated at 25°C. Fill the burette with ceric solution just prior to the titration to minimize any temperature change of the titrant.

Using a Calomel reference-platinum indicator electrode system, titrate with ceric to a potential of 800 to 820 mV, making certain the potential is maintained within these limits for 15 to 30 seconds. Back-titrate with ferrous ammonium sulfate to a potential of 700 to 720 mV or to the first visual change of the indicator from blue to tan.

### 3. Blanks

Weigh approximately the same amount of $ThO_2$ as in the sample into a 600-ml beaker. Continue as in Sections I.E.1.a or .b and I.E.2 of this Appendix. For $UO_2$ material, omit the $ThO_2$ addition.

### 4. Control Standards

For each level of uranium to be analyzed, prepare a control with the same ratio of uranium to thorium as in the sample.* For the $UO_2$-$ThO_2$ samples, pipette 25.00 ml of the appropriate standard uranium solution to each of two 600-ml beakers. For the $UO_2$ powder samples, pipette duplicate 25.00-ml aliquots to each of the 600-ml beakers.

Evaporate to dryness and cool. Add $ThO_2$ in the same quantity as the amount present in the $UO_2$-$ThO_2$ samples. Do not add any $ThO_2$ to controls prepared for the $UO_2$ samples. Continue as in Sections I.E.1.a or .b and I.E.2 of this Appendix.

## F. Reliability

Duplicate control standards, with verified uranium concentrations, are analyzed with each sample set. The recovery and range of the duplicate controls are used to accept or reject all sets of data. The acceptable limits for the mean and range of the duplicate controls are 99.65 to 100.35 and 0 to 0.70, respectively. Values obtained on samples accompanying controls that fall outside of these limits are invalidated, and the sample set is reanalyzed. All results reported are corrected for any bias indicated by the control standards. Control charts are maintained on a daily basis to verify day-to-day control and to indicate abnormal method variances. The samples must have a relative precision (1s) of 0.25 percent and a relative basis of 0.15 percent to meet core specifications.

Fluctuations of temperature in the laboratory beyond a 3°C range indicate that the observed oxidimetric titration values may be inaccurate. A 3°C temperature change of the titration solution will result in an additional ±0.10 percent relative precision error in the method. This increase in precision error may require rechecking of samples that would normally fall within the precision and bias limits noted above. Therefore, rigid temperature control must be instituted and maintained.

## G. Calculations

### 1. Normality of Ceric Standard

*a. Arsenious Oxide Standardization*—The normality of ceric when standardized with arsenious oxide is determined as follows:

$$N = \frac{A}{B \times C}$$

where

N = normality of ceric solution

A = amount of $As_2O_3$ in 25 ml, mg

B = net amount of ceric solution corrected for blank and ferrous back-titration, ml

C = milliequivalent weight of $As_2O_3$ (49.46 mg/milliequivalent).

*b. Uranium Oxide Standardization*—The normality of ceric when standardized with uranium oxide is determined as follows:

$$N = \frac{A}{B \times C}$$

where:

N = normality of ceric solution

A = amount of natural uranium in 25 ml, mg

B = net amount of ceric solution corrected for blank and ferrous back-titration, ml

C = milliequivalent weight of natural uranium (119.015 mg/milliequivalent).

### 2. Calculation Factor

Determine the calculation factor necessary for calculating the uranium content of the samples as follows:

$$CF = N \times 119.015^{**}$$

where:

CF = calculation factor (mg of uranium per ml of ceric solution)

N = normality of ceric solution.

### 3. Uranium Content of Samples

Calculate the uranium content of the samples as follows:

$$\%\ \text{Uranium} = \frac{CF \times B \times 100}{W}$$

where:

CF = calculation factor (mg of uranium per ml of ceric solution)

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*The Operational Chemistry Laboratory procedure is to analyze two control standards with each set of five samples. The two controls are randomly inserted in the sequence of samples.

**This milliequivalent weight is used for natural uranium. The milliquivalent weight of uranium for each blend of production material must be verified by using the appropriate isotopic assay of the $^{233}UO_2$ used in the blend.

B = net amount of ceric solution corrected for blank and ferrous back-titration, ml

W = weight of sample, mg.

## H. References

D-1. W. Davies and W. Gray, "A Rapid and Specific Volumetric Method For The Precise Determination of Uranium Using Ferrous Sulfate as Reductant," *Talanta 11*, 1203-11 (1964).

# II. THE SPECTROPHOTOMETRIC DETERMINATION OF NITROGEN IN $ThO_2$ AND $UO_2$-$ThO_2$

## A. Scope

This procedure describes the determination of nitrogen in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 10 to 60 ppm on a 0.5-g sample basis using a 5-cm light path for photometric measurement. This range can be extended by altering sample sizes or by using shorter path length absorption cells and larger nitrogen aliquots for calibration curves.

## B. Summary of Method

The sample is dissolved by refluxing in a sulfuric-phosphoric acid mixture. The resulting solution is made basic by the addition of a strong sodium hydroxide solution, and nitrogen is separated as ammonia by steam distillation. Ammonia is determined spectrophotometrically in the distillate with Nessler reagent.

## C. Apparatus

1. **Steam Distillation and Condenser Apparatus (see Figure D-1)**—The standard unit is modified by replacing the rubber stopper with a Teflon plug and replacing the Tygon tubing from the steam generator outlet to the distillation flask inlet with a glass tube. Ball-and-socket ground glass joints are used for greater flexibility.

2. **Boiling Flask**—125 ml.

3. **Spectrophotometer**—Beckman Model DU-2 or equivalent equipped with a 5-cm absorption cell.

4. **Volumetric Flask**—50 ml.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.

2. **Standard Ammonia Solution ($10 \mu g$ nitrogen/ml)**—Dissolve 3.819 g of ammonium chloride in water and dilute to 1 liter in a volumetric flask. Dilute 10.0 ml of this solution to 1 liter in a volumetric flask.

3. **Standard Ammonia Solution ($2 \mu g$ nitrogen/ml)**—Dilute 20.0 ml of the $10 \mu g$/ml standard ammonia solution (Item 2) to 100 ml in a volumetric flask.

4. **Phosphoric-Sulfuric Acid Solution**—Add 60 ml of water to a 1-liter beaker. Then add 600 ml of concentrated phosphoric acid to the beaker followed by 240 ml of concentrated sulfuric acid. Store in a 1-liter reagent bottle.

5. **Sodium Hydroxide (37.5%)**—Dissolve 600 g of sodium hydroxide in 1 liter of water.

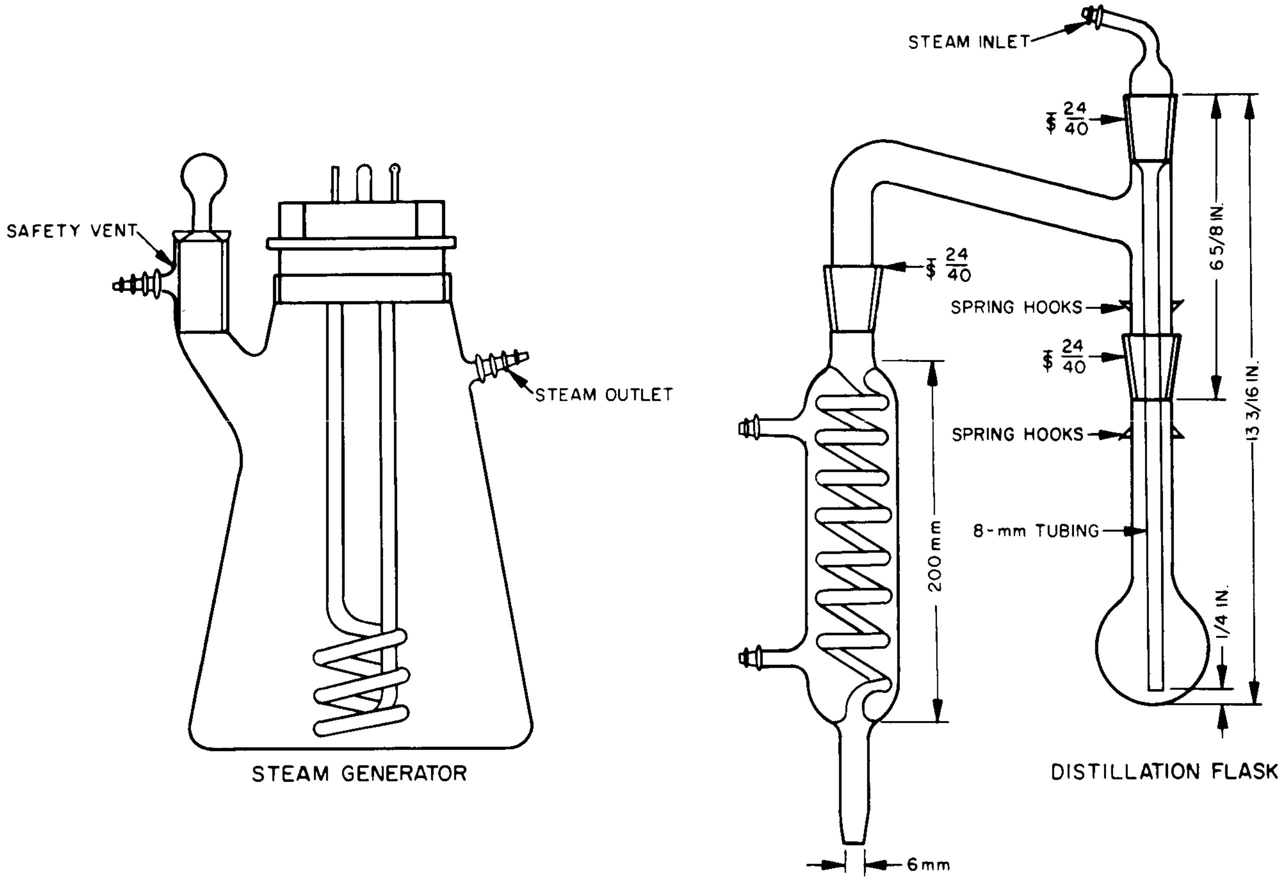
6. **Nessler Reagent**—Koch-McMeekin Formula from Scientific Products Division of American Hospital Supply, Catalogue Item B-5305 or equivalent. Dissolve by emptying the entire contents of the container into a beaker containing 900 ml of water. Rinse the container with 85 ml of water and add to the beaker. Mix well using a magnetic stirrer and stirring bar until the solid has completely dissolved. Allow to stand until cool and completely clear. Any slight sediment formed may be removed by decanting or filtering through glass wool or absorbent cotton. The solution will remain stable indefinitely when stored in a tightly stoppered reagent bottle.

Prepare all solutions in an ammonia-free atmosphere and store in tightly stoppered bottles. Boil all rubber stoppers for 30 minutes in a 10% sodium hydroxide solution and then rinse with water.

## E. Procedure

1. **Calibration Curve (0 to 30 $\mu g$ nitrogen)**

Pipette 0 (blank), 2.0, 4.0, 6.0, 8.0, 10.0, and 15.0 ml (0, 4, 8, 12, 16, 20, and 30 $\mu g$ of nitrogen) of the 2 $\mu g$/ml standard ammonia solution (Item 3 of Section II.D of this Appendix) into separate 50-ml volumetric flasks containing 25 to 30 ml of water. Pipette 1.0 ml of Nessler reagent into each flask. Dilute to volume, stopper, and shake well. Let stand 10 to 15 minutes. Transfer the solution to a 5-cm absorption cell. Adjust the spectrophotometer to the initial setting using a light band centered at



STEAM GENERATOR

DISTILLATION FLASK

**Figure D-1. Steam Distillation Apparatus for Nitrogen Determination in $ThO_2$ and $UO_2$-$ThO_2$**

410 mμ, a slit of 0.04 mm, and a photomultiplier in the circuit. While maintaining this adjustment, take photometric readings of the calibration solutions using deionized water in the reference cell. Correct for the blank and plot absorbance versus micrograms of nitrogen in 50 ml of solution.

### 2. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 0.5 g of the sample, weighed to the nearest mg, into a boiling flask. Add 15 ml of the phosphoric-sulfuric acid solution and heat gently until slight fumes of $SO_3$ appear. If the sample is not completely in solution, cover the flask with a watch glass. Heat at high heat until the sample is in solution. Cool to room temperature. Rinse the flask three times using no more than 30 ml of water for the total rinse, mix well, and cool.

While the samples are dissolving, fill the steam generating flask of the distillation apparatus with deionized water. Apply heat and pass steam through the distillation flask and into the condenser at a rate yielding approximately 50 ml of distillate in 10 minutes. Collect 50-ml portions of distillate until the analysis described in Section II.E.1 shows the apparatus to be free of ammonia. Add 25 to 30 ml of water to the distilling flask containing the sample and mix well. Immediately, add slowly 50 ml of 37.5% NaOH solution down the sidewall of the flask so as to form two layers. Connect the flask to the distillation apparatus and distill into a 50-ml volumetric flask, collecting approximately 40 ml of distillate. Pipette 1.0 ml of Nessler reagent to the flask, dilute to volume, and continue as in Section II.E.1 of this Appendix, reading each sample versus the deionized water reference solution.

### 3. Blanks

Two reagent blanks are run with each set of samples. Add 15 ml of the phosphoric-sulfuric acid solution to each of two boiling flasks and heat until slight fumes of $SO_3$ appear. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section II.E.2 of this Appendix. Use an average of the two blanks for the sample blank.

### 4. Control Standards

To prepare the control standards, pipette 5.0 ml of the 2 μg/ml standard ammonia solution (Item 3 of Section II.D of this Appendix) into two separate boiling flasks. Add 15 ml of the phosphoric-sulfuric acid solution to each flask. Heat gently until slight fumes of $SO_3$ appear. Treat the solutions from this point on in the same manner as samples, analyzing them as described in Section II.E.2 of this Appendix.

## F. Calculations

Correct for the average blank, determine the micrograms of nitrogen from the calibration curve, and calculate the nitrogen content of the samples as follows:

$$\text{ppm Nitrogen} = \frac{A}{B}$$

where:

A = nitrogen present, $\mu$g

B = weight of sample, g.

## G. References

The Analytical and Spectrochemical Analysis Laboratory procedure for the spectrophotometric determination of nitrogen in $ThO_2$ and $UO_2$-$ThO_2$ is given in Appendix C, Section I.

# III. THE FLUORIMETRIC DETERMINATION OF URANIUM IN $ThO_2$

## A. Scope

This procedure describes the determination of uranium in $ThO_2$ in the concentration range of 1 to 20 ppm on a 0.5-g sample basis. This range can be extended by changing the size of the aliquot used for the final uranium determination.

## B. Summary of Method

The sample is dissolved in a mixture of hydrofluoric and nitric acids. Acid-deficient aluminum nitrate solution containing tetra-n-propylammonium nitrate is added. Uranium is then extracted as tetra-n-propylammonium uranyltrinitrate with methyl isobutyl ketone. An aliquot of the organic phase is evaporated on a pellet of sodium-lithium fluoride in a small platinum dish, and the mixture is fused into a button. The characteristic uranium fluorescence emitted by the button under ultraviolet light is measured with a fluorimeter.

## C. Apparatus

**NOTE**

*All apparatus should be kept separate and used only for trace uranium analysis. Pipettes and other glassware should be cleaned by soaking for 1 hour in hot 8N $HNO_3$ and $K_2Cr_2O_7$-$H_2SO_4$ cleaning solution.*

1. **Galvanek-Morrison Fluorimeter**—Jarrell-Ash or equivalent.

2. **Platinum Dishes**—Stamped from 0.015- by 0.75-in. discs using Jarrell-Ash platinum dish-stamping die or equivalent.

   **NOTE**

   *The platinum dishes are reshaped as needed using the dish-forming tool. For cleaning purposes, the dishes are arranged so that no stacking results and are then immersed in warm 8N $HNO_3$ and left standing overnight. Boil in 8N $HNO_3$, cool, and rinse the dishes with deionized water. Add 6N HCl and boil 10 to 15 minutes; rinse again with deionized water and dry. The platinum dishes and fluoride discs should be handled only with forceps to prevent the introduction of fluorescent impurities.*

3. **Shaker**—Burrell wrist action or equivalent.

4. **Centrifuge.**

5. **Burner and Support**—Fisher burner and support or equivalent for the platinum dishes.

6. **Specimen Bottles**—50 ml with polypropylene caps.

7. **Heat Lamp.**

8. **Pipettes**—250 and 500 microliter.

9. **Polypropylene Bottles**—4 oz.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.

2. **Standard Uranium Solution** (100 $\mu$g uranium/ml)—Dissolve 0.1179 g of $U_3O_8$ in 5 ml of concentrated nitric acid. Transfer to a 1-liter volumetric flask and dilute to volume with water.

3. **Standard Uranium Solution** (10 $\mu$g uranium/ml)—Dilute 10.0 ml of the 100 $\mu$g/ml standard uranium solution (Item 2) to 100 ml in a volumetric flask.

4. **Standard Uranium Solution** (1 $\mu$g uranium/ml)—Dilute 10.0 ml of the 10 $\mu$g/ml standard uranium solution (Item 3) to 100 ml in a volumetric flask.

5. **Nitric Acid** (1.6N)—Dilute 100 ml of concentrated nitric acid to 1 liter with water.

6. **Hydrofluoric Acid** (29.4N)—Reagent grade.

7. **Hydrofluoric Acid** (2.94N)—Dilute 10 ml of concentrated hydrofluoric acid to 100 ml in a polypropylene bottle.

8. **Nitric Acid (13N)-Hydrofluoric Acid (0.05N) Solution**—Add 1656 ml of concentrated nitric acid to 310 ml of water in a 2-liter polyethylene bottle. Add 34 ml of 2.94N hydrofluoric acid.

9. **Tetra-n-propylammonium Hydroxide**—10% in water.

10. **Aluminum Nitrate Solution** (2.8M)—Transfer 1050 g of aluminum nitrate nonahydrate to a 2-liter beaker. Add water to a volume of 800 ml and warm on a hot plate. After dissolution, add 160 ml of ammonium hydroxide. Stir to dissolve the precipitate, cool to room temperature, and add 10 ml of 10% tetra-n-propylammonium hydroxide solution. Stir to dissolve the precipitate, transfer to a 1-liter volumetric flask, and dilute to volume with water. If the blanks are high and erratic, the aluminum nitrate may be discarded or a preliminary extraction with methyl isobutyl ketone is recommended to remove the uranium. Tetra-n-propylammonium hydroxide must be added again if this purifying extraction is done.

11. **Fusion Mixture (98% sodium fluoride - 2% lithium fluoride)**—Thoroughly blend 9 g of lithium fluoride and 454 g of sodium fluoride. Essentially uranium free lots of sodium fluoride and lithium fluoride must be selected for the fusion mixture.

12. **Methyl Isobutyl Ketone**—Reagent grade.

13. **Thorium Dioxide**—High purity.

## E. Procedure

### 1. Calibration Curve (0 to 20 $\mu$g uranium)

Pipette 0 (blank), 1.0, and 2.0 ml (0, 1, and 2 $\mu$g of uranium) of the 1 $\mu$g/ml standard uranium solution (Item 4 of Section III.D of this Appendix) and 0.5, 1.0, and 2.0 ml (5, 10, and 20 $\mu$g of uranium) of the 10 $\mu$g/ml standard uranium solution (Item 3 of Section III.D of this Appendix) into separate 250-ml platinum beakers, each containing 0.500 g of $ThO_2$ powder. Add 20 ml of the 13N nitric acid-0.05N hydrofluoric acid solution to each beaker. Take to near dryness. Evaporate the solutions until they become glossy in appearance and a few crystals appear. Do not heat to the point where most of the salts have crystallized or re-solution of the material becomes very difficult. Cool to room temperature and dissolve the salts in 5 ml of 1.6N nitric acid.

Transfer the solutions to 4-oz polypropylene bottles. Rinse each beaker twice with water, using no more than 5 ml of total wash solution. Add 25 ml of aluminum nitrate solution. Pipette 10.0 ml of methyl isobutyl ketone, cap tightly, and shake for 3 minutes using a mechanical shaker. Transfer to a specimen bottle, cap the bottle, and centrifuge for 3 minutes.

Place pellets containing approximately 0.4 g of fusion mixture into platinum dishes.

**NOTE**

*The fusion mixture can be measured readily using a 2-ml hypodermic syringe in which the end face has been cut parallel with the milliliter graduations.*

Pipette 0.25-ml aliquots of the methyl isobutyl ketone phase onto two separate pellets. Dry under a heat lamp. Fuse the pellets. The fusion technique will depend upon the type of fusion apparatus used.

**NOTE**

*Calibrate the burner so that reproducible conditions can be obtained for fusing the pellets. The temperature should be such that complete fusion of the pellet takes place during the second minute (approximately 900 °C). The total time for a fusion should be 3 minutes. Pellets that are fused during the first minute may have high or erratic readings.*

Allow the dish to cool (approximately 15 minutes) and read the fluorescence of the fused button. Correct the average of the readings for the blank. Construct a calibration curve by plotting corrected meter readings (microamperes) versus concentration (micrograms) per 0.25-ml aliquot.

### 2. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 0.5 g of the sample, weighed to the nearest mg, into a 250-ml platinum beaker. Add 20 ml of 13N nitric acid-0.05N hydrofluoric acid solution. Cover with a platinum lid. Heat the sample to a temperature just below boiling. At this temperature the sample dissolves rapidly. When the sample has completely dissolved, remove the platinum lid. Rinse the platinum lid with a minimum quantity of water and continue as in Section III.E.1 of this Appendix, starting with taking the solution to near dryness.

### 3. Control Standards

To prepare the control standards, weigh a 0.5-g sample of $ThO_2$ to the nearest mg. Transfer to a platinum beaker. Pipette 1.0 ml of the 1 $\mu$g/ml standard uranium solution (Item 4 of Section III.D of this Appendix) into the platinum beaker. Continue as in Section III.E.2 of this Appendix, starting with the addition of 20 ml of 13N nitric acid-0.05N hydrofluoric acid solution, and use the data obtained to calculate the recovery.

## F. Calculations

Determine the micrograms of uranium present in the blank by comparing the average milliampere reading with the calibration curve. Determine the micrograms of uranium present in the samples from the calibration curve and correct for the blank. Calculate the uranium content of the samples as follows:

$$\text{ppm Uranium} = \frac{40\,A}{B}$$

where:

A = uranium present, $\mu$g/0.25 ml

B = weight of sample, g.

## G. References

The Analytical and Spectrochemical Analysis Laboratory procedure for the fluorimetric determination of uranium in $ThO_2$ is given in Appendix C, Section III.

# IV. THE DETERMINATION OF THORIUM IN $ThO_2$ BY THE OXALATE PRECIPITATION-GRAVIMETRIC METHOD

## A. Scope

This procedure describes the determination of thorium in $ThO_2$ using a 0.5-g sample. Interfering elements are those that are precipitated as an oxalate or hydrolyzed in the dilute acid solution from which the thorium is precipitated as the oxalate. Yttrium, scandium, lanthanum, the lanthanide rare earths, niobium, and tantalum are known to interfere. Metals such as uranium, zirconium, and the alkaline earths do not interfere.

## B. Summary of Method

The sample is dissolved in a nitric-hydrofluoric acid mixture. After the sample is completely dissolved, boric acid is added to complex the fluoride, and the solution is evaporated to dryness. Hydrochloric acid is added to convert the thorium nitrate to thorium chloride and remove the catalytic quantity of fluoride as a boron-fluoride compound. The thorium is then precipitated as the oxalate from this solution. The precipitate is filtered, ignited to the oxide, and weighed.

## C. Apparatus

1. **Muffle Furnace**—Equipped with exhaust duct.

2. **Platinum Crucibles**—30 ml with lids.

3. **Filter Paper**—Whatman #40 or equivalent, 11 or 12.5 cm.

4. **Filter Tablet or Pulp**—Whatman or equivalent.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.

2. **Hydrofluoric Acid (2.94N)**—Dilute 10 ml of concentrated hydrofluoric acid to 100 ml in a polyethylene bottle.

3. **Nitric Acid (13N)-Hydrofluoric Acid (0.05N) Solution**—Add 1656 ml of concentrated nitric acid to 310 ml of water in a 2-liter polyethylene bottle. Add 34 ml of 2.94N hydrofluoric acid.

4. **Boric Acid**—Reagent grade powder.

5. **Ammonium Hydroxide (37.5M)**—Reagent grade.

6. **Hydrochloric Acid (6N)**—Add 500 ml of concentrated hydrochloric acid to 500 ml of water and dilute to 1 liter in a volumetric flask. Store in a polyethylene bottle.

7. **Oxalic Acid Reagent Solution (1.00M)**—Dissolve 126 g of $H_2C_2O_4 \cdot 2H_2O$ in 800 ml of water and dilute to 1 liter in a volumetric flask. Store in a polyethylene bottle.

8. **Oxalic Acid (0.39M)-Hydrochloric Acid (0.48M) Wash Solution**—Dissolve 35 g of $H_2C_2O_4 \cdot 2H_2O$ in 500 ml of water. Add 80 ml of 6N hydrochloric acid and dilute to 1 liter in a volumetric flask. Store in a polyethylene bottle.

9. **Thorium Dioxide**—High purity, ignited.

## E. Procedure

### 1. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 0.5 g of the sample, weighed to the nearest 0.1 mg, into a 400-ml beaker. Add 20 ml of the 13N nitric acid-0.05N hydrofluoric acid solution, rinsing down the beaker walls during the addition. Cover with a watch glass. Heat the sample to a temperature just below boiling. At this temperature the sample dissolves rapidly. Continue heating at this temperature until the sample is in solution (5 to 75 minutes). Remove the sample from the hot plate, cool 5 to 10 minutes, and then add 40 mg of boric acid. Rinse the beaker walls and watch glass three times with deionized water. Place the beaker on a hot plate, evaporate the solution to a moist paste, and cool. Do not take to dryness as the dried salt may spatter with possible loss of sample.

Add 10 to 15 ml of 6N hydrochloric acid. Place the beaker on a hot plate, evaporate the solution to a moist paste, and cool.

Add 10 to 15 ml of water and 14 ml of 6N hydrochloric acid. Warm to dissolve the salt, add one-half tablet of paper pulp, warm to mascerate the paper, and dilute to 250 ml. Add 2 drops of concentrated ammonium hydroxide and heat in a water bath to 80 to 85°C.

Slowly, while stirring, add 60 ml of 1.00M oxalic acid reagent solution. Stir well and allow to digest at 80 to 85°C for 2 hours or until the supernatant solution is clear. Add a few drops of the 1.00M oxalic acid reagent solution. The completeness of precipitation of the thorium oxalate is indicated by observation of no turbidity in the supernatant solution. If turbidity is observed, redigest for 2 hours at 80 to 85°C. Allow to stand overnight at room temperature.

Decant the supernatant solution through an 11- or 12.5-cm Whatman #40 filter paper or equivalent. Using the 0.39M oxalic acid-0.48M hydrochloric acid wash solution, transfer the precipitate to the filter paper and police the beaker with a polyethylene policeman. The beaker precipitate and filter paper should be washed a total of not less than eight times with the 0.39M oxalic acid-0.48M hydrochloric acid wash solution, allowing each washing to drain.

Transfer the filter paper with precipitate to a tared platinum crucible that has been preignited at 1000°C for 1 hour. Place in a cool, vented muffle furnace, heat to about 400°C with the door open, and hold until the paper has burned off. Cover the sample with a platinum lid. Take the furnace to 1000°C with the door shut and ignite the sample for 1 hour. Remove the crucible and cool in a desiccator for 1/2 hour. Weigh as $ThO_2$ to ±0.1 mg.

### 2. Control Standards

To prepare the control standards, weigh a 0.5-g sample of high purity $ThO_2$ to ±0.1 mg and transfer to a 400-ml beaker. Continue as in Section IV.E.1 of this Appendix, starting with the addition of the 13N nitric acid-0.05N hydrofluoric acid solution.

## F. Calculations

Calculate the thorium content of the samples as follows:

$$\%\ \text{Thorium} = \frac{A \times 0.8788 \times 100}{B}$$

where:

A = $ThO_2$ present, g

B = weight of sample, g.

## G. References

The Analytical and Spectrochemical Analysis Laboratory procedure for the determination of thorium in $ThO_2$ by the oxalate precipitation-gravimetric method is given in Appendix C, Section IV.

# V. THE CHROMATOGRAPHIC DETERMINATION OF CARBON IN $ThO_2$ AND $UO_2$-$ThO_2$

## A. Scope

This procedure describes the determination of carbon in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 10 to 2000 ppm on a 0.5-g sample basis. This range can be extended to 10,000 ppm by using sample weights as low as 0.1 g; however, sample homogeneity must be ensured to obtain a representative analysis.

## B. Summary of Method

The carbon analyzer utilizes the difference in thermal conductivity between helium and carbon dioxide to determine the carbon content of the sample. A crucible containing the sample and accelerators is placed in a high frequency induction furnace. Carbon in the sample is converted to carbon dioxide at a combustion temperature in excess of 1600°C. Metal oxides that are produced either remain in the crucible or are filtered out in a glass wool trap. The sulfur gases and any halides present are absorbed in a trap containing manganese dioxide and silver wire. Any carbon monoxide formed is converted to carbon dioxide in a heated catalyst furnace. Moisture is removed in an anhydrone trap mounted on the analyzer. Both carbon monoxide and moisture, if permitted to pass into the analyzer, will cause erroneous results. The carbon dioxide is carried by oxygen into a collection trap, which when heated sweeps the released carbon dioxide through a silica gel column to a thermal conductivity measuring cell. The imbalance in the bridge circuit containing the thermal conductivity cell is integrated and read directly as micrograms of carbon on a digital voltmeter (DVM).

## C. Apparatus

1. **Induction Furnace**—Leco No. 521-100 or equivalent.
2. **Low Carbon Analyzer**—Leco No. 589-600 or equivalent.
3. **Oxygen Purification Assembly**—Leco No. 516-000 or equivalent.
4. **Induction Furnace Crucibles**—Leco No. 528-035, 528-16, or equivalent.
5. **Combustion Tubes** (quartz)—Leco No. 550-120 or equivalent.
6. **High Temperature Tube or Muffle Furnace.**
7. **Leak-Check Seal Assembly**—Leco No. 589-911 or equivalent.
8. **Glass Wool**—Pyrex or equivalent.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Ascarite**—20 to 30 mesh
2. **Magnesium Perchlorate**—Anhydrous.
3. **Sulfuric Acid** (18M)—Reagent grade.
4. **Manganese Dioxide**—Burrell Sulsorbent No. 25-433 or equivalent.
5. **Silver Wire.**
6. **Accelerator Iron**—Leco No. 762-970 or equivalent.
7. **Accelerator Copper Ring**—Leco No. 550-184 or equivalent.
8. **Steel Samples**—National Bureau of Standards (NBS) with certified carbon content.

## E. Procedure

### 1. Preparation of Crucibles

Low carbon analysis requires that crucibles and pedestals be preburned prior to use. To accomplish this, place the crucibles and pedestals in the muffle furnace at a temperature of approximately 1000°C for 1 hour. This time may be shortened to approximately 15 minutes by using a tube furnace and an oxygen atmosphere maintained at an operating temperature of approximately 1200°C.

When cool, weigh 1.0 g of accelerator iron into each crucible. Heat the crucibles at approximately 900°C for 2 hours, cool, and store in a dry, closed container.

Crucible preparation may be omitted if sufficiently low carbon content crucibles are used in conjunction with low carbon iron chip accelerators.

### 2. Instrument Preparation and Leak Check

Place a plug of fine glass wool in the stem of the combustion tube and install the tube in the induction furnace. Replace daily the magnesium perchlorate and glass wool in the drying tube located on the left side of the analyzer.

Check the induction furnace for leaks by adjusting the oxygen line regulator to a reading of 8 psi. Open the valve on the purifying train and set the flowmeter at 1.5 liters/min. Plug the furnace exit tube on the upper left side of the analyzer using the leak-check seal assembly. Allow the pressure to build in the system to 8 lb and back off the valve on the regulator. If the regulator valve holds the pressure for 15 minutes, there is no leak in the furnace.

Check the analyzer for leaks by setting 20 lb of pressure on the helium tank regulator. With the valve on the rotometer wide open, adjust the helium flow regulator on the analyzer to the given flow rate for the analyzer. Plug the exit tube on the lower left side of the analyzer using the leak-check seal assembly. Allow the analyzer pressure to build; then back off the valve on the helium tank regulator. If the gage on the helium tank regulator holds 20 lb for 15 minutes, with no apparent movement of the gage needle, there is no leak in the analyzer.

### 3. Balancing the Analyzer

To balance the analyzer, turn on the DVM by turning the OFF-NORM-REV switch to the REV position. Allow the DVM to warm up for 15 minutes. Turn the RANGE switch to the *1.000* position. Place the SELECT control of the DVM on the *0* position. Adjust the zero control until the DVM indicates *0.0000*. Place the SELECT control in the AMP BAL position. Adjust the BAL control until the DVM indicates *0.0000*. Place the SELECT control in the SYSTEM BAL position. Adjust the SYSTEM BAL control until the DVM indicates *0.0000*. This adjustment is quite sensitive, hence the control should be rotated slowly until approximate DVM zero indication is achieved. Activate the locking mechanism on this control. It is normal that there be a slight wandering about *0* due to variations in oven temperature as the oven heater cycles. When the balancing is completed, leave the DVM switch in the REV position, set the selector switch to OPERATE, and turn on the filament power to the induction furnace, letting it warm for 15 minutes.

### 4. General Operating Procedure

Place the crucible on the pedestal of the induction furnace and lock the sealing assembly. Purge the system for 30 seconds with oxygen at a flow rate of 1.5 liters/min.

Turn on the BLANK, CLAMP, and TIMER switches and start the analysis by depressing the CYCLE switch, which turns on the furnace. The remainder of the analysis is automatic. The carbon content is read as micrograms of carbon on the DVM. Another sample can be loaded when the COLLECT light goes out; however, the READ light must be on and the trap temperature must be below 100°F before another analysis is begun.

### 5. Calibration

Condition the furnace tube by running two samples composed of 1 g of each accelerator.

Run the appropriate low point calibration standard. As soon as the trap temperature reaches the set value, the DVM will attempt to reach the value of the blank that is set into the instrument. The DVM will then proceed upward until a stable reading is reached. At this point, adjust the blank control until the actual value of the low point calibration standard is read on the DVM. Repeat procedure if required. Run the appropriate high point calibration standard, adjusting the SLOPE control until the actual value of the standard is read on the DVM. Verify the calibration by running both the low and high point calibration standards in duplicate. If the readings obtained on the standards are within ±5 percent of their actual value, the instrument is calibrated and ready for sample analysis. Maximum accuracy is attained by instrument calibration in the expected carbon range.

### 6. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Weigh a 0.5-g sample to ±1 mg and transfer to a preburned crucible.

Place the crucible on the pedestal of the induction furnace and lock the sealing assembly. Purge the system for 30 seconds with oxygen at a flow rate of 1.5 liters/min and continue as in Section V.E.4 of this Appendix.

### 7. Control Standards

To prepare the control standards, run an NBS standard of appropriate weight to give a carbon content in the mid-point range of the calibration curve. If the control value is within ±5 percent of the NBS value, sample analysis may begin. Failure of duplicate mid-point controls to reach their actual value within ±5 percent requires the instrument to be recalibrated.

## F. Calculations

$$\text{ppm Carbon} = \frac{A}{B}$$

where:

A = DVM carbon reading, $\mu$g

B = weight of sample, g.

## G. References

The Analytical and Spectrochemical Analysis Laboratory procedure for the chromatographic determination of carbon in $ThO_2$ and $UO_2$-$ThO_2$ is given in Appendix C, Section V.

# VI. THE PYROHYDROLYTIC DETERMINATION OF FLUORIDE IN $ThO_2$ AND $UO_2$-$ThO_2$ USING A SPECIFIC ION ELECTRODE

## A. Scope

This procedure describes the determination of fluoride in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 2 to 30 ppm on a 1-g sample basis. For related samples of higher concentration, the range can be extended to 1000 ppm since electrode response is Nernstian to this level and beyond.

## B. Summary of Method

Fluoride is separated from the sample as hydrofluoric acid with steam in a quartz tube at approximately 1050°C. Hydrofluoric acid is absorbed in water, any complexes of the fluoride (i.e., $HF_2$, etc.) being broken by the addition of a Total Ionic Strength Adjustment Buffer (TISAB). The concentration of the free fluoride is determined by a fluoride specific ion electrode.

## C. Apparatus

1. **Pyrohydrolysis Apparatus**—See Figure D-2.
2. **Quartz Combustion Boats**—3 in. long.
3. **Polypropylene Volumetric Flasks**—250 ml and 1 liter for preparation of fluoride solutions.
4. **Fluoride Ion Electrode**—Orion Model 94-09 or equivalent.
5. **Reference Electrode**—Orion Model No. 90-01 or equivalent.
6. **pH Meter**—Corning Model 112 or equivalent.
7. **Powerstat Variable Transformer**—10-amp capacity.
8. **Magnetic Stirrer and Stirring Bar.**
9. **Tripour Polypropylene Beakers**—50 ml, graduated to ±1.5% accuracy (Fisher Scientific #2-593-50A or equivalent).

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.
2. **Standard Fluoride Solution (100 μg fluoride/ml)**—Dissolve 0.221 g of sodium fluoride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 1 liter in a polypropylene volumetric flask.
3. **Standard Fluoride Solution (10 μg fluoride/ml)**—Dilute 25.0 ml of the 100 μg/ml standard fluoride solution (Item 2) to 250 ml in a polypropylene volumetric flask.
4. **Standard Fluoride Solution (1 μg fluoride/ml)**—Dilute 25.0 ml of the

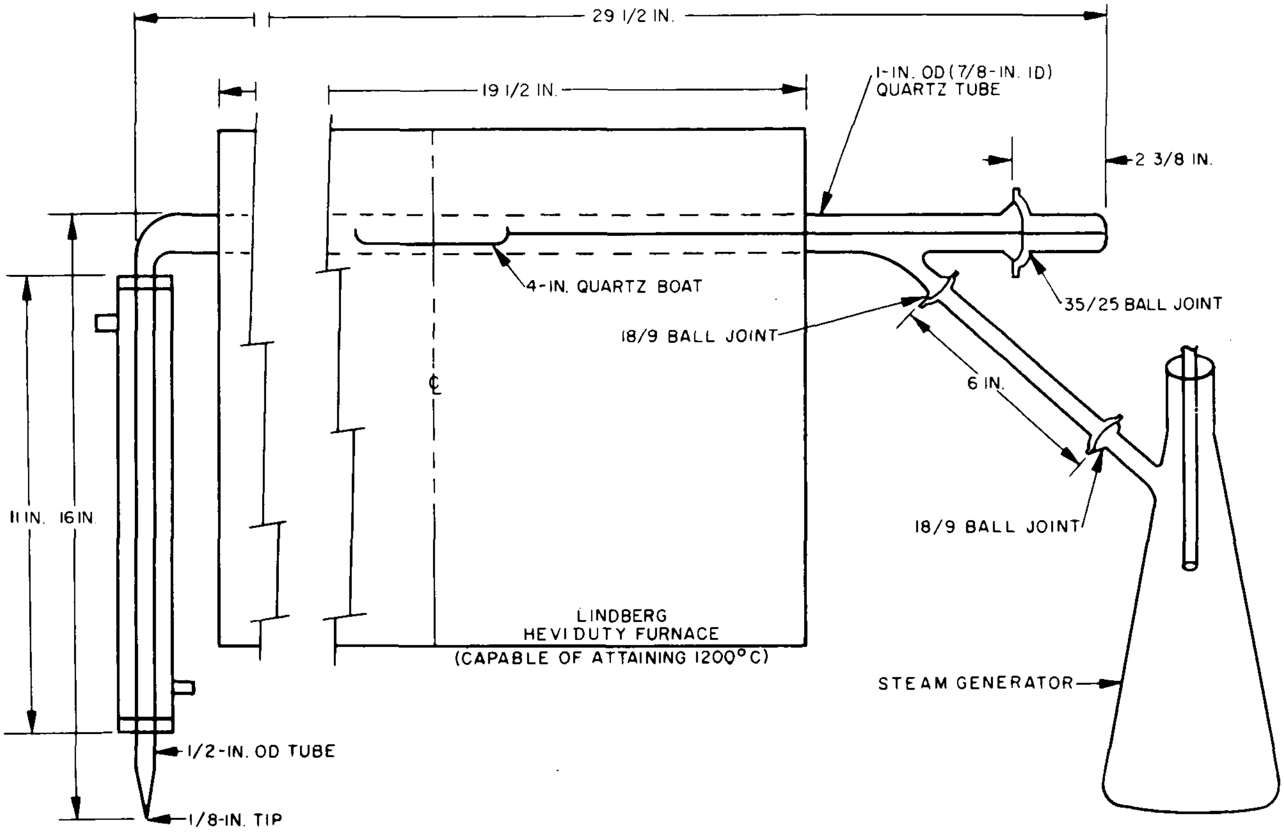


**Figure D-2. Pyrohydrolysis Apparatus for Fluoride Determination in $ThO_2$ and $UO_2$-$ThO_2$**

10 μg/ml standard fluoride solution (Item 3) to 250 ml in a polypropylene volumetric flask.

5. **Total Ionic Strength Adjustment Buffer (TISAB)**—Orion No. 94-09-09 or equivalent.

## E. Procedure

### 1. Calibration Curve (0 to 30 μg fluoride)

Pipette 0 (blank), 2.0, and 5.0 ml (0, 2, and 5 μg of fluoride) of the 1 μg/ml standard fluoride solution (Item 4 of Section VI.D of this Appendix) and 1.0, 2.0, and 3.0 ml (10, 20, and 30 μg of fluoride) of the 10 μg/ml standard fluoride solution (Item 3 of Section VI.D of this Appendix) into six 50-ml polypropylene beakers. Add 10 ml of TISAB solution to each beaker and dilute to 50 ml with water. Insert the fluoride ion electrode and reference electrode pair into the solution. Stir each solution with a magnetic stirrer and read the EMF of the electrode system after 10 minutes. Plot the millivolt readings on the linear axis and the fluoride ion concentration in micrograms per 50 ml of solution on the logarithmic axis of two-cycle semilog graph paper. After each measurement, rinse the electrodes with water and dry them by gently patting with soft, absorbent tissue. While it is not necessary to obtain a calibration curve for each set of samples, three calibration points should be run to ensure the validity of the curve.

### 2. Blanking the Pyrohydrolysis Apparatus

Insert a quartz boat in the pyrohydrolysis tube at approximately 1050°C and adjust the steam flow to produce 30 ml of distillate in 15 minutes. Blank the apparatus in this manner for 1 hour. Collect 30-ml portions of distillate and continue as in Section VI.E.1 of this Appendix, starting with the addition of the TISAB solution. Continue this process until 30 ml of distillate gives a constant millivolt reading within ±10 mV of the reagent blank, which is determined in accordance with Section VI.E.1 of this Appendix.

### 3. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 1.0 g of the sample, weighed to the nearest mg, to a blanked quartz boat. Place a 50-ml polypropylene beaker containing sufficient deionized water such that the condenser tip is below the water surface. Insert the boat quickly in the hot zone of the combustion tube, connect the steam line, and collect close to but under 40 ml of distillate. Treat the distillate in the same manner as in Section VI.E.1of this Appendix, starting with the addition of the TISAB solution.

### 4. Control Standards

To prepare the control standard, pipette 0.1 ml of the 100 μg/ml standard fluoride solution (Item 2 of Section VI.D of this Appendix) into a previously pyrohydrolyzed sample in a quartz boat. Dry the control in a desiccator. Treat the control as a sample, analyzing it as described in Section VI.E.3 of this Appendix, and use the data obtained to calculate the recovery.

## F. Calculations

Convert the millivolt readings to micrograms of fluoride by means of the calibration curve. Calculate the fluoride content of the samples as follows:

$$\text{ppm Fluoride} = \frac{A}{B}$$

where:

A = fluoride present, μg

B = weight of sample, g.

## G. References

The pyrohydrolytic analysis procedure for chloride ion determination is given in Section VII of this Appendix.

The Analytical and Spectrochemical Analysis Laboratory procedures for the pyrohydrolytic determination of chloride and/or fluoride in $ThO_2$ and $UO_2$-$ThO_2$ are given in Appendix C, Sections VI through VIII.

# VII. THE PYROHYDROLYTIC DETERMINATION OF CHLORIDE IN $ThO_2$ AND $UO_2$-$ThO_2$ USING A SPECTROPHOTOMETER

## A. Scope

This procedure describes the determination of chloride in $ThO_2$ and $UO_2$-$ThO_2$ in the concentration range of 3 to 25 ppm on a 2-g sample basis using a 10-cm light path for photometric measurement. This range can be extended by using dilution techniques, altering sample sizes, or using shorter path length absorption cells and larger chloride aliquots for calibration curves.

## B. Summary of Method

Chloride is separated from the sample as hydrochloric acid by pyrohydrolysis with steam in a quartz tube at approximately 1050°C. The chloride reacts with mercuric thiocyanate, releasing thiocyanate ions which in turn react with ferric ions to produce the red ferric thiocyanate complex. The intensity of the color measured at 470 mμ is proportional to the chloride content.

## C. Apparatus

1. **Pyrohydrolysis Aparatus**—See Figure D-3.

2. **Quartz Combustion Boats**—3 in. long.

3. **Spectrophotometer**—Beckman Model DU-2 or equivalent equipped with 10-cm absorption cells.

4. **Powerstat Variable Transformer**—10-amp capacity.

5. **Magnetic Stirrer and Stirring Bar.**

6. **Volumetric Flask**—50 ml.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilutions and in the preparation of all reagents.

2. **Standard Chloride Solution** (100 μg **chloride/ml)**—Dissolve 0.1648 g of sodium chloride or 0.2103 g of potassium chloride, previously dried at 100 to 110°C for 1 hour, in water and dilute to 1 liter in a volumetric flask.

3. **Standard Chloride Solution** (10 μg **chloride/ml)**—Dilute 10.0 ml of the 100 μg/ml standard chloride solution (Item 2) to 100 ml in a volumetric flask.

4. **Nitric Acid** (6**N**)—Dilute 190 ml of concentrated nitric acid to 500 ml with water.

5. **Ferric Ammonium Sulfate Solution**—Dissolve 49 85 g of $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ in 300 ml of 6N nitric acid and dilute to 500 ml in a volumetric flask. Allow the solution to stand 24 hours before use and store in a brown bottle.

6. **Mercuric Thiocyanate Solution**—Add 7.5 g of mercuric thiocyanate to 500 ml of methyl alcohol and stir for 1 hour with a magnetic stirrer. Filter the solution through Whatman No. 41 or 41H filter paper or equivalent. If the filtrate is not clear, allow the solution to stand 24 hours and refilter. Repeat this filtration process until a clear solution is obtained.

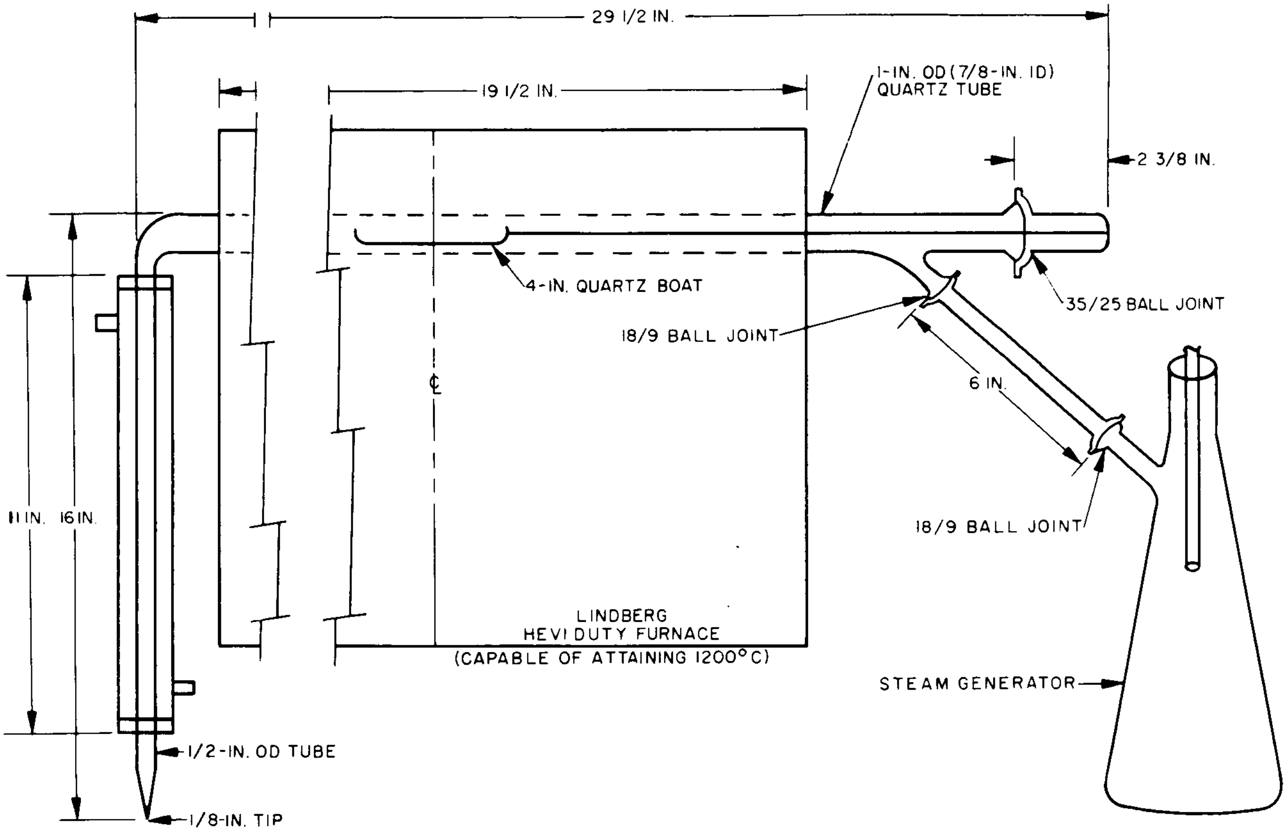


Figure D-3. Pyrohydrolysis Apparatus for Chloride Determination in $ThO_2$ and $UO_2$-$ThO_2$

## E. Procedure

### 1. Calibration Curve (0 to 50 $\mu g$ chloride)

Pipette 0 (blank), 1.0, 2.0, 3.0, 4.0, and 5.0 ml (0, 10, 20, 30, 40, and 50 $\mu g$ of chloride) of the 10 $\mu g$/ml standard chloride solution (Item 3 of Section VII.D of this Appendix) to separate 50-ml volumetric flasks and dilute with water to approximately 40 ml. Add 2.0 ml of the ferric ammonium sulfate solution, rinse down the neck of the flasks, and mix by swirling the flasks. Add 2.0 ml of the mercuric thiocyanate solution and mix again by swirling. Care should be taken not to agitate the mercuric thiocyanate solution or to transfer undissolved mercuric thiocyanate to the volumetric flasks. Dilute to volume with water, mix well, and allow to stand for 15 minutes. Read the absorbance at 470 m$\mu$ in 10-cm cells using deionized water in the reference cell. Correct for the blank and plot absorbance versus micrograms of chloride in 50 ml. While it is not necessary to obtain a calibration curve for each set of samples, three calibration points should be run with each set of samples to ensure the validity of the curve.

### 2. Blanking the Pyrohydrolysis Apparatus

Insert a quartz boat in the pyrohydrolysis tube at approximately 1050°C and adjust the steam flow to produce 30 ml of distillate in 15 minutes. Blank the apparatus in this manner for 1 hour. Collect 30-ml portions of distillate, transfer to 50-ml volumetric flasks, and dilute to approximately 40 ml. Continue as in Section VII.E.1 of this Appendix, starting with the addition of the ferric ammonium sulfate solution. Continue this process until 30 ml of distillate gives an absorbance reading within 0.005 to 0.01 of the reagent blank, which is determined in accordance with Section VII.E.1 of this Appendix.

### 3. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 3.0 g of the sample, weighed to the nearest mg, to a blanked quartz boat. Quickly place the boat in the hot zone of the combustion tube, connect the steam line, and collect approximately 30 ml of distillate. Transfer the distillate to a 50-ml volumetric flask, dilute to approximately 40 ml, and continue as in Section VII.E.1 of this Appendix, starting with the addition of the ferric ammonium sulfate solution.

### 4. Control Standards

To prepare the control standard, pipette 1.0 ml of the 10 $\mu g$/ml standard chloride solution (Item 3 of Section VII.D of this Appendix) into a previously pyrohydrolyzed sample in a quartz boat. Dry the control in a desiccator. Treat the control as a sample, analyzing it as described in Section VII.E.3 of this Appendix, and use the data obtained to calculate the recovery.

## F. Calculations

Correct for the blank, determine the micrograms of chloride from the calibration curve, and calculate the chloride content of the samples as follows:

$$\text{ppm Chloride} = \frac{A}{B}$$

where:

A = chloride present, $\mu g$

B = weight of sample, g.

## G. References

The pyrohydrolytic analysis procedure for fluoride ion determination is given in Section VI of this appendix.

The Analytical and Spectrochemical Analysis Laboratory procedures for the pyrohydrolytic determination of chloride and/or fluoride in $ThO_2$ and $UO_2$-$ThO_2$ are given in Appendix C, Sections VI through VIII.

# VIII. THE POLAROGRAPHIC DETERMINATION OF URANIUM VI IN $UO_2$ AND $UO_2$-$ThO_2$

## A. Scope

This procedure describes the determination of $U^{+6}$ in $UO_2$ and $UO_2$-$ThO_2$ using a single-sweep polarographic technique. The $U^{+6}$ content is used to calculate the O/U ratio of $UO_2$ and $UO_2$-$ThO_2$.

## B. Summary of Method

The sample is dissolved in a hot, concentrated oxygen-free phosphoric-sulfuric acid solution. The $U^{+6}$ content is subsequently determined by single-sweep polarography. In single-sweep polarography, the entire analysis takes place with one drop of mercury and one scan of voltage sweep from the polarographic analyzer. The rapid scan causes those ions in the vicinity of the mercury drop to be quickly reduced, resulting in a peak-shaped polarogram. Since the scan is quite rapid, a cathode-ray oscilloscope is used to capture and retain the resultant polarograms. A trace-recording camera is used to photograph the spectra where a permanent record is required. The increase in sensitivity due to the fast scan when compared with classical methods is considerable. The method also permits greater resolution of adjacent peaks through the use of derivative mode of analysis.

## C. Apparatus

1. **Polarographic System**—Chemtrix Model SSP-5A or equivalent.

2. **Dropping Mercury Electrode Assembly**—Chemtrix Model 105 or equivalent.

3. **Trace-Recording Camera**—Tektronix C-12 or equivalent.

## D. Reagents

All reagents used in this procedure meet or exceed the American Chemical Society specifications for reagent grade chemicals.

1. **Deionized Water**—Use deionized water for sample dilution and in the preparation of all reagents.

2. **Standard Uranium Solution (5 mg $U^{+6}$/ml)**—Dissolve 1.1793 g of National Bureau of Standards 950a $U_3O_8$ in 10 ml of 8M nitric acid. Fume to dryness several times with 5-ml portions of 9M sulfuric acid. Dilute to 200 ml with 4N sulfuric acid in a volumetric flask.

3. **Standard Uranium Solution (50 $\mu$g $U^{+6}$/ml)**—Dilute 1.0 ml of the 5 mg/ml standard uranium solution (Item 2) to 100 ml in a volumetric flask.

4. **Sulfuric Acid (4N)**—Dilute 56 ml of concentrated sulfuric acid to 500 ml with water.

5. **Sulfuric Acid (9M)**—Dilute 500 ml of concentrated sulfuric acid to 1 liter with water.

6. **Nitric Acid (8M)**—Dilute 500 ml of concentrated nitric acid to 1 liter with water.

7. **Phosphoric-Sulfuric Acid Solution (2:1)**—Prepare a solution containing two parts concentrated phosphoric acid to one part concentrated sulfuric acid and deaerate with argon for 1 hour.

8. **Thorium Dioxide**—High purity, ignited.

9. **Uranium Dioxide**—High purity.

10. **Nitrogen & Argon**—High purity.

11. **Mercury**—High purity.

## E. Procedure

### 1. Calibration Curve (0 to 200 $\mu$g $U^{+6}$)

The calibration curve described in this procedure is for use with low-level $U^{+6}$ samples. Hence, this calibration curve will be varied to encompass the $U^{+6}$ content of the samples.

Pipette 0 (blank), 1.0, 2.0, 3.0, and 4.0 ml (0, 50, 100, 150, and 200 $\mu$g of $U^{+6}$) of the 50 $\mu$g/ml standard uranium solution (Item 3 of Section VIII.D of this Appendix) into clean, dry, 50-ml volumetric flasks into which approximately 1.0 g of $ThO_2$ has been added. $ThO_2$ is omitted if samples are pure $UO_2$. Add 15 ml of deaerated phosphoric-sulfuric acid solution and heat the flask until the solution is clear. Remove the flask from the hot plate, cool, and dilute to volume with water.

Transfer a portion of the solution to the polarographic cell and allow the solution to reach operating temperature (30 ±0.2°C) while deaerating with inert gas.

Using the instrument parameters listed in Table D-2, initiate a scan from the Type 105 assembly and store the resulting polarogram on the Type 564B oscilloscope. Measure the limiting current ($I_a$) corrected for residual current (blank) at −0.50 volt. At least three scans of each calibration point should be run and a permanent record of the data should be obtained by means of a trace-recording camera. A regression fit of the diffusion current ($I_d$) versus concentration values is obtained from a linear regression fit program and the resulting equation is plotted on linear graph paper. Note that $I_a$ is actually measured as $dI_a/dT$; likewise $I_d$ is measured as $dI_d/dT$ and $I_d = I_a - \text{residual}$..

### 2. Sample Preparation and Analysis

Grind the sample using the appropriate procedure as described in Appendix E, Section I. Transfer approximately 1.0 g (0.5 g for $UO_2$) of the sample, weighed to the nearest mg, into a dry, 50-ml volumetric flask. Add 15 ml of deaerated phosphoric-sulfuric acid solution to the flask and heat on a hot plate until the sample is dissolved and a clear solution is obtained. Allow the flasks to cool and dilute to volume with water. Transfer a portion of the sample solution into the polarographic cell and record several scans. Measure the $I_a$ values for each scan corrected for residuals.

## F. Calculations

To calculate the mole ratio of oxygen to uranium in the samples (O/U), first determine the provisional atom fraction of excess oxygen (A) as follows:

$$A = \frac{50 \times C}{W \times CF \times 1000}$$

where:

$C$ = concentration of $U^{+6}$ in sample solution, $\mu g/ml$

$W$ = weight of $UO_2$ in sample solution, mg

$CF$ = composition factor of uranium in $UO_2$.

Determine the corrected atom fraction of excess oxygen ($A_c$) as follows:

$$A_c = A(1 + 0.1A).$$

Then

$$O/U = 2.000 + A_c.$$

## G. References

The Analytical and Spectrochemical Analysis Laboratory procedure for the polarographic determination of $U^{+6}$ in $UO_2$ and $UO_2$-$ThO_2$ is given in Appendix C, Section IX.

### TABLE D-2. POLAROGRAPHIC SYSTEM INSTRUMENT PARAMETERS

**Type 564B**

Display Switches — Both in STORE position

Calibrator — Off

Focus — Adjusted for maximum clarity

Astigmatism — --

Intensity — Minimum setting that will retain trace

Scale Illumination — Power OFF

**Type 305**

Position — Optional

Input — Channel *A* and/or *B*

Current Component — 5.00; both channels

A gain — Fully counterclockwise

Slope Component — Adjusted for normal mode; turned fully counterclockwise for derivative mode

X-10 — 1X

Filter — In

Mode — Optional; will depend on sample makeup

Microamps/Division — Adjusted for maximum-peak height

## TABLE D-2. (Cont)

### Type 205

Position — Adjustable

Mode — Sawtooth

Sweep — Single

Sweep Time — 0.2 to 0.1 sec

Start Potential — 0.1 volt

Potential Range — 1.0 volt

Meter Switch — Positive

Polarity — Positive

*Delay Time — 2.3 sec

### Type 105

The drop dislodger is adjusted until the rate of dislodging is slightly shorter than the natural drop time.

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*Delay time will vary with different capillaries.

# APPENDIX E

# OPERATING PROCEDURES

# APPENDIX E

# OPERATING PROCEDURES

## I. OPERATIONAL CHEMISTRY LABORATORY GRINDING PROCEDURES FOR $ThO_2$ AND $UO_2$-$ThO_2$ PELLETS

### A. Scope

These procedures describe the grinding of $ThO_2$ and $UO_2$-$ThO_2$ pellets as required for the production certification procedures in Appendices B and D. The applicable grinding technique for each production certification procedure is given in Table E-1.

### B. Summary of Method

There are four procedures used for grinding. One or a combination of the following procedures may be used:

1. Plattner mortar and pestle
2. Zirconium mortar and pestle
3. Pulverit 5 planetary ball mill grinder
4. Pulverit 0 grinder.

### C. Apparatus

The necessary equipment for performing each of the grinding procedures is as follows:

1. **Plattner Mortar and Pestle**
   - a. Plattner mortar and pestle
   - b. Adjustable gap magnet, Edmund Scientific Catalogue No. 70,810 or equivalent.
   - c. Hammer
   - d. Chisel.

2. **Zirconium Mortar and Pestle**
   - a. Zirconium mortar and pestle
   - b. Hammer.

3. **Pulverit 5 Planetary Ball Mill Grinder**
   - a. Laboratory planetary ball mill, Geoscience Pulverit 5 or equivalent
   - b. Agate grinding vessels and lids
   - c. Agate grinding balls of four different diameters (approximately 1, 5/8, 3/8, and 1/4 in.).

TABLE E-1. APPLICABLE GRINDING TECHNIQUE FOR OPERATIONAL CHEMISTRY LABORATORY PROCEDURES

| Procedure | Initial Grinding* | Final Grinding* |
|---|---|---|
| Total uranium | D.2.a | D.2.d (agate) |
| Total thorium, trace uranium, and rare earths | D.2.b | D.2.c or D.2.d (agate) |
| Emission spectrographic | D.2.b | D.2.d (zirconium) |
| Nitrogen, carbon, chloride, fluoride, and $U^{+6}$ | D.2.a | D.2.d (agate) |

**NOTE**

*All pellets are ground to a consistency of approximately 200 mesh.*

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*The entries in this column refer to the applicable section of this Appendix.

4. **Pulverit 0 Grinder**
   a. Electromagnetic laboratory micromill, Geoscience Pulverit 0 or equivalent
   b. Agate or zirconium grinding vessel
   c. Agate or zirconium grinding ball.

## D. Procedures

### 1. Preparation

Articles to be used for grinding should be cleaned thoroughly with a Kimwipe or equivalent wetted with acetone. (Water should never be used to clean the grinding articles.) After drying the grinding articles with Kimwipes (or equivalent), ensure that there are no powder residues, lint, or paper fibers remaining. Place all used Kimwipes (or equivalent) in a covered metal waste can at the end of each shift, permitting sufficient time for the acetone to evaporate from the Kimwipes (or equivalent) prior to placing them in the metal can.

### 2. Pellet Grinding

*a. Plattner Mortar and Pestle*—Transfer up to 10 g of pellet or pellet chunks to the Plattner mortar. If a pellet weighs more than 10 g, break the pellet into chunks with a hammer and chisel and transfer up to 10 g into the Plattner mortar. Break the pellet into 1/16-in. or less chips by repeatedly striking the pestle with a hammer. After transferring this portion to a plastic vial, repeat the crushing operation until the entire pellet has been reduced to pieces less than 1/16 in. For the removal of iron, slowly rotate the vial through the magnetic field of an adjustable gap magnet by moving from the bottom to the top of the vial. Remove the iron particles from the vial at the end of each pass. Repeat until three successive passes yield no additional iron particles. Place the lid on the plastic vial and hold for further grinding.

*b. Zirconium Mortar and Pestle*—After transferring the pellets to the zirconium mortar, break them into small chips by striking the pestle with a hammer or using the pestle itself. Transfer an appropriate portion of the pellet chips to a plastic sample vial and hold for further grinding. The required particle size may also be obtained by continued hand grinding of the sample with the zirconium mortar and pestle.

*c. Pulverit 5 Planetary Ball Mill, Grinder or Equivalent*—After the pellets have been broken into chips using a zirconium mortar and pestle, transfer 100 to 200 g to an agate grinding vessel. Also, place two (approximately 5/8-in. to 1-in. diameter) agate balls and three (approximately 1/4-in. to 3/8-in. diameter) agate balls into the grinding vessel. The best grinding action occurs when the grinding vessel is approximately two-thirds filled. Place the agate lid on the vessel and transfer the samples into a polyethylene bag. Secure the polyethylene bag about the vessel and lid and place it upon the planetary grinder, being careful to tighten the security cables on the grinding vessel. Tighten the locknut firmly enough that the clamping screw will withstand all attempts to unscrew it. After securing the three grinding vessels, set the Plexiglass cover in place. Insert the thickest of the three metal pins on the Plexiglass cover into the safety switch of the grinder. Grind the samples at a setting of *3 1/2 right* for approximately 60 minutes. If only one or two samples are to be ground, permit the remaining vessels or vessel to rotate empty. After grinding transfer the material to a vial.

*d. Pulverit 0 Grinder or Equivalent*—After the pellets have been broken into chips using either a Plattner or zirconium mortar and pestle, transfer up to 9 g (7 g for total uranium and/or total thorium) to the agate or zirconium grinding vessel. Place the grinding ball in the vessel and place the vessel in the grinding unit. Secure the lid over the vessel. Grind the sample at a setting of *2* for 10 to 15 minutes, then change the setting to *9* for 40 to 60 minutes. The grinder must be level for proper operations. (Alterations in the grinder level are made with the three grinder legs.) When the grinder is level, the powder in the vessel will rise and fall evenly around the grinding ball. Upon completion of grinding, transfer the powder to a vial.

# II. PREPARATION OF EMULSION CALIBRATION CURVES FOR OPERATIONAL CHEMISTRY LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

## A. Scope

This procedure describes the preparation of emulsion calibration curves for the Operational Chemistry Laboratory emission spectrochemical procedures. These curves are used to convert percent transmission readings obtained from a microphotometer into relative intensity values.

## B. Summary of Method

Emulsion calibration curves will vary both with emulsion type and also with different production lots for the same emulsion. These curves are also affected to various degrees by the wavelength of light used, the duration and intermittency of exposure, the conditions of photographic development, and the slit width and general optical design of both the spectrograph and the microphotometer. A relative intensity obtained by referring a measured percent transmission to such a curve is accurate only if the sample spectrogram was produced under the same conditions as the emulsion calibration curve.

Quantitative spectrochemical analysis accuracy depends upon the methods used for calibrating emulsions and interpreting the data. From the standpoint of accuracy, a calibration procedure employing a two-step filter has been used. The use of the two-step method ensures more uniform vertical illumination than a several-step method since it requires a smaller slit. It is also fast and provides an easy method for periodic rechecks.

A series of exposures of the radiant energy emitted by iron using d-c arc excitation is recorded. In each of the resulting spectra, each line has a light step and a dark step. The preliminary curve is prepared by plotting the light step versus the dark step on linear graph paper. The final emulsion calibration curve is prepared by plotting the transmission values obtained from the preliminary curve as a Seidel function versus the relative intensities as a logarithmic function.

## C. Apparatus

1. **Spectrograph**—Baird-Atomic dual grating spectrograph with two individual 30,000 lines/inch gratings capable of being utilized simultaneously or individually. Grating *A* is blazed to obtain maximum efficiency and intensity at 2500 A in the second order, while grating *B* is blazed for 3000 A in the second order. The second order reciprocal linear dispersion has been determined to be 1.95 A/mm.

2. **Excitation Source**—Baird-Atomic Model RE-1 or equivalent, capable of a range from 3 to 30 amps.

3. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent.

4. **Calculator**—Jarrell-Ash 30-100 Seidel calculating board or equivalent.

5. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent.

## D. Reagents and Materials

1. **Electrodes**—Met Bay C-1, iron self-electrode (Spex Industries), or equivalent.

2. **Photographic Plates**—Eastman Kodak SA #1 and SA #3 or equivalent.

3. **Developer**—Eastman Kodak #D-19 or equivalent.

4. **Stop Bath**—1% acetic acid.

5. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

6. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Procedure

### 1. Excitation and Exposure Parameters

Arc the iron electrode according to the conditions listed in Table E-2.

### 2. Photographic Processing

Process the plate in accordance with the procedure described in Section III of this Appendix.

### 3. Preparation of Preliminary Curve

Utilizing the microphotometry procedure described in Section IV of this Appendix, read successive steps of the iron lines selected and obtain an even distribution of transmission values between 97 and 3 percent. Measure sufficient spectral lines within wavelength increments of 100 to 200 A to determine any shift in the slope or gamma of the preliminary curve.

Prepare the preliminary curve by plotting on linear coordinate paper the light step as the ordinate and the dark step as the abscissa. Draw the best smooth curve through the points, making sure the curve passes through 0 and 100 percent transmission. This curve represents the percent transmission relationship between any two hypothetical lines that have a given intensity ratio of 1.585, obtained by using a 100/63 percent transmission filter at the slit.

### 4. Preparation of Emulsion Calibration Curve

From the preliminary curve, construct a table of successive percent transmission values similar to Table E-3, starting at 97 percent in the light step as the upper limit. Record the percent transmission value in the dark step corresponding to 97 percent in the light step. Now use this percent transmission value determined in the dark step as the point in the light step to obtain the next dark step value. Continue this process until a dark step percent transmission value of less than 3 is obtained.

The 97 percent transmission value of the table is arbitrarily assigned an intensity value of 0.10. The next percent transmission value is 1.585 times more intense and is therefore assigned the value 0.1585. The intensity for the next value is 1.585 times 0.1585 or 0.2512. Continue in this manner until all percent transmission values of the table have a corresponding intensity value.

Using the Seidel calculating board, plot the percent transmission values as a Seidel function on the ordinate and the relative intensities as a logarithmic function on the abscissa from the data in the table.

### TABLE E-2. EXCITATION AND EXPOSURE CONDITIONS OF ELECTRODES FOR PREPARATION OF EMULSION CALIBRATION CURVES
(Operational Chemistry Laboratory)

| | |
|---|---|
| **Excitation:** | D-c arc |
| **Current:** | 5 amps |
| **Exposure Time:** | Preburn—2 sec |
| | Exposure—Exposure varies. Six exposures of 1, 2, 3, 4, 5, and 10 sec will be suitable for most wavelength regions. |
| **Electrodes:** | Upper—Met Bay C-1 or equivalent |
| | Lower—Iron electrode |
| | Gap distance—4 mm |
| **Slit Width:** | 20 $\mu$ |
| **Slit Height:** | 3 mm |
| **Spectral Region:** | 2400 to 4000 A |
| **Grating:** | *B* |
| **Filter:** | 100% illuminator |
| | Two-step 100/63% neutral density filter at slit |

#### 5. Preparation of Emulsion Calibration Strip

To facilitate the determination of the corresponding relative intensity for a percent transmission reading, a calibration strip is prepared. From each point on the emulsion calibration curve with an integral ordinate value, draw a line perpendicular to the abscissa and mark it with the ordinate percent transmission value.

#### 6. Calculation of Relative Intensity

Shift the calibration strip to line up a percent transmission value of 97 with a relative intensity of 0.10 on the logarithmic scale. Move the vertical scale mount to the percent transmission value of interest and note the corresponding relative intensity value on the logarithmic scale.

## III. PHOTOGRAPHIC PROCESSING AND DARK ROOM PROCEDURES FOR OPERATIONAL CHEMISTRY LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

### A. Scope

This procedure describes the photographic process and the recommended procedure for processing spectrographic plates used in the Operational Chemistry Laboratory emission spectrochemical procedures such as Eastman Kodak SA #1 and SA #3.

### B. Summary of Method

The photographic process can be described as consisting of four distinct steps: (1) development, (2) termination of development, (3) fixing, and (4) washing.

#### 1. Development

After exposing a photographic emulsion to light, radiation that is absorbed acts upon the silver halide crystals, producing minute particles of free silver within the crystals. These exposed silver halide crystals comprise the latent image. After immersing the plate in the developing agent, Eastman Kodak #D-19 or equivalent, a reaction between the agent and the silver ions is started by the latent-image silver. A few silver ions are reduced to free silver, which then acts as a catalyst to continue the reduction process between more silver ions and the developing agent. The reduction process produces the spectral lines observed on the photographic plate.

### TABLE E-3. FORMAT OF TABLE FOR EMULSION CALIBRATION CURVE PREPARATION

| Percent Transmission | Relative Intensity |
|---|---|
| $T_1$ = 97 | 0.1000 |
| $T_2$ = ___ | 0.1585 |
| $T_3$ = ___ | 0.2512 |
| $T_4$ = ___ | 0.3982 |
| $T_5$ = ___ | 0.6311 |
| $T_6$ = ___ | 1.000 |
| $T_7$ = ___ | 1.585 |
| $T_8$ = ___ | 2.512 |
| $T_9$ = ___ | 3.982 |
| $T_{10}$ = ___ | 6.311 |
| $T_{11}$ ~3 | 10.00 |

### 2. Termination of Development

After the desired degree of development is attained, the development action is terminated by immersing the plate in an acetic acid bath. This stop bath prevents aerial oxidation of the developing agent, which could produce stains on the emulsion. By using the stop bath, the surface of the emulsion is matched more closely with the acidic nature of the fixer solution and excessive carry-over of the alkaline developer into the fixer is prevented. The amount of emulsion swelling is also controlled by the stop bath, which allows the emulsion-hardening properties of the fixer solution to be more efficient.

### 3. Fixing

After termination of development, the plate is immersed in the fixer solution containing ammonium thiosulfate and a hardener. The hardener is added to prevent excessive swelling and softening of the emulsion during washing, thus minimizing susceptibility to physical damage. The fixer solution should meet the following requirements: (1) it must completely dissolve the unexposed silver halides, (2) it must form salts with the dissolved silver halides so they will not decompose during washing, (3) it must not attack the gelatin or emulsion support, and (4) it must not seriously affect the silver grains of the developed image.

### 4. Washing

After fixing and hardening, the plate is washed. Washing is necessary to remove the residual ammonium thiosulfate, which will attack the silver image and convert it to a sulfide. To prevent any deposits from being left on the plate due to washing, the plate is immersed in a photo-flo solution and rinsed with deionized water. The plate is then dried by a forced filtered-air blower.

## C. Apparatus

1. **Photographic Processor**—Zeebac Model 3100 photoprocessor or equivalent, equipped with stainless steel tanks for developer, stop, fixer, and photo-flo rinse solutions. All trays are immersed in a constant temperature bath maintained at 20 ±0.5°C. Agitation is provided as a slow back-and-forth movement, allowing the developer to flow gently over the emulsion surface, thus maintaining a normal development rate. Agitation is also provided for the fixer solution to shorten clearing time.

2. **Plate Washer**—A compartment within the photoprocessor that provides a continuous stream of water to remove the fixer solution from the plate.

3. **Plate Drier**—A resistance type heater with blower within the photoprocessor that provides a constant flow of warm or ambient-temperature air to dry the emulsion without softening.

4. **Timer**—Gra Lab Model 300 darkroom timer or equivalent.

5. **Water Chiller**—Kreonite Model KR 100 or equivalent, capable of supplying water at or below 20°C.

6. **Temperature Blender**—Kreonite Model KTB251 or equivalent, capable of controlling the temperature to 20 ±0.5°C.

7. **Plateholder**—Zeebac Model 3100-A-0400 or equivalent, designed to hold two 4-in. by 10-in. photographic plates.

8. **Safelight with Filter**—Eastman Kodak safelight or equivalent with Wratten No. 1 filter or equivalent.

9. **Refrigerator**—Capable of storing plates at 40 to 50°F to maintain their quality. Relative humidity should not exceed 60 percent. Packages of plates removed from the

refrigerator should be allowed to reach room temperature before opening to prevent condensation of moisture on the plates.

## D. Reagents and Materials

1. **Photographic Plates**—Eastman Kodak SA #1 and SA #3 or equivalent.
2. **Developer**—Eastman Kodak #D-19 or equivalent.
3. **Stop Bath**—1% acetic acid.
4. **Fixer Solution**—Eastman Kodal Rapid Fixer or equivalent.
5. **Photo-flo Bath**—Eastman Kodak Photo-flo 600 Solution or equivalent.

## E. Procedure

Remove exposed spectrographic plates from the camera and place them in a plateholder under safelight illumination. Sufficient time should be allowed for solutions in trays to come to equilibrium at 20 ±0.5°C. Process the plates according to the following times and order:

1. Developer—4 min
2. Stop bath—30 sec
3. Fixer solution—5 min
4. Wash—5 min
5. Photo-flo bath—30 sec.

After completion of the photo-flo bath, rinse the plates with deionized water and place them in the drier. Dry the plates for 5 minutes with warm air and force ambient-temperature air over them for 5 minutes to allow them to cool.

It is advisable to precondition newly prepared developer prior to plate development. This is necessary because the reactivity of freshly prepared developer declines rapidly with the first few plates developed until a stable reactivity plateau is reached. Therefore, retain used developer; when new developer is prepared, make a 3:1 dilution of new to old developer.

# IV. MICROPHOTOMETRY PROCEDURE FOR OPERATIONAL CHEMISTRY LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

## A. Scope

This procedure describes the recommended practice required for correct measurement of the spectral line intensities on photographic plates used in the Operational Chemistry Laboratory emission spectrochemical procedures.

## B. Summary of Method

A photographic plate containing the emitted spectra of samples and standards as images of the slit of a spectrograph is inserted in the front carriage of the microphotometer. A reference plate for alignment and line identification is inserted in the rear carriage. After alignment, setting of slit width and height, and making transmission range adjustments, measurements of the percent transmission of selected lines are taken.

The percent transmission readings are obtained in the following manner. The light from a mercury lamp is projected by a condensing system onto the photographic plate. A projection of the two plates magnified to 15X is displayed on the viewing screen. A split glass rhomb located directly under the sample plate has a 0.05-mm wide aluminum mirror that reflects the light from the region of the plate where the spectral line of interest lies. The image of the mirror appears on the viewing screen and acts as the fiducial mark. As the photographic plate is scanned slowly across the aluminum mirror, the images of the spectral lines move across the slit. The line images are of an intensity directly proportional to the light transmitted by the images on the plate. The light transmitted by the images is reflected from the edge of the rhomb by total internal reflection and passed down the light tube through the focus lens. It is reflected back by a mirror through an adjustable slit to the photomultiplier. The current output of the tube is proportional to the percent transmission of the line. By setting the digital reading to read *0* when all light is cut off and to read *100* when the light passes through a clear, unexposed portion of the emulsion, the proportionality constant becomes unity. Therefore, the digital display reads directly in percent transmission.

After reading the background and line transmission for each line of interest, refer the measurements to the emulsion calibration curve and convert them to relative intensities.

## C. Apparatus

1. **Microphotometer**—Jarrell-Ash Model 21-300 or equivalent with the following features:
   - a. *Slit Height*—Variable in increments of 0.1, 0.5, 0.7, 1.2, 1.6, and 2.0 mm and rotatable parallel with spectral lines up to ±7°.
   - b. *Slit Width*—Continuously variable from 0 to 25$\mu$.
   - c. *Light Measurement*—Photomultiplier detection system.
   - d. *Screen Magnification*—15X.
   - e. *Readout*—Digital with capabilities of being locked on the spectral line peak reading.

## D. Procedure

1. Turn on the master switch, and after 5 seconds, push the ignitor button. The mercury projection lamp should receive power, and as the lamp warms up the screen will slowly become brighter.
2. Permit the microphotometer-measuring electronics to warm up for a period of approximately 30 minutes to ensure maximum stability.
3. Insert a master plate in the rear carriage and a sample plate in the front carriage of the microphotometer with the emulsion side down.
4. Adjust the focus of the two projected fields.
5. Make a rough alignment of the two plates by sliding the sample plate by hand until the iron spectrum or characteristic spectral lines of the plates coincide.
6. Make the final alignment by adjusting the alignment knob on the right of the front carriage.
7. Using the master plate, locate and identify the spectral line whose percent transmission is to be determined.
8. Adjust the position of the sample plate with the lateral and transverse scanning knobs to a clear unexposed portion of the plate near the line to be measured.
9. Slide an opaque card over the top of the sample plate or close the occulter and set the digital reading to *0* with the zero control.
10. Remove the card or open the occulter to a position that just includes the length of the line to be measured. To minimize the effects of graininess in the emulsion, use as large an occulter setting as possible.
11. Open the slit exit to about one-third of the slit width used on the spectrograph when the exposure was taken.
12. Turn the sensitivity control until the digital reading is nearly 100 percent.

**NOTE**

*Do not set the sensitivity control to 100 on the background near the line. This is tantamount to subtracting logarithmic functions and will result in dividing the relative intensities of the line by the background rather than performing a subtraction of the intensities.*

13. Adjust the digital reading to exactly 100 percent with the span control.
14. Recheck the 0- and 100-percent readings and adjust if necessary.
15. Move the line to be measured slightly to the right of the vertical fiducial mark on the screen.
16. Adjust the lateral racking knob until the area of interest is centered on the enclosed area by the two fiducial marks chosen by the occulter setting.
17. Adjust the sample plate or rotate the slit to ensure the spectral lines are parallel with the fiducial mark.
18. Press either the foot switch or small push button to initiate a scan.
19. Read the transmission for each line of interest as well as its corresponding background. To obtain a background transmission, scan from the left of the line and note the reading. As the spectral line transmission is being displayed, switch the scalock switch to maximum. The scalock will then lock on the lowest percent transmission reading. Release the scalock, continue scanning to the right of the line, and note the background reading. The mean of the two background readings will give a good approximation of the background transmission. If spectral complexity prohibits obtaining background readings on both sides of the line, use only one background reading, obtained from the side with no interference. Maintain consistency in measuring backgrounds in the same location and on the same side of the line.
20. Reset 0- and 100-percent transmission each time a new element line is to be measured.
21. Upon completion of all measurements of the desired spectral lines and their corresponding backgrounds, refer the measurements to the emulsion calibration curve and convert them to relative intensities.

# V. PREPARATION OF EMULSION CALIBRATION CURVES FOR ANALYTICAL AND SPECTROCHEMICAL ANALYSIS LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

## A. Scope

This procedure describes the preparation of emulsion calibration curves for the Analytical and Spectrochemical Analysis Laboratory emission spectrochemical procedures. These curves are used to convert percent transmission readings obtained from a microphotometer into relative intensity values.

## B. Summary of Method

Emulsion calibration curves will vary both with emulsion type and also with different production lots for the same emulsion. These curves are also affected to various degrees by the wavelength of light used, the duration and intermittency of exposure, the conditions of photographic development, and the slit width and general optical design of both the spectrograph and the microphotometer. A relative intensity obtained by referring a measured percent transmission to such a curve is accurate only if the sample spectrogram was produced under the same conditions as the emulsion calibration curve.

A series of exposures of the radiant energy emitted by iron using d-c arc excitation is attenuated in known ratios by a rotating step sector located at the slit of the stigmatic spectrograph. The line intensities are measured photometrically, and preliminary curves are prepared from the measured transmission values on linear coordinate paper. The final emulsion calibration curve is prepared by plotting the transmission values obtained from the preliminary curve as a Seidel function versus the relative intensities as a logarithmic function.

## C. Apparatus

1. **Spectrograph**—Either of the following two spectrographs can be used:

   a. 3.4-meter Jarrell-Ash with a 15,000 lines per inch grating in a Wadsworth mounting or equivalent. The second order reciprocal linear dispersion is 2.6 A/mm with a resolution of 0.15 A. The image of the slit is focussed vertically on the collimating mirror by means of a cylindrical lens (45-cm focal length, horizontal axis) located at the entrance slit. The plateholder will accommodate two 4-in. by 10-in. photographic plates.

   b. Hilger instrument with quartz and glass optics for dispersing radiant energy. For normal ultraviolet and visible operation, an image of the source is focussed at the collimating lens by means of a spherical lens, F-1025, which has a focal length of 30 cm and is located at the slit.

2. **Excitation Source**—Any source of excitation capable of supplying a 220-v, fully rectified output of 5 amps.

3. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Jarrell-Ash Model 200, or equivalent.

4. **Calculator**—Applied Research Laboratories Dunn-Lowry calculator, Jarrell-Ash calculating board, Model JA-3001, or equivalent.

5. **Rotating Step Sector**—Seven steps, step ratio of 1.585.

6. **Photographic Processor**—Jarrell-Ash "Photoprocessor," Model 3410 or equivalent.

## D. Reagents and Materials

1. **Preformed Spectrographic Electrodes**—High purity; specific types indicated in Section V.E of this Appendix.

2. **Iron Rods or Powder**—See Section V.E of this Appendix.

3. **Photographic Plates**—Eastman Kodak SA #1 and SA #3 or equivalent.

4. **Developer**—Eastman Kodak #D-19 or equivalent.

5. **Stop Bath**—1% acetic acid.

6. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

## E. Excitation and Exposure Parameters

### 1. Excitation Parameters

a. **D-c Arc**
   - Current—5 amps.
   - Applied voltage—220 volts.

b. **Electrode System**
   - Upper (counter)—1/8-in.-diameter pointed; National Carbon L-4036, United Carbon 1992, or equivalent.
   - Lower (sample, anode)—Iron globule formed at the end of a 1/4-in.-diameter iron self-electrode or mounted on a 0.24-in.-diameter graphite electrode.
   - Analytical gap—4 mm.

### 2. Exposure Conditions

Exposure conditions are presented in Table E-4.

## F. Photography and Processing

Process the plate in accordance with the procedure described in Section VI of this Appendix.

## G. Preparation of Preliminary Curve

Utilizing the microphotometry procedure described in Section VII of this Appendix, read successive steps of the iron lines selected and obtain an even distribution of transmission values between 97 and 3 percent. Measure sufficient spectral lines within wavelength increments of 100 to 200 A to determine any shift in the slope or gamma of the preliminary curve.

Prepare the preliminary curve by plotting on linear coordinate paper the light step as the ordinate and the dark step as the abscissa. Draw the best smooth curve through the points, making sure the curve passes through 0 and 100 percent transmission. This curve represents the percent transmission relationship between any two hypothetical lines that have a given intensity ratio of 1.585, obtained by using a rotating step sector (Item 5 of Section V.C of this Appendix) at the slit.

## H. Preparation of Emulsion Calibration Curve

From the preliminary curve, construct a table of successive percent transmission values similar to Table E-5, starting at 97 percent in the light step as the upper limit. Record the percent transmission value in the dark step corresponding to 97 percent in the light step. Now use this percent transmission value determined in the dark step as the point in the light step to obtain the next dark step value. Continue this process until a dark step percent transmission value of less than 3 is obtained.

The 97 percent transmission value of the table is arbitrarily assigned an intensity value of 0.10. The next percent transmission value is 1.585 times more intense and is therefore assigned the value 0.1585. The intensity for the next value is 1.585 times 0.1585 or 0.2512. Continue in this manner until all percent transmission values of the table have a corresponding intensity value.

Using the Seidel calculating board, plot the percent transmission values as a Seidel function on the ordinate and the relative intensities as a logarithmic function on the abscissa from the data in the table.

### TABLE E-4. EXPOSURE CONDITIONS OF ELECTRODES FOR PREPARATION OF EMULSION CALIBRATION CURVES

**(Analytical and Spectrochemical Analysis Laboratory)**

| | Wadsworth | | | Hilger |
|---|---|---|---|---|
| Slit width, μ | 30 | | | 10 |
| Slit height, mm | 18 | | | 18 |
| Spectral region, A | 2400 to 4000 | | | 2100 to 2650 |
| Collimating mask, in. | 5/8 by 5 1/4 | | | None |
| Grating mask, in. | 2 by 2 1/2 | | | None |
| Pre-exposure time, sec. | 2 | | | 2 |
| *Exposure time, sec. | **Spectrogram** | **Veeder (approximate)** | **Sector** | **Exposure Time** |
| | 1 | 15 | No | 15 |
| | 2 | 35 | Yes | 25 |
| | 3 | 55 | Yes | 50 |
| Filter | Rotating step sector located at the slit of the spectrograph, speed >600 rpm | | | Rotating step sector located at the slit of the spectrograph, speed >600 rpm |
| Exterior lens | None | | | 1025 spherical, focal length 300 mm, located at the slit |

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*Exposure times will vary with emulsion batches. A test plate may be necessary to establish optimum exposure conditions.

### TABLE E-5. FORMAT OF TABLE FOR EMULSION CALIBRATION CURVE PREPARATION

| Percent Transmission | Relative Intensity |
|---|---|
| $T_1$ = 97 | 0.1000 |
| $T_2$ = ____ | 0.1585 |
| $T_3$ = ____ | 0.2512 |
| $T_4$ = ____ | 0.3982 |
| $T_5$ = ____ | 0.6311 |
| $T_6$ = ____ | 1.000 |
| $T_7$ = ____ | 1.585 |
| $T_8$ = ____ | 2.512 |
| $T_9$ = ____ | 3.982 |
| $T_{10}$ = ____ | 6.311 |
| $T_{11}$ ~3 | 10.00 |

## I. Preparation of Emulsion Calibration Strip

To facilitate the determination of the corresponding relative intensity for a percent transmission reading, a calibration strip is prepared. The emulsion calibration curve may be projected to a horizontal scale for use with the Dunn-Lowry calculator or equivalent. Care must be exercised to ensure that the log relative intensity scale of the plot has the same scale size or scale parameter as the log scale on the calculator.

## J. Calculation of Relative Intensity

Shift the calibration strip to line up a percent transmission value of 97 with a relative intensity of 0.10 on the logarithmic scale. Move the vertical scale mount to the percent transmission value of interest and note the corresponding relative intensity value on the logarithmic scale.

# VI. PHOTOGRAPHIC PROCESSING AND DARK ROOM PROCEDURES FOR ANALYTICAL AND SPECTROCHEMICAL ANALYSIS LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

## A. Scope

This procedure describes the photographic process and the recommended procedure for processing spectrographic plates used in the Analytical and Spectrochemical Analysis Laboratory emission spectrochemical procedures such as Eastman Kodak SA #1 and SA #3.

## B. Summary of Method

The photographic process can be described as consisting of four distinct steps: (1) development, (2) termination of development, (3) fixing, and (4) washing.

### 1. Development

After exposing a photographic emulsion to light, radiation that is absorbed acts upon the silver halide crystals, producing minute particles of free silver within the crystals. These exposed silver halide crystals comprise the latent image. After immersing the plate in the developing agent, Eastman Kodak #D-19 or equivalent, a reaction between the agent and the silver ions is started by the latent-image silver. A few silver ions are reduced to free silver, which then acts as a catalyst to continue the reduction process between more silver ions and the developing agent. The reduction process produces the spectral lines observed on the photographic plate.

### 2. Termination of Development

After the desired degree of development is attained, the development action is terminated by immersing the plate in an acetic acid bath. This stop bath prevents aerial oxidation of the developing agent, which could produce stains on the emulsion. By using the stop bath, the surface of the emulsion is matched more closely with the acidic nature of the fixer solution and excessive carryover of the alkaline developer into the fixer is prevented. The amount of emulsion swelling is also controlled by the stop bath, which allows the emulsion-hardening properties of the fixer solution to be more efficient.

### 3. Fixing

After termination of development, the plate is immersed in the fixer solution containing ammonium thiosulfate and a hardener. The hardener is added to prevent excessive swelling and softening of the emulsion during washing, thus minimizing susceptibility to physical damage. The fixer solution should meet the following requirements: (1) it must completely dissolve the unexposed silver halides, (2) it must form salts with the dissolved silver halides so they will not decompose during washing, (3) it must not attack the gelatin or emulsion support, and (4) it must not seriously affect the silver grains of the developed image.

4. **Washing**

After fixing and hardening, the plate is washed. Washing is necessary to remove the residual ammonium thiosulfate, which will attack the silver image and convert it to a sulfide. To prevent any deposits from being left on the plate due to washing, the plate is rinsed with deionized water and partially dried with a photographic sponge. This preliminary sponging removes large water droplets that could cause staining of the emulsion. The plate is then dried by a forced filtered-air blower.

## C. Apparatus

1. **Photographic Processor**—Jarrell Ash Model 3410 or equivalent, equipped with stainless steel tanks for developer, stop, and fixer solutions. All trays are immersed in a constant temperature water bath maintained at 20 ±0.5°C. Agitation is provided for even distribution of developer over the emulsion surface, thus maintaining a normal development rate. Agitation is also provided for the fixer solution to shorten clearing time.

2. **Plate Washer**—A compartment within the photoprocessor that provides a continuous stream of water to remove the fixer solution from the plate.

3. **Plate Drier**—A resistance type heater with blower within the photoprocessor that provides a constant flow of warm or ambient-temperature air to dry the emulsion without softening.

4. **Timer**—Gra Lab Model 300 darkroom timer or equivalent.

5. **Water Chiller**—Capable of supplying water at or below 20°C.

6. **Plateholder**—Designed to hold one or more plates during photographic processing.

7. **Safelight with Filter**—Eastman Kodak safelight or equivalent with Wratten No. 1 filter or equivalent.

8. **Refrigerator**—Capable of storing plates at 40 to 50°F to maintain their quality. Relative humidity should not exceed 60 percent. Packages of plates removed from the refrigerator should be allowed to reach room temperature before opening to prevent condensation of moisture on the plates.

## D. Reagents and Materials

1. **Photographic Plates**—Eastman Kodak SA #1 and SA #3 or equivalent.

2. **Developer**—Eastman Kodak #D-19 or equivalent.

3. **Stop Bath**—1% acetic acid.

4. **Fixer Solution**—Eastman Kodak Rapid Fixer or equivalent.

5. **Sponges**—Dupont photographic type or equivalent.

## E. Procedure

Remove exposed spectrographic plates from the camera and place them in a plateholder under safelight illumination. Sufficient time should be allowed for solutions in trays to come to equilibrium at 20 ±0.5°C. Process the plates according to the following times and order:

1. Developer—4 min
2. Stop bath—30 sec
3. Fixer solution—5 min
4. Wash—5 min.

After completion of the washing step, rinse the plates with deionized water, partially dry them with a photographic sponge, and place them in the drier. Dry the plates for 5 minutes with warm air and force ambient-temperature air over them for 5 minutes to allow them to cool.

It is advisable to precondition newly prepared developer prior to plate development. This is necessary because the reactivity of freshly prepared developer declines rapidly with the first few plates developed until a stable reactivity plateau is reached. Therefore, retain used developer; when new developer is prepared, make a 3:1 dilution of new to old developer.

# VII. MICROPHOTOMETRY PROCEDURE FOR ANALYTICAL AND SPECTROCHEMICAL ANALYSIS LABORATORY EMISSION SPECTROCHEMICAL PROCEDURES

## A. Scope

This procedure describes the recommended practice required for correct measurement of the spectral line intensities on photographic plates used in the Analytical and Spectrochemical Analysis Laboratory emission spectrochemical procedures.

## B. Summary of Method

A photographic plate containing the emitted spectra of samples and standards produced by an optical spectrograph is inserted in the sample plateholder of the microphotometer. A reference plate for alignment and line identification is inserted in the master plateholder of the microphotometer. The spectra on both plates are represented as images of the slit of the spectrograph that have been reflected and dispersed by the diffraction grating of the spectrograph.

The microphotometer projects an image of the two plates onto a screen with a magnification of 14 to 20X. A line of light is also projected through the sample plate and is focused on the light-sensitive plate of a photocell or photomultiplier tube, which converts its intensity to an electronic signal that is amplified and measured by a galvanometer. After plate alignment, focusing, and transmission range adjustments, measurements of each selected spectral line and its adjacent background are made. The background reading is obtained by reading the percent transmission of the light through the photographic plate immediately adjacent to the spectral line. The spectral line reading is obtained by scanning the line itself by intersecting the line of light, thus reducing the actual percent transmission reading on the galvanometer in proportion to the density of the line. The minimum reading obtained by this process is recorded as the peak (area of maximum intensity) of the selected line. Resultant values obtained for each spectral line and its adjacent background are converted to relative intensities through the use of the emulsion calibration curve. The spectral line relative intensity is then corrected for background contributions by subtracting the relative intensity of the adjacent background from the relative intensity of the spectral line.

## C. Apparatus

1. **Microphotometer**—National Spectrographic Laboratories "Spec Reader," Model MM-102 or equivalent with the following features:

   a. *Slit Height*—Fixed, 1.75 mm.
   b. *Slit Width*—8, 12, and 16$\mu$.
   c. *Light Measurement*—Photocell.
   d. *Screen Magnification*—20X.
   e. *Voltage Regulation*—External Stabiline automatic voltage regulator or equivalent.
   f. *Readout*—Galvanometer scale.

2. **Microphotometer**—Jarrell-Ash Model 21-050 or equivalent with the following features:

   a. *Slit Height*—Variable from 0.5 to 2.0 mm.
   b. *Slit Width*—Variable from 0 to 50$\mu$.
   c. *Light Measurement*—Photomultiplier tube.
   d. *Screen Magnification*—14X.
   e. *Voltage Regulation*—Line voltage fluctuations compensated for by second servo photomultiplier tube built into instrument which serves as a balance for the analytical photomultiplier tube.
   f. *Readout*—Galvanometer scale.

3. **Microphotometer**—National Spectrographic Laboratories (Baird/Atomic) Model XM-102 or equivalent with the following features:

   a. *Slit Height*—Variable in increments of 0.5, 0.75, 1.0, 1.25, and 1.5 mm.
   b. *Slit Widths*—Variable in increments of 3.5, 7, 10, and 17$\mu$.
   c. *Light Measurement*—Photomultiplier tube.
   d. *Screen Magnification*—20X.
   e. *Voltage Regulation*—External Stabiline automatic voltage regulator or equivalent.
   f. *Readout*—Digital with capability of being locked on the spectral line peak reading.

## D. Procedure

A general step-wise spectrographic plate-reading procedure applicable to all three microphotometers follows, with special notes as required for the individual instruments:*

1. Turn on the master switch in the DIM position and permit each instrument to warm up for a period of approximately 20 minutes for maximum stability.
2. Insert a master plate in the rear carriage and a sample plate in the front carriage of the microphotometer.
   a. NSL #1—Plate emulsion side up with the first sample nearest the operator.
   b. JACO—Plate emulsion side down with last standard nearest the operator.
   c. NSL #2—Plate emulsion side down with the last standard nearest the operator.
3. Illuminate the screen on the BRIGHT setting.
4. Align the sample plate with the master plate. This is accomplished by sliding the plate by hand in its plateholder until the spectral lines on the sample plate coincide with the spectral lines on the master plate. A spectrum of iron or certain characteristic $ThO_2$ spectral line groupings on each plate may be utilized for this coarse alignment. The fine alignment can be made with the fine adjustment wheel located on the plateholder

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*Individual instruments are referred to in the following manner:
1. National Spectrographic "Spec Reader," Model MM-102 = NSL #1
2. Jarrell-Ash Model 21-050 Microphotometer = JACO
3. National Spectrographic Model XM-102 = NSL #2.

carriage of each instrument. When the two plates have been aligned, spectral wavelengths of interest can be located and identified.

5. Focus the sample plate, if necessary, to obtain a sharp image of emulsion granularity.
6. Check the focus of the line of light. This step is primarily necessary for the NSL #2 instrument due to the extreme sensitivity of its photomultiplier and amplifier system. This focus is checked by observing the line-of-light image on the screen through an eyepiece. No color should appear on the fringe of this image. If green or red is present, the focus should be readjusted by turning the condensing lens located in the head of the instrument.
7. Choose the slit height to be utilized on instruments where adjustment is possible. This height is chosen with reference to the slit height utilized on the spectrograph from which the plate was obtained. Slit height should be slightly less than the spectral line heights to be measured. When a slit height is changed, a "profile" must be run to obtain maximum percent transmission readings for the new setting. This is accomplished by manually moving the slit across the line of light and observing the digital readout.
8. Set the slit width to approximately one-third the width of the slit utilized on the spectrograph.
9. Using the master plate, locate and identify the spectral line of the element to be measured.
10. Adjust the 0 and 100 percent transmission readings. Position the plate so that the line-of-light image on the screen is on a blank area of the sample plate at the same wavelength as the spectral line to be measured.
    a. 0 Percent Adjust—This adjustment is accomplished by placing an opaque object (no light transmittance or reflectance) in a position at plate level so as to intercept the line of light. The 0 percent can then be adjusted to read an actual *0* on the galvanometer scale or digital readout.
    b. 100 Percent Adjust—With the plate in the same position, the opaque object can be removed to permit the total light to be transmitted through the clear area of the photographic plate. The 100 percent can then be adjusted to read an actual *100* on the galvanometer scale or digital readout.
11. Repeat Step 10 until reproducibility of the 0 and 100 percent transmission readings is obtained.
12. Set the scan speed on instruments where a selection is available. A speed must be chosen that will permit the instrument to reach the absolute minimum for the darkest spectral line of interest.
13. Adjust the sample plate by physically repositioning it in the plateholder so that all spectral lines are parallel with the line of light as observed on the projection screen.
14. Read spectral transmissions for each spectral line of interest as well as its adjacent background.

    a. Background Reading—Obtain background transmission readings by scanning and recording the background readings to the immediate right and immediate left of the line as observed on the projection screen. Average the two readings thus obtained for a final background transmission reading. If conditions (spectral complexity or diffuse spectral line edge) prohibit obtaining background readings on both sides of the spectral line, use only one background reading, obtained from the side with no interference. When only one reading is obtainable, consistency must be maintained to measure the background on the same side and in the same location for all samples.

    b. Spectral Line Reading—Obtain the spectral line transmission reading as the minimum transmission reading obtained on the galvanometer scale or digital readout by scanning the line itself across the line of light. For maximum accuracy and precision the acceptable transmission range for reading a spectral line should be from 5 to 90 percent.

15. Recheck the 0 and 100 percent transmission readings in accordance with Step 10 upon completion of reading a spectral line of interest in all samples and standards. An indicated drift in excess of ±5 percent in the 100 percent reading indicates excessive instrumental drift and necessitates discarding values previously obtained for that particular spectral line and rereading the line and background for all samples and standards.

16. Repeat Step 10 each time a new wavelength is to be measured.

17. Upon completion of all measurements of the desired spectral lines and their corresponding backgrounds on a plate, refer the measurements to the emulsion calibration curve for calculations.

18. Obtain the relative intensity for each line and background transmission from the emulsion calibration curve. Correct the relative intensity of each line for background by subtracting the relative intensity of the background for that particular line from the relative intensity of the line. Utilize these corrected relative intensities for final concentrational determinations for each element of interest.

# VIII. CALIBRATION PROCEDURE FOR ANALYTICAL BALANCES

## A. Scope

This procedure describes a system for complete analytical balance maintenance on a quarterly basis. Balances covered by this procedure include the Mettler H14, H10 (four place), and H20 (five place).

## B. Summary of Method

The continuous analytical balance maintenance includes precalibration, calibration, and postcalibration procedures. The precalibration procedure includes inspecting, cleaning, and leveling the balance. The calibration procedure includes setting of both the zero range and the vernier deflection and calibration of the balance weights. All weights used to calibrate the balance must be equivalent to class *S*, National Bureau of Standards. The postcalibration procedure includes recording of appropriate data and evaluation of these data regarding listed specifications.

## C. Precalibration

### 1. Inspection of Balance

Before calibration, visually inspect the balance, checking the beam, knife edges, weights, mirrors, and mechanical parts for dust, corrosion, and needed repairs.

### 2. Cleaning of Balance

Clean the balance pan before any weighings are attempted. Care should be taken to avoid jarring the pan, which could result in the secondary knife edge falling from its support plane. The pan may also be cleaned by carefully removing it from the beam and chamber. The mirrors within the balance may be cleaned with a piece of chamois or lens paper. When making internal adjustments or repairs, the beam, weights, or anything supported by the beam must not be touched. The operator must wear clean vinyl gloves when performing internal operations. Tools needed for internal operations or repairs must also be thoroughly cleaned.

### 3. Leveling of Balance

Level the balance before calibration by turning the three leveling feet under the balance until the leveling bubble on the balance top is within the inscribed circle.

## D. Calibration

### 1. Setting the Zero Range (see Reference E-1)

With the adjustment lever turned to the full release position and the tare turned off (larger black knob turned counterclockwise until the *T* is aligned with the indicating pointer), turn the zero knob until the vernier reads *0*. If the indicating dot on the zero dial is greater than 20 degrees to the left or right of the indicating line inscribed on the balance surface, the balance zero will need an internal adjustment.

Before internally adjusting the zero, turn the adjustment lever to the arrest position and remove the top cover of the balance. (The internal zero adjustment is the counterweight supported on a threaded rod pointing to the rear of the balance.) One full turn of this weight will adjust the vernier 14 scale division lines on the H20 and seven scale division lines on both the H10 and H14. Turn this weight until a *00* reading on the vernier can be centered within the external index fork. If the internal zero is adjusted, the vernier deflection must be adjusted.

### 2. Setting the Vernier Deflection (see Reference E-1)

Place a 100-mg weight on the pan of the H20 and a 1-g weight on the pan of the H10 and H14. The H20 must read exactly *0.10000* and the H10 and H14 must read exactly *1.0000*. If these readings cannot be obtained, refer to Section VIII.D.1 of this Appendix for zero adjustment. Without arresting the balance, turn the weight control knob to *0*. The vernier scale should read exactly *100*. If this reading cannot be obtained, an internal adjustment of the scale deflection weight must be made. (The vernier adjustment is the counterweight supported on a threaded rod pointing to the top of the balance.) One full turn of the scale deflection weight corresponds to a scale division of 0.4 on the H20 and a scale division of 0.2 on the H10 and H14. Repeat the procedures for checking scale deflection after each adjustment and recheck the zero range.

### 3. Calibrating the Balance Weights

The weights should be the same temperature as the balance. To achieve this, set the weights in the balance chamber for 1/2 hour before using them for balance calibration.

On the Mettler H20, make the check for vernier linearity by putting weight loads of 10, 30, and 50 mg on the pan and recording the corresponding reading on the balance. Make the check for vernier linearity on the H10 and H14 by putting weight loads of 100, 300, and 500 mg on the pan and again recording the corresponding readings.

Each weight in the balance must be compared with a class *S* weight. Weights to be checked on the H20 include 0.1, 0.2, 0.3, 0.6, 1.0, 2.0,.3.0, 6.0, 20, 40, and 80 g. Weights to be checked on the H10 and H14 include 1.0, 2.0, 3.0, 6.0, 10, 20, 40, 80, and 160 g. Obtain two readings by using the same mass as the load. Obtain the second reading for the H20 by using smaller weights totaling 0.1 g less than the load giving a 100-mg reading on the vernier. Obtain the second reading for the H10 and H14 by dialing balance weights 1 g less than the weight load.

## E. Postcalibration

### 1. Recording Data

Record the balance number and the balance location. In addition, record the class *S* weight load used on a particular balance and the corresponding two balance readings for that particular weight. Note if the vernier span was used to arrive at these readings. If the data recorded meet the specification of the Operational Chemistry Laboratory (see Section VIII.E.2 of this Appendix), place an acceptance sticker with the balance number, the month, and the year the balance is to be recalibrated and the operators initials on the balance or the window of the glove box containing the balance.

### 2. Operational Chemistry Laboratory Specifications

The balance weight readings must not differ from a class *S* weight by an amount greater than the following:

| Weight Range (g) | Deviation (mg) |
|---|---|
| 0.00000 to 0.09999 | 0.04 |
| 0.10000 to 1.00000 | 0.06 |
| 1.00001 to 10.00000 | 0.10 |
| 10.00001 to 160.00000 | 0.50 |

If the above specifications of the balance cannot be attained, affix a separate tag to the balance or on the window of the glove box containing the balance, along with the tag mentioned in Section VIII.E.1 of this Appendix, with data stating which of the balance weights do not satisfy the specifications.

A balance must carry an active calibration tag at all times unless it is tagged, "Do not use for fuel certification work until calibrated." Such a tag must be dated and signed at the time the calibration has expired.

## F. References

E-1. "Mettler H10/H20/H14-Instructions," Mettler Instrument Corporation, Princeton, N. J.

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