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The Radiochemistry of Selenium

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The Radiochemistry of Selenium

G. W. LEDDICOTTE

Oak Ridge National Laboratory
Oak Ridge, Tennessee

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Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of selenium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of selenium which might be included in a revised version of the monograph.

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G. W. LEDDICOTTE
Oak Ridge National Laboratory
Oak Ridge, Tennessee

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II. RADIOACTIVE NUCLIDES OF SELENIUM

The radioactive nuclides of selenium that are of interest in the radiochemistry of selenium are given in Table I. This table has been compiled from information appearing in reports by Strominger, et al.,[1] and by Hughes and Harvey.[2]

Table I: The Radioactive Nuclides of Selenium

Radionuclide	Half-life	Mode of Decay	Energy of Radiation	Produced by
Se^{71}	4.5 m	β^+	β^+, 3.4 γ, 0.16	As-dp-4n
Se^{72}	9.7 d	EC		As-dp-3n, Se-γ-2n, Se-n-3n
Se^{73m}	44 m	β^+	β^+, 1.7	Se-γ-n, Se-n-2n, As-d-4n
Se^{73}	7.1 h	β^+, EC	β^+, 1.29, 1.65 γ, 0.36, 0.066	Se-γ-n, Se-n-2n, As-d-4n
Se^{75}	127 d	EC	γ, 0.265, 0.136 0.28, 0.405	Se-n-γ, As-p-n, As-d-2n
Se^{77m}	17.5 s	I.T.	γ, 0.162	Se-n-γ, U fission
Se^{79m}	3.90 m	I.T.	γ, 0.096	Se-n-γ, U fission, Br-n-p
Se^{79}	6×10^4 y	β^-	β^-, 0.16	Se-n-γ, U fission
Se^{81m}	56.8 m	I.T.	γ, 0.103	Se-n-γ, Se-d-p, Br-n-p, U fission
Se^{81}	18.2 m	β^-	β^-, 1.38	Se-n-γ, Se-d-p, Br-n-p, U fission
Se^{83m}	69 s	β^-	β^-, 1.5, 3.4 γ, 1.01, 2.02, 0.65, 0.35	Se-n-γ, U fission
Se^{83}	25 m	β^-	β^-, 1.5 γ, 0.35	Se-n-γ, Se-d-p, U fission, Th fission
Se^{84}	3.3 m	β^-		U fission
Se^{85}	40 s	β^-		U fission
Se^{86}	17 s	β^-		U fission

III. THE CHEMISTRY OF SELENIUM AND ITS APPLICATION TO THE RADIOCHEMISTRY OF THE SELENIUM RADIONUCLIDES

Radiochemistry is probably best described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some form so that an absolute measurement of its radioactivity, radiation energies and half-life can be made, or (2) to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or

(3) to complete a radioactivation analysis being used to determine the stable element concentration in a particular sample material. In order to be an aid in accomplishing any one of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either carrier or carrier-free separation methods.

Generally, "carrier" methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of that element through the separation method. In "carrier-free" separations, i.e., radiochemical techniques used mostly for absolute radioactivity measurements (see (1) above), it is required that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactivity measurements.

In most instances, radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electrolysis and the subsequent presentation of the isolated radioelement in a form suitable for a measurement of the radioelement's radioactivity. One major difference exists between carrier radiochemistry and more conventional techniques in that it is not always necessary to recover completely the added amount of "carrier" element, since a radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element, and any loss of the radioactive species is proportional to the "loss" of carrier during the separation process.

Colorimetric, polarographic and volumetric analysis techniques are seldom used in radiochemistry, because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed. However, some of the developments used in these analysis techniques may be useful in radiochemistry. Appendix A lists some of

the more recent references cited for the determination of selenium by these analysis techniques.

The following information is intended to give some general idea of the behavior of selenium and its compounds and how this behavior can be used in devising radiochemical analysis methods for the radionuclides of selenium. More detailed information can be obtained either from the references given in this section or from the general references given in Section I of this monograph.

A. The General Chemistry of Selenium

Selenium is found associated with sulfur and sulfides. Native sulfides, such as pyrite, chalcopyrite, and zinc blends, are the usual sources of selenium. The flue dusts obtained from the roasting of seleniferous ores and from the sludge formed in the lead chambers used in manufacturing processes for sulfuric acid are also highly enriched in selenium. The selenium in these materials is usually brought into solution by a treatment with sulfuric acid and sodium nitrate. In this treatment, it is converted into selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4, and finally precipitated as elemental selenium when sulfur dioxide is passed through the solution.

1. Metallic Selenium

Selenium, like sulfur, exists in at least three allotropic forms, or modifications. These modifications may be characterized as crystalline, metallic, and amorphous selenium. Only the crystalline and metallic forms have been well characterized. Metallic selenium is gray and forms hexagonal crystals; whereas, crystalline selenium is a loose powder composed of at least two varieties of red, monoclinic crystal forms. The gray, metallic selenium is the more stable of the two modifications. It is relatively insoluble in carbon disulfide while the red, monoclinic form is soluble in carbon disulfide. Gray selenium can be obtained by heating any other form at temperatures of from 200-230°.

The amorphous form is red in color and a solid which may be regarded as a supercooled liquid of great viscosity. This form is usually produced when selenite in an acid solution is reduced by sulfur dioxide. An extraction of amorphous selenium with carbon disulfide will yield amber to dark red solutions. When these solutions are evaporated slowly below room temperature, the monoclinic forms of selenium are obtained.

Selenium will burn in air with a characteristic smell. It will combine with the halogens, hydrogen and many metals. Selenium is not attacked by non-oxidizing acids, but when heated it will dissolve in concentrated sulfuric acid, nitric acid and caustic alkalis.

2. Compounds of Selenium

Selenium can form compounds having oxidation states of -2 (the selenides), +4 (the selenites) and +6 (the selenates). Polyselenides, such as $NaSe_2$ and $NaSe_3$, are known, but they are less stable than the polysulfides. Latimer[3] reports the following potentials:

a) Acid Solution

$$H_2Se \xrightarrow{0.40} Se \xrightarrow{-0.74} H_2SeO_3 \xrightarrow{-1.15} SeO_4^{--}$$

b) Base Solution

$$Se^{--} \xrightarrow{0.92} Se \xrightarrow{0.366} SeO_3^{--} \xrightarrow{-0.05} SeO_4^{--}$$

Selenium (like sulfur and tellurium) reacts with other elements in a manner similar to oxygen. However, it will not combine directly with tellurium or sulfur. Unlike oxygen, selenium is able to combine directly with all of the halogens except iodine. It will burn in air to produce selenium dioxide, SeO_2, but will not react directly with nitrogen. Selenium will dissolve in concentrated nitric acid but will not react with concentrated alkali solutions. The most stable compounds of selenium are those with oxygen, chlorine, and electropositive elements such as the alkalis.

Selenium is electronegatively bivalent towards hydrogen and the metals. In its electropositive behavior, selenium exhibits a valence of +4 in its compound formation with most elements. An exception exists in its combina-

tion with fluorine; here a valence state of +6 is exerted. In general, the compounds of selenium, sulfur and tellurium are analogous to each other; the principal difference is in the lower stability of selenium (and tellurium) compounds.

The most important compounds formed by selenium include oxides, oxyacids, oxyhalides, halide compounds, hydrogen compounds, and alkyls. Table II lists the more important of these compounds and gives information about their solubilities.

a) The Oxide, Oxyacid, and Oxyhalide Compounds

Oxygen compounds having valences of +2, +3, or +5 do not exist. Also, poly-acids of sulfur are not known. The most stable oxide of selenium is selenium dioxide, SeO_2. SeO_2 is produced by burning selenium in oxygen or air. Pure SeO_2 is composed of brilliant white needles. It sublimes readily and can be melted without decomposition. In the vapor state, it has a yellow-green color. SeO_2 will dissolve in water, concentrated sulfuric acid and alcohol. Monoethyl esters of selenious acid, H_2SeO_3, can be formed if the alcohol solution is evaporated. Selenium dioxide can combine with hydrogen chloride to form $SeO_2 \cdot 2HCl$, and it will form similar double compounds with other substances. SeO_2 can easily be reduced to elemental selenium.

In its combination with water, SeO_2 will form selenious acid, H_2SeO_3. H_2SeO_3 can also be prepared by dissolving powdered selenium metal in dilute nitric acid. H_2SeO_3 is deliquescent and forms crystals that are colorless, hexagonal prisms. Selenious acid is a weak dibasic acid; the salts of this acid are either acid or neutral selenites. The selenites are colorless. In aqueous solution, the neutral selenites have a basic reaction and are presented in the solution as hexahydroxo ions, $[Se(OH)_6]^{=}$.

H_2SeO_3 can be reduced to selenium by such agents as sulfur dioxide. The reduction process must be carried out in the presence of hydrochloric acid since selenopolythionic acids (acids in which sulfur is partly replaced by selenium) are formed. These acids are decomposed by hydrochloric

Table II: Solubility of Selenium Compounds[a]

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	Se_2Br_2	Decomposes	Decomposes	Decomposes in alcohol; soluble in CS_2, chloroform, C_2H_5Br.
	$SeBr_4$	Decomposes	Decomposes	Soluble in CS_2, chloroform, C_2H_5Br, HCl.
	$SeBrCl_3$ $SeBr_3Cl$			Insoluble in CS_2.
	Se_2N_2Br	Insoluble	Decomposes	Slightly soluble in CS_2.
Chlorides	Se_2Cl_2	Decomposes	Decomposes	Decomposes in alcohol and ether; soluble in CS_2, CCl_4, chloroform, benzene.
	$SeCl_4$	Decomposes	Decomposes	Decomposes in acids and alkalis; slightly soluble in CS_2.
Fluorides	SeF_4	Decomposes	Decomposes	
	SeF_6	Decomposes		
Iodide	Se_2I_2	Decomposes	Decomposes	
	SeI_4	Decomposes	Decomposes	
Nitride	Se_4N_4	Insoluble	Insoluble	Insoluble in alcohol and ether; slightly soluble in benzene, acetic acid, and CS_2.

Table II (Continued)

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Oxides	SeO_2	Soluble	Soluble	Soluble in alcohol, acetone, benzene, acetic acid.
	SeO_3	Decomposes slightly	Decomposes slightly	Soluble in alcohol and H_2SO_4; insoluble in ether, benzene, chloroform, CCl_4.
	$SeSO_3$	Decomposes	Decomposes	Soluble in H_2SO_4; insoluble in SO_3.
Oxy-Salts	$SeOBr_2$	Decomposes	Decomposes	Soluble in CS_2, CCl_4, chloroform, H_2SO_4, benzene.
	$SeOCl_2$	Decomposes	Decomposes	Soluble in CS_2, CCl_4, chloroform, benzene.
	$SeOF_2$	Insoluble	Insoluble	Soluble in alcohol, CCl_4.
Sulfides	SeS	Insoluble	Insoluble	Insoluble in ether; soluble in CS_2.
	SeS_2	Insoluble	Insoluble	Decomposes in HNO_3, aqua regia; soluble in $(NH_4)_2S$.

[a] Additional information appears in "Handbook of Chemistry and Physics, 42nd Ed., 1960-61," Chemical Rubber Publishing Company, Cleveland (1960).

acid so that elemental selenium is produced. Selenium can also be precipitated from a solution of selenious acid by other reducing agents, such as sodium dithionite, hydrazinium or hydroxylammonium salts, and hydrogen iodide. Hydrogen sulfide will produce a mixed sulfur and selenium precipitate.

The oxidation of H_2SeO_3 with strong oxidizing agents like chlorine or bromine produces selenic acid, H_2SeO_4. Selenic acid is a stronger oxidizing agent than sulfuric acid. Mixtures of concentrated H_2SeO_4 and concentrated HCl can dissolve gold and platinum in the same was as aqua regia. Selenic acid will react only slowly with reducing agents containing chloride and bromide ions. Selenious acid and free halogens are products of these reactions. Much more slow reactions occur with sulfurous acid; elemental selenium and H_2SO_4 are formed as products of these reactions. If H_2SeO_4 is reduced by hydrazine-hydrochloric acid mixture at 60°, elemental selenium will be produced.

The salts of selenic acid, the selenates, are readily prepared either by fusing selenium, selenides, or SeO_2 with potassium nitrate, or by treating solutions of selenites with chlorine or by electrolytically oxidizing a selenite solution.[4] The selenate compounds like the sulfates are insoluble; however, they are less stable towards heat than the sulfates. They are crystalline in form and lose oxygen and deflagrate when heated on charcoal to form selenides. They can form double salts, and, in most instances, these salts resemble the alums.

Selenium can form oxyhalide compounds of the type, $SeOX_2$. Known as the selenyl halides and existing as $SeOF_2$, $SeOCl_2$, and $SeOBr_2$, they are usually prepared by the reaction of the halide upon mixtures of selenium and selenium dioxide. The selenyl halides have a high reactivity and are less stable than the oxyhalides of sulfur. They can be hydrolyzed completely with water to form selenious acid, H_2SeO_3, and the corresponding halide acid. Selenyl halides are unstable when heated and will rapidly decompose to yield SeO_2, free halogen and lower halides, e.g. Se_2X_2.

Selenium(IV) oxychloride, $SeOCl_2$, has found much use as the parent solvent for use in studies concerned with the inorganic reactions of acids, bases, and salts.[5-7]

b) Halogen Compounds

Selenium halogen compounds are usually more stable than the corresponding sulfur compounds. Selenium can be combined directly with chlorine, fluorine, and bromine to form Se_2Cl_2, $SeCl_4$, SeF_4, Se_2Br_2, and $SeBr_4$. Tetraiodide compounds of selenium, i.e., SeI_4, etc., are not known. All of these compounds, except $SeCl_4$ and $SeBr_4$, are colorless liquids. $SeCl_4$ is a colorless crystal, and $SeBr_4$ is a yellow solid. The dihalides, $SeCl_2$ and $SeBr_2$, are vapors and are formed by the thermal decomposition of other selenium halides, such as $SeCl_4$ and Se_2Br_2. The selenium monohalides decompose rapidly in water and are soluble in a variety of nonaqueous solvents. The tetrahalides are highly reactive in water and decompose to give selenium dioxide (or the corresponding acid) and the halogen acid.

Selenium also forms a hexavalent compound with fluorine, SeF_6. Prepared by a direct combination of the elements, SeF_6 is a stable, colorless gas and like the sulfur compound, SF_6, is relatively unreactive. For example, SeF_6 will react with ammonia only at temperatures above 200°. SeF_6, like SF_6, is inert toward water at room temperature.

Several of the selenium halogen compounds can form complex acids by adding on hydrogen halide. For example, $SeBr_4$ will combine with HBr to form hexabromoselenic acid, $H_2(SeBr_6)$. Hexabromoselenates and hexachloroselenates have been formed by the reaction of alkali halide salts upon these complex acids. The solubilities of these salts resemble the solubilities of the selenates.

c) Hydrogen Compounds

Selenium will combine directly with hydrogen to form hydrogen selenide, H_2Se. H_2Se has properties similar to H_2S but is less stable than H_2S. It is a colorless gas, which can be easily liquified and solidified. It is more soluble in water than H_2S and will combine with water to form unstable

hydrates. Hydrogen selenide is a stronger acid than hydrogen sulfide.

H_2Se can form both acid selenides, M^1HSe, and neutral selenides, M_2^1Se. The alkali and alkaline earth metals can combine with additional selenium to form polyselenides, $M_2^1Se_x$, in the same way as these metals form polysulfides with sulfur. The alkali selenides are colorless in the pure state. The heavy metal selenides, prepared by the action of hydrogen selenide on solutions of the heavy metal salts, are more or less strongly colored. Like the metal sulfides, they are insoluble in water, and some of them are insoluble in acids.

d) Alkyl Compounds

The distillation of neutral or acid alkali selenides with potassium alkyl sulfates produces alkyl selenides, SeR_2 (where R = the alkyl group) and alkyl selenomercaptans, SeRH. The alkyl selenides are volatile liquids with pungent and repulsive odors. They readily combine with, or add on, halogens or oxygen to form such compounds as $(C_2H_5)_2SeCl_2$ or $(C_2H_5)_2SeO$. In addition, they can add on alkyl iodides to form such compounds as alkyl selenoniums, e.g. $(C_2H_5)_3SeI$. These compounds are strong bases and, when treated with moist silver oxide, will form the corresponding hydroxide.

e) The Nitride and Sulfide Compounds

Selenium can combine directly with nitrogen to form selenium nitride Se_4N_4. Se_4N_4 is an amorphous orange-yellow, brick-red, crystalline solid. It is slightly hydroscopic; however, it is insoluble in water. It is only slightly soluble in benzene, acetone, acids and carbon disulfide.

Selenium combines with sulfur to form selenium monosulfide, SeS, and selenium disulfide, SeS_2. SeS is an orange-yellow powder that is insoluble in water and ether, but very soluble in carbon disulfide. SeS_2 is a bright red-yellow powder; it is insoluble in water and will only decompose in aqua regia and nitric acid. It is soluble in ammonium sulfide.

The interaction of selenium with sulfur also forms selenium sulfur oxide, $SeSO_3$, a green-yellow powder which decomposes in water but is soluble

in H_2SO_4. Selenium sulfur oxytetrachloride, $SeSO_3Cl_4$, is also known. It decomposes in cold water.

B. The Analytical Chemistry of Selenium

As it has already been pointed out elsewhere in this monograph, the use of a known amount of inactive selenium carrier in a separation method almost always makes it practical to obtain the selenium carrier in a weighable form in the final stage of the separation procedure used. If this is done, the radionuclide can be concentrated into a small mass for the radioactivity measurements, and any loss of the "carrier" during the analysis can be easily accounted for.

Selenium (like tellurium) can be qualitatively detected or quantitatively determined by reducing its salts contained in strong acid solutions to elemental selenium with either sulfur dioxide,[8] sulfur dioxide in acetone,[9] hydroxylamine hydrochloride,[10] hydrazine,[11,12] ammonium sulfite,[13] and tin(II) chloride.[14] Seath and Beamish[15] recommend that SO_2 plus hydroxylamine hydrochloride as the best method of producing elemental selenium. The hydroxylamine hydrochloride precipitations may be made from hydrochloric, tartaric, or citric acid solutions. Duval,[16] from his pyrolysis studies, recommends that elemental selenium be isolated by reducing it with tin(II) chloride.[14] However, it would appear from Duval's pyrolysis curves that any one of the other reductants could be used if drying temperatures of 100° or less for the selenium were employed.

Many other substances, such as potassium iodide, titanous chloride, metals such as zinc or aluminum, and phosphorus and hypophosphorus acids, can be used to reduce selenides (or tellurides) to the metal in a cool acid solution.[17] Although usually considered as being unsuited for quantitative work because the reaction products are occluded, some investigators have used them effectively to obtain selenium in a weighable form. For instance, Challis[18] has used hypophosphorus acid to determine selenium (and tellurium) in copper. Similarly, Evans[19] has used hypophosphate as a reductant.

In addition to the gravimetric determination of selenium as the metal, Ripan-Tilici[20] and Spacu[21] have shown that selenium can be determined as lead selenate. In order to obtain it in this form, selenium must be oxidized to the hexavalent state with H_2O_2 and precipitated by a lead salt solution.

Either the metal or the lead selenate can be used to obtain the selenium "carrier" and the selenium radionuclide(s) in a form suitable for a radioactivity measurement, after they have been isolated from a stable and/or radioactive nuclide mixture. The information that follows generally reports on current ideas used in isolating and determining inactive selenium. It should not be inferred that it is always necessary to radiochemically separate the desired selenium radioisotope in a precipitible form before the radioactivity measurements. Sometimes it would be sufficient to accept and use, for example, one of the phases obtained in solvent extraction, or an aliquot from the eluate obtained from an ion-exchange separation column, or a portion of a paper chromatogram, in the radioactivity measurements.

1. Separation by Precipitation

Selenium is usually separated from most elements by the use of various reducing agents in acid solutions. Hillebrand, et al.,[22] report that selenium (as well as tellurium) can be initially separated from most elements by reduction with sulfur dioxide in 3.7 to 4.8 N hydrochloric solution. Gold, palladium and small amounts of antimony, bismuth, copper, and other elements are also reduced under the same conditions and by use of other reducing agents.

Gold can be separated by filtration after the mixed metal precipitate has been digested for some time in a dilute nitric acid solution. The selenium can then be separated by a precipitation with sulfurous acid or hydroxylamine hydrochloride.[10] Quadrivalent selenium (and tellurium) can also be separated from other elements by saturating an acid solution with hydrogen sulfide.[22] Sexivalent selenium can be completely precipitated from a 12 N HCl solution at room temperature.[23] Sulfides of the copper sub-

group may interfere under the same conditions.

In their studies, Seath and Beamish[15] and Noakes[24] showed that nitrates, Cu^{+2} and Au^{+3}, interfered in the reduction of selenium (and tellurium) to elemental selenium (or tellurium). The nitrates were removed by evaporation with HCl and NaCl; Cu^{+2} and Au^{+3} were separated before the reduction with hydroquinone.[25,26]

Selenium (and tellurium) can be gathered in a ferric hydroxide precipitate. Wells[27] reports that 0.1 to 0.2 g of trivalent iron must be present and concentrated ammonium added in excess to effect this separation of selenium from other elements. Schoeller[28] also has used ammonium hydroxide and ferric nitrate to gather selenium (and tellurium) from solutions of ores and metals. The ammonium hydroxide precipitation eliminated interferences from copper and nitrates. Selenium (and tellurium) are separated from Fe^{+3} by a reduction of an acid solution with stannous chloride. Selenium can be separated from tellurium by a brominated hydrochloric acid solution of the metals followed by a precipitation of selenium with sulfur dioxide.

Bode[29] has shown that a separation of selenium from tellurium can be effected in a 5 N HCl solution by using a solution of tetraphenylarsonium chloride. Te^{+6} will precipitate. Bromide, iodide, fluoride, nitrate, Mo^{+6} and W^{+6} will interfere.

2. Separation by Volatility

Selenium (or tellurium) in the selenide (or telluride) form can be separated from metals whose chlorides are nonvolatile by passing chlorine gas into a hot solution.[30] Hydrochloric acid gas can be used instead of chlorine to separate either Se^{+4} or Se^{+6}. Selenium can be separated from tellurium by a distillation method in which hydrochloric acid gas is passed into a sulfuric acid solution.[31] The distillate is caught in cold water and Se^{+6} precipitated by adding sulfur dioxide. Either Se^{+4} or Se^{+6} can be quantitatively separated from tellurium by passing carbon dioxide gas into a hydrobromic-phosphoric acid solution.[32] $SeOCl_2$ and

$SeOBr_2$ (as well as $TeOCl_2$ and $TeOBr_2$) are volatile from 6 N HCl[33] or 6 N HBr[34-36] solutions at temperatures above 100°. Arsenic, antimony, tin and germanium also are volatile under these conditions.

3. Separation by Electrolytic Methods

Electroseparation and electrogravimetry methods for selenium are not well defined. Only a few applications of electroanalysis techniques exist for the determination of selenium by amperometry and coulometry. However, it would appear that a consideration of these investigations might be profitable for use in radiochemistry. For example, Lingane and Niedrach[37] report on the titration of Se^{+4} with cupric copper in an ammoniacal medium. Se^{+4} is reduced to Se^{+2} and cupric selenide is only slightly soluble in this medium. The potential of the dropping electrode is at a value at which the tetraammino cupric ions and the selenite ions are reducible; its value will increase when excess cupric ion is added. Rowley and Smith[38] have used a coulometric titration of thiosulfate for the determination of Se^{+4}. Two back titration procedures were followed. In one, an excess of iodide is added to a strongly acidic selenious acid solution and iodine liberated and reduced with sodium thiosulfate solution with the excess thiosulfate being determined by coulometric titration. In the second procedure, excess thiosulfate is added so that the selenious acid is reduced to selenopentathionate, SeS_4O_6, and the excess thiosulfate determined by coulometric titration with iodine. More accurate results (± 0.1% for several hundred micrograms) were obtained by use of the second method.

4. Separation by Solvent Extraction

Solvent extraction methods used as separation methods for other analysis techniques can often be adapted for use in radiochemistry and can be quite useful in separating the desired radionuclide from a sample by either a carrier-free or carrier radiochemistry method. Morrison and Freiser[39] have recently reviewed the applications of ion association and chelate complex systems to the determination of most of the elements. Some of these

systems are applicable for use as separation processes in the radiochemistry of selenium.

a) Ion Association Systems

Kitahara[40] has reported that Sn^{+2} and Sn^{+4} can be completely extracted, while Se^{+4} (and As^{+3}, Sb^{+3} and Mo^{+6}) is only partially extracted (about 4%) from HF solutions of varying concentrations by ethyl ether and a 4:1 volume ratio of organic to aqueous phase. Using equal volumes of HF and ethyl ether, Bock and Herrman[41] have shown that only Nb^{+5}, Ta^{+5}, and Re^{+7} were extracted in amounts greater than 50% while Se^{+4} (as well as Sn^{+2}, Sn^{+4}, As^{+3}, As^{+5}, Te^{+4}, Ge^{+4}, P^{+5}, V^{+3}, V^{+5}, Mo^{+6}, and Sb^{+3}) was only partially extracted. However, the extractions of Se^{+4} and the other ions increased with increasing HF concentration. Stevenson and Hicks[42] report that Se^{+6} (as well as Te^{+6}, Fe^{+3}, Ga^{+3}, Sb^{+5}, and As^{+3}) can be extracted by diisopropyl ketone from a mineral acid-hydrofluoric acid (6 M HCl-0.4 M HF) aqueous system. Se^{+4} (as well as Sb^{+3}, As^{+5}, and Te^{+4}) is only slightly extracted under these conditions. In this same study, it was shown that Se^{+4} (and Te^{+6} and Ta^{+5}) could be extracted by diisopropylketone from a 6 M H_2SO_4-0.4 M HF system.

At least 30% Se^{+4} can be extracted from a mixture of metal bromides (4 M to 6 M HBr) into ethyl ether.[43] Au^{+3}, Ga^{+3}, In^{+3}, Tl^{+3}, Sb^{+5}, Sn^{+2}, Sn^{+4}, and Fe^{+3} quantitatively extract from this system; As^{+3}, Sb^{+3}, and Mo^{+6} extract slightly, whereas, Cu^{+2} and Zn^{+2} do not.

Scadden and Ballou[44] have shown that less than 5% Se^{+4} (and Te^{+4}) will extract into 0.06 M or 0.6 M di-n-butyl phosphoric acid (DBPA), either as carrier-free or as macroquantities, from a 1 M HNO_3 solution. The volume ratio used in these studies was 1:1 (organic/aqueous). Yttrium, tin, molybdenum, niobium, tantalum, zirconium and indium are extracted in concentrations varying from 5 to 95% or greater from the same system.

Selenium (as well as Te, Fe, Ge, Sn, As, and Sb) can be quantitatively extracted into methyl isobutyl ketone from various concentrations of hydrochloric acid.[45] This study determined the approximate tendencies of ex-

tractability for metallic salts of these and other elements.

b) Chelate Complex Systems

Selenium as the sodium diethyldithiocarbamate salt can be extracted from an acid solution (pH3) with ethyl acetate.[46,47] Se^{+4} (and Te^{+4} will also form a complex in an acid solution (pH5-6) by use of a 0.2% solution of sodium diethyldithiocarbamate.[48] The complex can be extracted into carbon tetrachloride. The addition of a 5% solution of EDTA to the system assists in masking out other extractable elements. Cheng[49] has shown that a 5% aqueous diaminobenzidine hydrochloride solution will form a selenium complex in a formic acid-water system which can be extracted at a pH of 6-7 by toluene. Fe^{+3}, Cu^{+2}, V^{+5} and other oxidants interfere; however, the Fe^{+3} and Cu^{+2} interferences can be eliminated by EDTA complexing at pH 2-3. Tellurium does not interfere.

5. Separation by Ion Exchange Resins

Kraus and Nelson[50] report that selenite (Se^{+4}) shows good absorption on an anion resin column as a chloride complex. As an example, this behavior of Se^{+4} has made it possible to separate it from As^{+3} and Br^{-} by use of solutions of various NH_4Cl concentrations. As^{+3} is removed by elution with 0.01 M NH_4Cl; Se^{+4} with 0.50 M NH_4Cl; and Br^{-} with 5.0 M NH_4Cl. Attebury, et al.,[51] and Aoki[52] report that selenium and tellurium can be separated by adsorption upon an anion resin column from 3 M HCl. A mixture of 1 M HCl and 1 M NH_4CNS was used as the eluant.

Lederer and Kertes[53] used selenite and tellurite ions in a study concerned with the use of a Dowex resin-paper. Optimum conditions for separation were calculated by considering the relationship of the ion adsorption with the pH of the aqueous acid used as eluant.

6. Separation by Paper Chromatography

Levi and Danon[54] have used paper chromatography to separate mixtures of Bi^{210}, Pb^{210}, Po, Se, and Te in nitric acid solutions. A butanol-propanol mixture was used as the solvent and a good separation of each element was obtained. Crouthamel and Gatrousis[55] also report on a similar separa-

tion of Se, Te, Po, and Bi by paper chromatography. Specific separations of selenium (as Se^{+4}) from tellurium (as Te^{+4}) in HCl, HNO_3, and HBr have been studied by Burstall, et al.,[56] Lederer,[57] and Weatherley.[58] Solvents such as mixtures of butanol-methanol, butanol-water, and butanol-HCl were used to effect the separation.

IV. DISSOLUTION OF SAMPLES CONTAINING SELENIUM

When dissolving selenium-containing samples, it is necessary to use techniques that will minimize the loss of selenium by volatilization.[59] Selenium is easily volatilized from boiling concentrated acid but not from dilute acid. The presence of alkali salts do not prevent the volatilization of selenium. No loss of selenium occurs if sulfuric acid or perchloric acid solutions of selenious acid are evaporated to dense fumes.[60] If chlorides and bromides are present, varying amounts of selenium will be lost during fuming.

Some selenides attack platinum during a fusion process. It is best to use a porcelain or nickel crucible. The fusion can be done with sodium peroxide or a mixture of sodium carbonate and niter in a nickel crucible. Fusions with potassium or KCN are not recommended because volatilization can occur.

Ores or minerals containing selenides can be decomposed by heating to a dull redness in a current of chlorine and collecting the volatilie chlorides in dilute hydrochloric acid. Small amounts of selenium in pyrites, shales, soils, water, vegetation, grains, and animal matter have been released from these materials by distilling with hydrobromic acid.[61] Gorsuch,[62] in a series of radiochemical investigations concerned with the recovery of trace elements from organic matter, has evaluated a number of dissolution methods for recovering trace selenium from similar materials. The results of these studies showed that selenium was lost by volatilization.

Any one of the above dissolution techniques can be adapted for use in the radiochemistry of the selenium radionuclides. The addition of inactive

selenium carrier to the mixture before dissolution begins will assist in achieving an exchange of the radionuclide with the carrier atoms.

V. SAFETY PRACTICES

No matter what method is used to decompose a sample, adequate safety precautions should be followed. The toxicology of most elemental compounds have been reported by Pieters and Creyghton,[63] and it should be consulted for information on handling selenium-containing materials safely.

Safety practices in handling radioactive sample materials is always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in widespread contamination. Thus, some source of information on safe-handling practices in processing radioactive samples should be consulted before a radiochemical analysis is undertaken. One such source is that which is given in the Oak Ridge National Laboratory's Master Analytical Manual.[64] Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE SELENIUM RADIONUCLIDES

The analysis of sample materials containing selenium radionuclides may be completed either by a direct (nondestructive) measurement of the radioactivity of the particular radionuclide or by obtaining the radionuclide in some form by radiochemically processing the radioactive sample. The use of either technique is dependent upon the selenium radionuclides being measured, and such characteristics as the radionuclide's half-life, the type of radiations it emits as it decays, and the energy of the radiations must be considered in selecting the radioactivity measurement technique to be followed.

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of selenium. The chief radioisotopes of selenium usually encountered by the radiochemist are Se^{75} (127 d), Se^{81m} (56.8 m), Se^{81} (18.2 m) and Se^{83} (25 m). These isotopes are produced as a result either of a number of nuclear reactions on stable isotopes of selenium or on the stable isotopes of other elements. The radioactivity of

any of these selenium radionuclides can be analyzed and measured by standard Geiger-Mueller, gamma scintillation and proportional counting techniques.[65-68] Okada[69] has recently reported on the use of gamma spectrometry to detect and determine the radioactivity of Se^{75} (121 d) in a nondestructive analysis of neutron-irradiated sulfur, ammonium compounds and ores for trace selenium. Putman and Taylor[70,71] have also reported on a similar technique for determining trace selenium in glass. Erion, et al.,[72] and Fineman, et al.,[73] have also determined trace selenium in sulfur and ore concentrates by a nondestructive analysis method.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR SELENIUM

The radiochemical procedures that now exist for the determination of the selenium radionuclides have been evolved from each investigator's choice of ideas and techniques similar to those expressed in Section III of this monograph. In most of the procedures to be cited, a carrier technique has been used to separate the radionuclide from the radioactive mixture. Gest and Edwards[74] report on the preparation of carrier-free selenium radioactive tracer using a Szilard-Chalmers reaction. No other specific carrier-free separations for the selenium radionuclides appear in the current literature; however, it should be possible to use any volatility, solvent extraction, or chromatography separation procedure to serve as a means of obtaining essentially carrier-free radioactive selenium. In particular, that part of Schindewolf's[75] separation procedure concerned with the anion-exchange separation of radioactive selenium and tellurium from neutron-irradiated stony meteorites appears to be usable for a carrier-free selenium separation. Likewise, the studies of Kraus and Nelson[50] and others[51,52] suggest possible carrier-free separations for the radioactive selenium isotopes.

The carrier radiochemical procedures that follow have originated from analyses either in work on the preparation and use of radioactive tracers[76] or fission product analysis,[77] or in the use of radioactivation analysis.[78,79] In particular, radiochemical separations (see Procedures 1 to 3) have been

used in radioactivation analysis concerned with the determination of microgram and submicrogram amounts of selenium in metals and alloys;[80] animal tissues, vegetation, and body fluids;[80] waters;[81-83] ores, slags, and gaseous mixtures[73] and stony meteorites.[74] A detailed procedure of the use of radioactivation and the radiochemical separation method followed in the determination of trace selenium in metals and alloys[80] and biological materials[80] and water[81-83] appears in the ORNL Master Analytical Manual.[84]

In the radiochemical procedures that follow, special information regarding the procedure's use, the type of nuclear bombardment, the type of material analyzed, separation time, etc., appears as part of each procedure. Whenever possible, an evaluation of each procedure is made with regard to its use in the decontamination of other radioactive species from the radioactive selenium isotopes.

PROCEDURE 1

Procedure Used In: Radioactivation analysis

Method: Volatility and precipitation

Element Separated: Selenium

Type of Material Analyzed: Metals and alloys,[80] biological materials (animal tissues, body fluids),[80] waters.[81-83]

Type of Nuclear Bombardment: $Se^{74}(n,\gamma)Se^{75}$ (Se^{75}: 121 d)
$Se^{80}(n,\gamma)Se^{81m}$ (Se^{81m}: 57 m)
$Se^{80}(n,\gamma)Se^{81}$ (Se^{81}: 18 m)

Procedure By: Leddicotte, G. W. (reported by Leddicotte[84])

Chemical Yield of Carrier: 75-80%

Separation Time: 1.5 hours

Degree of Purification: Studies with radioactive tracers of As, Te, Sn, Sb, Na show that decontamination is better than 10^6 for each

Equipment Required: Neutron source and standard laboratory equipment

Procedure

A. Irradiation of Sample Materials

1. Irradiate known amounts of test (Note 1) and comparator (0.025 to 0.030 g of selenium metal to nearest 0.1 mg) samples (Note 2) in a neutron flux of at least 5×10^{11} $n/cm^2/sec$ for 16 hours (Note 3). Use small quartz tubes, polyethylene bottles or aluminum foil to contain the samples.

B. Preparation of Irradiated Samples for Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 100-ml volumetric flask, then dissolve it in a small measured volume of 6 M HNO_3; then dilute the solution to 100 ml with water. Mix well, using safe-handling practices for radioactive materials.

2. Pipet a 1.00 ml aliquot of this solution into a second 100 ml volumetric flask; dilute to volume with water. Mix well.

3. Pipet a 1.00 ml aliquot of this solution into a 125-ml glass distillation flask. By means of a volumetric pipet, add to the same distillation flask 2.00 ml of a standard carrier solution of known selenium concentration (Note 4). Also add 1 ml each of holdback carriers of arsenic, copper, cobalt, iron, sodium, and strontium (Notes 5 and 6). Continue with Part C below.

II. The Test Sample(s)

1. If the sample is a metal or alloy, quantitatively transfer the irradiated test portion from the quartz tube or aluminum wrap to a 125-ml glass distillation flask, and then add, by means of a volumetric pipet, to the same distillation flask 2.00 ml of a standard carrier solution of known selenium concentration. Also add 1 ml each of holdback carriers of arsenic, copper, cobalt, iron, sodium and strontium (Notes 5 and 6). To this mixture, add dropwise enough concentrated mineral acid to completely dissolve the sample. If necessary, heat the mixture to effect solution. Continue with Part C below.

2. If the sample is an aqueous liquid, pipet an aliquot of the irradiated portion into a 125-ml glass distillation flask. By means of a volumetric pipet, add to the same distillation flask 2.00 ml of a standard carrier solution of known selenium concentrations. Also add 1 ml each of holdback carriers of arsenic, copper, cobalt, iron, sodium, and strontium (Notes 5 and 6). Continue with Part C below.

3. If the sample is biological material (plant ash, tissue ash, body fluid, etc.) or if it is an organic liquid (a petrochemical or one of its derivatives), pipet a known aliquot, or quantitatively transfer the total amount of solid, to a 125-ml glass distillation flask. Then add, by means of a volumetric flask, to the same distillation flask 2.00 ml of a standard carrier solution of known selenium concentration. Also add 1 ml each of holdback carriers of arsenic, copper, cobalt, iron, sodium and strontium (Notes 5 and 6). To this mixture, add 3 ml of H_2O, 1 ml of 6 M HCl, and 15 ml of HNO_3-$HClO_4$ mixture. Also, put 2 or 3 glass beads into the flask, then heat the solution at a moderate temperature (60°C) until all of the HNO_3 is removed and $HClO_4$ condenses on the neck of the flask (Note 7). Digest the mixture in this manner from 1-2 hours. Remove the flask from the hot plate; cool it and then continue with Part C below.

C. Radiochemical Separation of Selenium

1. Add 10 ml of concentrated hydrochloric acid (HCl) and 10 ml of 48% hydrobromic acid (HBr) to the distillation flask. Connect a condensor (of the type shown in Figure 1) to the distillation flask and place a 50-ml glass centrifuge tube at the end of the distillate tube. Add 10 ml of water (or alkali solution) to the centrifuge tube. Cool the tube by placing it in an ice bath.

2. Connect the condenser head to an air flow and begin bubbling air through the mixture in the distillation flask. Heat the flask (an open flame can be used) to boiling. Continue distillation process for at least 5 minutes. (Note 8)

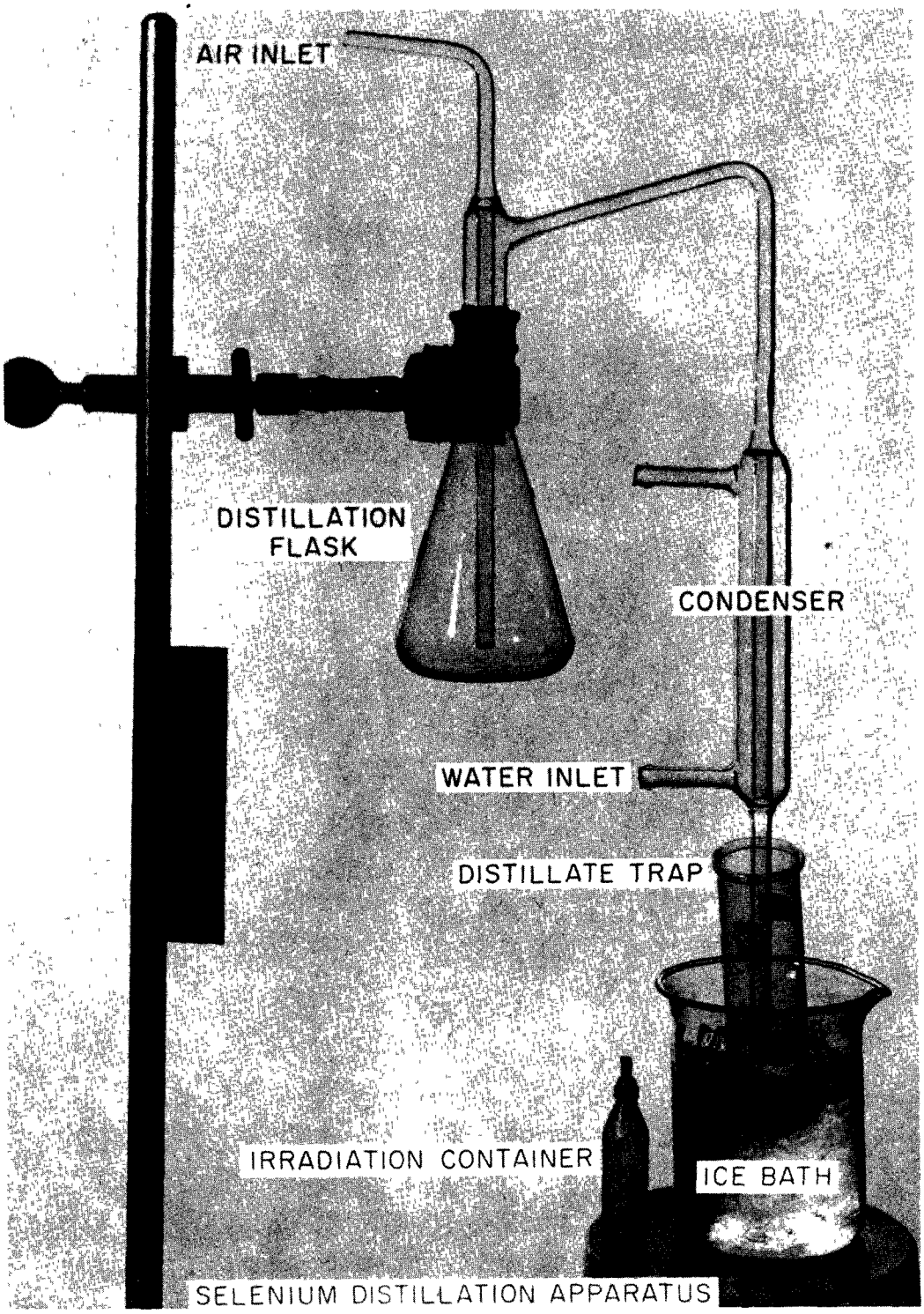
AIR INLET
DISTILLATION FLASK
CONDENSER
WATER INLET
DISTILLATE TRAP
IRRADIATION CONTAINER
ICE BATH
SELENIUM DISTILLATION APPARATUS

Figure 1

3. Remove the centrifuge tube containing the distillate fraction from the ice bath; then, neutralize the solution by adding conc. NH_4OH dropwise to it (Note 9).

4. Acidify the solution with 2 ml of conc. HCl. Add 4 ml of 6% H_2SO_3 solution. Stir the mixture until the selenious acid is reduced to elemental selenium. Centrifuge the mixture; discard the supernatant liquid.

5. Wash the precipitate once with 15 ml of hot water. Centrifuge; discard the wash liquid. Add a 10-ml volume of hot water to the tube. Stir.

6. Filter off the selenium metal through a tared filter paper (Munktells No. 00 or Whatman No. 42) that is held in a Hirsch funnel; wash the precipitate twice with 10-ml portions each of H_2O, 95% ethyl alcohol and ether.

7. Dry the precipitate for 30 minutes in a drying oven at 110°C (Note 10). Weigh the selenium metal precipitate (Note 11) and filter paper on an analytical balance. Then mount the precipitate for the radioactivity measurements. Continue with Part D below.

D. Measurement of the Radioactivity from Se^{75} (and/or Se^{81} or Se^{81m}) and Calculation of Inactive Selenium Content of the Original Sample

1. a) The analysis involving the measurement of Se^{81} must be completed by beta counting. Se^{81} has a half-life of 18.2 m and decays to stable Br^{81} only by the emission of 1.38 Mev beta radiations. These measurements can be made by means of a Geiger-Mueller counter.

b) The analysis involving the measurement of Se^{75} and Se^{81m} must be completed by gamma counting. Se^{75} has a half-life of 121 days and decays by means of electron capture and gamma radiations of various energies (chiefly, 0.121, 0.136, 0.27, 0.28, 0.405 Mev, plus others). Se^{81m} has a half-life of 57 minutes and decays to Se^{81} (18.2 m) by isomeric transition with the emission of 0.103-Mev gamma radiations. These measurements can be made by means of a gamma scintillation counter or a gamma scintillation spectrometer. In the use of the latter instrument, the major gamma radiations are measured.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment, half-life of the selenium radioactive isotope measured and the sample weights of the test and comparator samples. A comparison of these corrected radioactivities becomes a measure of the stable selenium content of the test sample:

$$\text{Percent Stable Se in Test Sample} = \frac{\text{Corrected Radioactivity of Se in Test Sample}}{\text{Corrected Radioactivity of Se in Comparator Sample}} \times 100$$

NOTES:

1. At least 0.10 gram portions of solid samples (metals, alloys, tissue, etc.) should be used. Liquid samples (water, body fluids, etc.) having volumes of at least from 1 to 20 milliliters should be used.

2. Comparator sample may be either selenium metal or a solution of a selenium compound. If a solution is used, it should contain at least 20 micrograms per aliquot used; an aliquot of the irradiated solution can be pipetted directly to the distillation flask.

3. The Oak Ridge National Laboratory Graphite Reactor was used for the irradiation. The sensitivity of the method is such that 2×10^{-8} gram of selenium can be determined. The sensitivity can be improved by use of higher neutron fluxes.

4. As selenious acid, H_2SeO_3; Se^{+4} concentration equals 10 milligrams per milliliter.

5. Holdback carriers should be made up to contain 5 milligrams per milliliter of desired elemental species.

6. Solutions of ions of other elements may also be added as holdback carriers.

7. If the biological material is a fatty substance, a wet digestion with HNO_3-H_2SO_4 mixture should be used to effect a solution of the material.

8. Tellurium, arsenic, antimony or germanium can follow wholly, or in part, through this distillation procedure. In most of the materials anal-

ized by this method, the radioactive contaminants were usually in minor concentrations or completely eliminated in the reduction of selenium to elemental form.

9. The Br_2 color of the solution disappears during neutralization.

10. If Se^{81} or Se^{81m} radioactivity is to be measured, this part of the procedure can be completed after the radioactivity measurements.

11. By comparing the final weight of the selenium metal precipitate obtained here with the theoretical yield expected for the amount of selenium carrier added, it is possible to determine the chemical yield of the experiment. The chemical yield correction is then used to determine the amount of Se^{75} (and/or Se^{81} or Se^{81m}) recovered during the separation process.

PROCEDURE 2

Procedure Used In: Radioactivation analysis

Method: Volatility and precipitation

Element Separated: Selenium

Type of Material Analyzed: Ore concentrates, slags, waste gases[73]

Type of Nuclear Bombardment: $Se^{74}(n,\gamma)Se^{75}$ (Se^{75}: 121 d)

Procedure by: Fineman, et al.[73]

Chemical Yield of Carrier: 50-80%

Separation Time: Several hours

Degree of Purification: Excellent from other volatile radionuclides

Equipment Required: Neutron source and standard laboratory equipment

Procedure

1. Samples (0.1-1 g) irradiated in a nuclear reactor for 14 days at a flux of 4×10^{11} $n/cm^2/sec$.

2. After irradiation, a weighed amount of selenium (10-100 mg) was mixed thoroughly with sample and the mixture fused in a nickel or iron

crucible with 25 grams of Na_2O_2 at a temperature of 900°-1000°C.

3. Cake dissolved in 50 ml of water. Solution cooled and then neutralized with (1:1) H_2SO_4. At least 50 ml more of conc. H_2SO_4 was added to solution and the mixture boiled for 15 minutes to precipitate SeO_2. Solution filtered and volume reduced by evaporation to 100 ml. Cooled and then transferred to a distillation flask.

4. Mixture distilled with HBr (48%) and Br_2. Distillate collected in 10 ml of H_2O. (40-50 ml of distillate collected)

5. Selenium precipitated from distillate with NH_4OH-HCl-hydrazine sulfate. Precipitate collected by filtration, then dried at 105°C, weighed, and mounted for the radioactivity measurement.

6. The Se^{75} gamma radioactivity was measured by use of a 3" x 3" NaI(Tl) scintillation crystal.

7. Comparator samples were irradiated and processed in a similar manner to obtain the selenium concentration of the materials being analyzed.

PROCEDURE 3

Procedure Used In: Radioactivation analysis

Method: Fusion, precipitation and ion exchange

Element Separated: Selenium as Se^{75} (121 d)

Type of Material Analyzed: Stony meteorites(74)

Type of Nuclear Bombardment: $Se^{74}(n,\gamma)Se^{75}$ (Se^{75}: 121 d)

Procedure by: Schindewolf(74)

Chemical Yield of Carrier: Quantitative

Separation Time: Several hours

Degree of Purification: Decontamination of > 10^4 for Ag, Ce, Co, Cs, Hg, Ir, Nb, Ru, Sb, Sc, Ta, Zn and Zr

Equipment Required: Neutron source and standard laboratory equipment

Procedure

1. Powdered meteorite samples weighing 0.050 to 0.20 gram were irradiated in the Argonne National Laboratory CP-5 reactor.

2. After irradiation, 0.020 gram each of selenium and tellurium was added to the irradiated sample and the mixture fused in a nickel crucible with 1-2 grams of Na_2O_2.

3. After cooling, the cake was dissolved in 6 N HCl and the mixture boiled. Selenium and tellurium reduced to elemental form with SO_2 gas.

4. Precipitate dissolved in aqua-regia and the solution made basic with NH_4OH. Impurity scavenge made with $Fe(OH)_3$.

5. Solution was acidified with HCl and the selenium and tellurium adsorbed on a Dowex-1 (100-200 mesh) anion exchange resin column. Selenium can be separated from tellurium by eluting it from the column with 3 to 5 column volumes of 3 N HCl.

6. The acid solution was then treated with SO_2 gas to reduce selenium to the elemental form. Precipitate collected by filtration, weighed and mounted for the radioactivity measurement.

7. The Se^{75} gamma-radioactivity was measured by use of a 3" x 3" NaI (Tl) scintillation crystal.

8. Comparator samples were irradiated and processed in a similar manner to obtain the selenium concentrations of the meteorite.

PROCEDURE 4

Procedure Used in: Preparation of Radioactive tracers

Method: Volatility and precipitation

Element Separated: Selenium

Type Material Bombarded: Arsenic

Type of Nuclear Bombardment: 194 Mev deuterons

Procedure by: H. Hopkins, Jr. (reported by Meinke[76])

Separation Time: 45 minutes

Chemical Yield of Carrier: > 90%

Decontamination: Radiochemically pure by factor of ~ 100

Equipment Needed: Standard

Procedure

1. Dissolve As metal in minimum 10 N HNO_3.
2. Add 5 mg Se carrier, evap. to near dryness to remove excess HNO_3.
3. Make up to 3 ml with 1 N HCl, add $NH_2OH \cdot HCl$ until Se starts to ppt from hot soln.
4. Add 1 ml 1 N KI, heat 5 min, centrifuge off mixture of Se and I_2.
5. Dissolve with minimum fuming HNO_3, repeat precipitation.

PROCEDURE 5

Procedure Used In: Preparation of radioactive tracers

Method: Volatility and precipitation

Element Separated: Selenium

Type Material Bombarded: Bismuth metal

Type of Nuclear Bombardment: 184" cyclotron (388 Mev alphas; 348 Mev protons; 194 Mev deuterons)

Procedure by: Goeckerman (reported by Meinke[76])

Separation Time: 1 hour

Chemical Yield of Carrier: ~ 90%

Decontamination: ~ 10^4 from fission and spallation products.

Equipment Needed: As indicated in Procedure

Procedure

1. To aliquot of HNO_3 soln. of target, add 10 mg Se and Te, 10 ml conc. HBr, and 0.5 ml liquid Br_2 in a glass still. Distill in air stream

to 3 ml residue, into 5 ml sat. Br_2 water in ice bath.

2. Keep at ice temp. and reduce to Se (red) with SO_2 or $NH_2OH \cdot HCl$. Add aerosol and centrifuge.

3. Dissolve Se in few drops conc HNO_3, add 10 ml conc. HCl and reduce with SO_2 in an ice bath. Centrifuge with aerosol.

4. Repeat $SeBr_4$ distillation and Se pptns as often as necessary for desired purity.

5. Ppt Se, filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry 10 min. at 110°C. Weigh as Se.

PROCEDURE 6

Procedure Used In: Determination of fission product activities in plant process solutions

Method: Volatility and precipitation

Element Separated: Selenium as Se^{75}

Type of Material Analyzed: Fission product solutions(77)

Type of Nuclear Bombardment: Uranium fission

Procedure by: Glendenin and Winsberg(85)

Chemical Yield of Carrier: 80%

Separation Time: 1 hour

Degree of Purification: Excellent

Equipment Required: Standard laboratory equipment

Procedure

1. Place not more than 5 ml of sample (Note 1) in a glass still and add 2 ml of Se carrier and 10 ml of conc. HBr. Distill the Se (hood) into 5 ml of water contained in a 50 ml centrifuge tube placed in an ice bath. Continue the distillation until no more than 2-3 ml of solution remains in the distillation flask (Note 2).

2. Pass SO_2 rapidly (Note 3) through the distillate (in an ice bath) until the red precipitate of Se is coagulated (2-3 minutes), centrifuge, and wash with 10 ml of water (Note 4).

3. Dissolve the Se by heating with 5-10 drops of conc. HNO_3, evaporate nearly to dryness, and take up in 10 ml of conc. HCl. Place in an ice bath and precipitate the Se with SO_2 as in step (2).

4. Repeat step (3).

5. Transfer the Se with 5-10 ml of water onto a weighed paper (Note 5) in a small Hirsch funnel and filter with suction. Wash 3 times with 5 ml of ethanol, and 3 times with 5 ml of ether. Dry at 110°C for 10 minutes, weigh as elementary Se, and mount.

NOTES:

1. If the sample contains a large amount of nitrate, add the Se carrier and boil down to about 1 ml before distilling with HBr.

2. The distillation of Se is practically complete at this point. The solution should not be taken to dryness.

3. A rapid stream of SO_2 hastens precipitation and aids in coagulation.

4. A few drops of aerosol solution prevents "scum" formation and aids in centrifugation.

5. The filter paper is washed with ethanol and ether and dried under the conditions of the procedure before weighing.

PROCEDURE 7

Procedure Used In: Carrier-free separation of selenium radioactivity

Method: Szilard-Chalmers reaction

Radioelement(s) Separated: Se^{83} (25 m), Se^{81m} (59 m), Se^{81} (17 m), and Se^{75} (121 d)

Procedure by: Gest and Edwards[74]

Procedure

1. One (1.0) gram of ammonium selenite (Note 1) irradiated in the ORNL Graphite Reactor for 30 minutes.

2. After irradiation, selenite was dissolved in 3 N HCl and extracted with CS_2 (Notes 2 and 3).

3. CS_2 fraction evaporated to dryness and the selenium taken up in conc. HNO_3.

NOTES:

1. Ammonium selenite prepared by neutralizing SeO_2 solutions with NH_4OH and crystallized with acetone.

2. 20% of the selenium activity found in CS_2 fraction.

3. In a second method, a 6 N HCl solution of the irradiated selenite was filtered through a fine sintered-glass filter. Much of the radioactivity was deposited on the filter. 28% of the original selenium radioactivity removed by passing boiling conc. HNO_3 through the filter.

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APPENDIX A

Some References on the Determination of Selenium by Colorimetry, Polarography, and Other Analysis Methods

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USAEC Office of Technical Information Extension, Oak Ridge, Tennessee