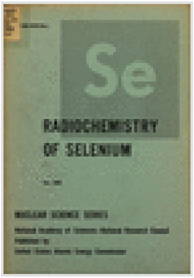

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Radiochemistry of Selenium

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Union Carbide Corporation
Mining and Metals Division
Research Center
Tuxedo, New York

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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 radiochemistry and nuclear chemistry. Support for the activities of this and other subcommittees of the Committee on Nuclear Science is provided by a grant from the National Science Foundation.

The Subcommittee has concerned itself with preparation of publications, encouraging and supporting activities in nuclear education, sponsoring symposia on selected current topics in radiochemistry and nuclear chemistry, and investigating special problems as they arise. A series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques is being published. Initiation and encouragement of publication of articles on nuclear education in various subject areas of chemistry have occurred, and development and improvement of certain education activities (e.g., laboratory and demonstration experiments with radioactivity) have been encouraged and assisted. Radioactive contamination of reagents and materials has been investigated and specific recommendations made.

This series of monographs has resulted from the need for comprehensive compilations of radiochemical and nuclear chemical information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or with a specialized technique. The U. S. Atomic Energy Commission has sponsored the printing of the series.

Comments and suggestions for further publications and activities of value to persons working with radioactivity are welcomed by the Subcommittee.

N. E. Ballou, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This monograph on the radiochemistry of selenium is one in a series covering the radiochemistry of essentially all the elements. It is a revised and expanded version of an earlier monograph. In it are included reviews of nuclear and chemical properties of selenium, discussions of methods of sample dissolution and of separation reactions, descriptions of counting techniques, and a compilation of radiochemical separation procedures for selenium as found in the literature.

As new information accumulates on chemical and nuclear properties of selenium and on separation and measurement techniques, consideration will be given to further revision of this monograph. Consequently as additional information becomes available in both published and unpublished form, readers are encouraged to bring it to the attention of the author for possible inclusion in future editions of this monograph.

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I. GENERAL REFERENCES ON INORGANIC AND ANALYTIC CHEMISTRY OF SELENIUM

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III. TABLE OF THE ISOTOPES OF SELENIUM

The radioactive nuclides of selenium 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 in the Nuclear Data Sheets(2). Figure 1 shows the selenium portion of the Chart of Nuclides(3) including the adjacent elements.

TABLE I

TABLE OF ISOTOPES OF SELENIUM

Isotope	Isotopic Abundance (%)	Half-life	Type of Decay	Energy (MeV)	Particle Reactions
Se^{70}		~44 m	β^+		$As^{75}(d,7n)Se^{70}$
Se^{71}		4.5 m	β^+	β^+, 3.4 γ, 0.16	$As^{75}(d,6n)Se^{71}$
Se^{72}		8.4 d	EC,β^+	γ, 0.046	$As^{75}(d,5n)Se^{72}$
Se^{73m}		44 m	β^+	β^+, 1.7 γ, 0.88	$As^{75}(d,4n)Se^{73m}$; $Se^{74}(\gamma,n)Se^{73m}$; $Se^{74}(n,2n)Se^{73m}$
Se^{73}		7.1 h	β^+,EC	β^+, 1.29,1.65 γ, 0.36,0.066	$As^{75}(d,4n)Se^{73m}$; $Se^{74}(\gamma,n)Se^{73}$; $Se^{74}(n,2n)Se^{73}$
Se^{74}	0.87%				
Se^{75}		121 d	EC no β^+	γ, 0.265,0.136 0.28 ,0.405	$Se^{74}(n,\gamma)Se^{75}$; $As^{75}(p,n)Se^{75}$; $As^{75}(d,2n)Se^{75}$
Se^{76}	9.02%				
Se^{77}	7.58%				
Se^{77m}		17.5 s	IT	γ, 0.162	$Se^{76}(n,\gamma)Se^{77m}$; U fission
Se^{78}	23.52%				
Se^{79m}		3.9 m	IT	γ, 0.096	$Se^{78}(n,\gamma)Se^{79m}$; $Se^{80}(n,2n)Se^{79m}$; $Br^{79}(n,p)Se^{79m}$; U fission

TABLE I (Continued)

Isotope	Isotopic Abundance (%)	Half-life	Type of Decay	Energy (MeV)	Particle Reactions
Se^{79}		6.5×10^{4} y	β^-	β^-, 0.16	$Se^{78}(n,\gamma)Se^{79}$; U fission
Se^{80}	49.82%				
Se^{81m}		56.8 m	IT	γ, 0.103	$Se^{80}(n,\gamma)Se^{81m}$; $Br^{81}(n,p)Se^{81m}$; $Se^{80}(d,p)Se^{81m}$; U fission
Se^{81}		18.2 m	β^-	β^-, 1.38	$Se^{80}(n,\gamma)Se^{81}$; $Se^{80}(d,p)Se^{81}$; $Se^{82}(\gamma,n)Se^{81}$; $Br^{81}(n,p)Se^{81}$; U fission
Se^{82}	9.19%				
Se^{83m}		70 s	β^-	β^-, 1.5, 3.4 γ, 1.01, 2.02, 0.65, 0.35	$Se^{82}(n,\gamma)Se^{83m}$; U fission
Se^{83}		25 m	β^-	β^-, 1.5 γ, 0.35	$Se^{82}(n,\gamma)Se^{83}$; $Se^{82}(d,p)Se^{83}$; U fission and Th fission
Se^{84}		3.3 m	β^-		U fission
Se^{85}		40 s	β^-		U fission
Se^{86}		17 s	β^-		U fission

FIGURE I: Partial chart of the nuclides showing selenium.

IV. FEATURES OF SELENIUM CHEMISTRY OF CHIEF INTEREST TO THE RADIOCHEMIST

1. INTRODUCTION

Selenium is found associated with sulfur and sulfides. The usual sources are the native sulfides such as pyrite, chalcopyrite, and zinc blende. Flue dusts from the roasting of seleniferous ores, and the sludge formed in the lead chambers used in sulfuric-acid manufacturing processes are also highly enriched sources. Selenium in these materials is usually brought into solution by 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.

Some of the chemical and physical properties of elemental selenium are summarized in Table II. Data have been compiled from publications by Hopkins(4) and by Latimer(5).

2. THE METALLIC STATE

Selenium, like sulfur, exists in at least three allotropic forms, or modifications: crystalline, metallic, and amorphous. Only the crystalline and metallic forms have been well characterized. The crystalline form (a loose powder composed of at least two varieties of red, monoclinic, crystals) is prepared by crystallization from carbon disulfide, in which it is soluble. Gray, metallic selenium is the most stable modification and forms hexagonal crystals. It is relatively insoluble in carbon disulfide, is a good conductor of electricity, and is less active chemically than the other forms. Gray selenium is prepared by heating any of the other forms at temperatures of from 200 to 230°C. Amorphous selenium is obtained in two forms: (1) red powder produced by reducing a selenite in an acid solution with sulfur dioxide; and (2) vitreous or glassy selenium, black in color and described as a super-cooled liquid. Both amorphous forms are soluble in carbon disulfide.

Selenium will burn with a characteristic odor, and will combine directly with hydrogen, oxygen, the halogens, and many other metals. It is not attacked by non-oxidizing acids; but when heated, it will dissolve in concentrated sulfuric acid, nitric acid, or caustic alkalis. Nitric acid oxidizes selenium to H_2SeO_3.

3. THE OXIDES

The most stable compound of Se (and its only well-defined oxide) is selenium dioxide (SeO_2) produced by burning selenium in oxygen or air. Pure SeO_2 is composed of brilliant white needles. It sublimes readily but can be melted

TABLE II

CHEMICAL AND PHYSICAL
PROPERTIES OF SELENIUM

Atomic Weight	78.96
Specific Gravity (solid)	4.26-4.79
Color (solid)	dark red
Melting Point	170-217°C
Boiling Point	688°C
Atomic Volume (approx.)	18C
Heat of Formation, H_2X (Cals.)	-25.1
Atomic Radius	1.5 Angstrom

Ionization Potentials

Ion	Volts
I	9.751
II	21.514
III	30.079
IV	42.902
V	73.109

Oxidation Potentials (volts) at 25°C

(a) Acid solution

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

(b) Base solution

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

without decomposition. In the vapor state, it has a yellow-green color. Selenium dioxide will dissolve in water, concentrated sulfuric acid, or alcohol. It can combine with hydrogen chloride to form $SeO_2 \cdot 2HCl$, and will form similar double compounds with other substances. It can easily be reduced to elemental selenium.

The characteristic burning odor of selenium is reported by Berzelius(6) to be due to the formation of a suboxide, SeO. It is also reported that a mixture of SeO_2 and SeO_3 is produced when selenium reacts with oxygen in an electrical discharge. Selenium trioxide is decomposed in water to form selenic acid, and is stable to 185°C, at which temperature it decomposes to oxygen and SeO_2.

4. OXIDATION STATES

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.

Selenium is electronegatively bivalent towards hydrogen and the metals. In its electropositive behavior, selenium has a valence of +4 in compounds formed with most elements; but in combination with fluorine it has a valence of +6. In general, the compounds of selenium, sulfur, and tellurium, behave similarly and are analogous to each other. The principal difference is in the lower stability of the selenium (and tellurium) compounds, which are easily decomposed to the element by heat or reducing agents.

5. SALTS

5.1 Soluble Salts

Selenium dioxide is a true anhydride, five parts dissolving in one part of water. In combination with water, SeO_2 will form selenious acid (H_2SeO_3). The alkali selenites (Li_2SeO_3, Na_2SeO_3, K_2SeO_3, Rb_2SeO_3, Cs_2SeO_3) are all soluble in water, as are the acid selenites or hydroselenites of the type $MHSeO_3$. Table III lists some of the more important soluble compounds of selenium.

5.2 Insoluble Salts

The selenate compounds of lead, barium and calcium, like the corresponding sulfates, are insoluble; however, they are less stable to heat than the sulfates.

Hydrogen selenide 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 that these metals form polysulfides with sulfur. Pure alkali selenides are colorless. 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 heavy metal sulfides, they are insoluble in water, and some are insoluble in acids.

Selenium can combine directly with nitrogen to form selenium nitride (Se_4N_4), which is insoluble in water, and only slightly soluble in benzene, acetone, acids, and carbon disulfide.

Selenium combines with sulfur to form selenium monosulfide, (SeS) and selenium disulfide (SeS_2). Selenium monosulfide is insoluble in water and ether, but very soluble in carbon disulfide. Selenium disulfide

TABLE III

SOLUBILITY OF SELENIUM COMPOUNDS

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	Se_2Br_2	decomposes $(Se + H_2SeO_3 + HBr)$	decomposes	Decomposes in alcohol; soluble in CS_2, chloroform, C_2H_5Br.
	$SeBr_4$	decomposes $(SeOBr_2 + HBr)$	decomposes	Soluble in CS_2, chloroform, C_2H_5Br, HCl.
	$SeBrCl_3$			Insoluble in CS_2.
	$SeBr_3Cl$			
	Se_2N_2Br	insoluble	decomposes	Slightly soluble in CS_2.
Chlorides	Se_2Cl_2	decomposes $(Se + H_2SeO_3 + HCl)$	decomposes	Decomposes in alcohol and ether; soluble in CS_2, CCl_4 chloroform, benzene.
	$SeCl_4$	decomposes $(SeOCl_2 + HCl)$	decomposes	Decomposes in acids and alkalis; slightly soluble in CS_2.
Fluorides	SeF_4	decomposes $(SeOF_2 + HF)$	decomposes	
	SeF_6	decomposes	decomposes	
Iodides	Se_2I_2	decomposes $(Se + H_2SeO_3 + HI)$	decomposes	
	SeI_4	decomposes $(SeOI_2 + HI)$	decomposes	
Nitrides	Se_4N_4	insoluble	insoluble	Insoluble in alcohol and ether; slightly soluble in benzene, acetic acid and CS_2.
Oxides	SeO_2	soluble	soluble	Soluble in alcohol, acetone, benzene, acetic acid.
	SeO_3	decomposes slightly $(SeO_2 + Se)$	decomposes slightly	Soluble in alcohol and H_2SO_4; insoluble in ether, benzene, chloroform, CCL_4.
	$SeSO_3$	decomposes $(SeO_2 + SO_2)$	decomposes	Soluble in H_2SO_4; insoluble in SO_3.
Oxy-Salts	$SeOBr_2$	decomposes $(H_2SeO_3 + HBr)$	decomposes	Soluble in CS_2, CCl_4, chloroform, H_2SO_4, benzene
	$SeOCl_2$	decomposes $(H_2SeO_3 + HCl)$	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 $(NH_4)_2S$.

is insoluble in water and will decompose only in aqua regia or nitric acid. Table III lists some of the more important insoluble compounds of selenium. Additional information on solubilities appears in the "Handbook of Chemistry and Physics"(7).

5.3 Non-isotopic Carriers

In some cases, a high specific activity selenium source must be prepared. A non-isotopic carrier, chemically similar to selenium, must be used rather than inactive selenium. Tellurium meets these requirements and can be used to separate small quantities of radioactive selenium. High-purity (99.999%) tellurium is available commercially. Total halogens, sulfur, and selenium do not exceed 5 ppm by chemical analysis. Garrison, et al.(8) reported a procedure in which they separated radioactive selenium from an arsenic target using tellurous acid, precipitating tellurium with sulfur dioxide. They reported that 95% of the selenium carries, and can then be separated from tellurium by distillation.

5.4 Coprecipitation

Microgram quantities of selenium can be collected by coprecipitation on ferric hydroxide. The weight of the iron present should be 30 times that of the selenium(9). The iron is precipitated with an excess of ammonium hydroxide. A method(10) for separating small amounts of selenite and selenate ions is based on the coprecipitation of the selenite ion with iron hydroxide at pH 8.4-8.6. Under these conditions, the selenate ion is not coprecipitated.

6. COMPLEX IONS

Several of the selenium halogen compounds can form complex acids by adding on hydrogen halide ions. For example, $SeBr_4$ will combine with HBr to form hexabromoselenic acid (H_2SeBr_6). Hexabromoselenates and hexachloroselenates have been formed by the reaction of alkali halide salts upon these complex acids. Their solubilities resemble those of the selenates.

7. CHELATES

Selenium forms a chelate in an acid solution with sodium diethldithiocarbamate that can be extracted (pH 3) with ethyl acetate(11,12). The complex can be extracted into carbon tetrachloride(13), and tellurium is also extracted.

Bode and Arnswold(14) reported the quantitative extraction of the SeIV chelate of diethyldithiophosphate from 10N HCl into CCl_4, only 40% of the tellurium being extracted.

Cheng(15) has shown that a 5% aqueous diaminobezidine hydrochloride solution will form a selenium complex in a formic acid-water system that can be extracted into toluene at pH 6-7. Although Fe^{+3}, Cu^{+2}, V^{+5} and other oxidants interfere, the Fe^{+3} and Cu^{+2} interferences can be eliminated by EDTA complexing at pH 2-3. Tellurium forms a complex that is extracted but does not interfere in the colorimetric analysis.

8. VOLATILE 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, 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, form the corresponding hydroxide.

9. PRINCIPAL ANALYTICAL METHODS

9.1 Gravimetric

The gravimetric determination of selenium is carried out by weighing the element after it has been precipitated by reduction in strong acid solution with either sulfur dioxide or hydroxylamine hydrochloride(16).

9.2 Volumetric(16)

9.2.1 Selenic acid is reduced by hydrochloric or hydrobromic acid. The halogen is caught in a solution of potassium iodide and titrated with arsenite and thiosulfate.

9.2.2 Selenious acid is reduced by hydriodic acid followed by titration of the liberated iodine with thiosulfate.

9.2.3 Selenious acid in hydrochloric acid solution is reduced by a known excess of sodium thiosulfate. The excess thiosulfate is then titrated with standard iodine solution.

9.2.4 Selenious acid is oxidized by an excess of standard permanganate solution in sulfuric acid solution. The excess permanganate is titrated with ferrous sulfate or oxalic acid solution.

9.3 Colorimetric

9.3.1 3,3'-Diaminobenzidine reacts with Se to form an intense yellow compound (piazselenol). Cheng(15) reported a procedure for determining traces of Se by extracting this compound into toluene and measuring the color spectrophotometrically at a wave length of 420 mμ.

9.3.2 2,3-Diaminonaphthalene also reacts with Se to form a piazselenol which is a reddish precipitate. It may be extracted into toluene and measured spectrophotometrically at a wave length of 380 mμ(17).

9.3.3 Selenious acid liberates iodine quantitatively by oxidation of iodide ion. The blue color is developed with a cadmium-iodide starch reagent and measured spectrophotometrically at a wave length of 615 mμ(18).

V. SELENIUM SEPARATION REACTIONS

1. SEPARATION BY PRECIPITATION

Selenium is separated from most elements by the use of reducing agents in acid solutions. Hillebrand, et al.(16) report that Se (and Te) can be initially separated from most elements by reduction with SO_2 in 3.7 to 4.8$\underline{N}$ HCl solution. Gold, Pd, and small amounts of Sb, Bi, Cu, and other elements are also reduced under the same conditons. Gold can be separated by filtration after the mixed metal precipitate has been digested for some times in a dilute HNO_3 solution. The selenium can then be separated by precipitation with H_2SO_3 or hydroxylamine hydrochloride.

Quadrivalent selenium or tellurium can be separated from other elements by saturating an acid solution with H_2S(19). Sexivalent selenium and tellurium can be completely precipitated from 12$\underline{N}$ HCl solution at room temperature(20). Sulfides of the copper subgroup may interfere under the same conditions.

In their studies, Seath and Beamish(21) and Noakes(22) showed that nitrates of Cu^{+2} and Au^{+3} interfered in the reduction of Se (or Te) to elemental Se (or Te). The nitrates were removed by evaporation with HCl and NaCl, and Cu^{+2} and Au^{+3} were separated before the reduction with hydroquinone(23,24).

Selenium (and tellurium) may be separated from many elements by reduction of an acid solution with stannous chloride. Selenium and tellurium are precipitated and can be separated by a brominated HCl dissolution of the metals followed by a precipitation of Se with SO_2(25).

Bode(26) has shown that a separation of Se from Te can be effected in a 5N HCl solution using a solution of tetraphenylarsonium chloride. Tellurium^{+6} will precipitate and bromide, iodide, fluoride, nitrate, Mo^{+6}, and W^{+6} will interfere.

Ripan-Tilici(27) and Spacu(28) have shown that Se can be determined as lead selenate. To obtain this form, Se must be oxidized to the hexavalent state with H_2O_2 and precipitated by a lead salt solution.

2. SEPARATION BY SOLVENT EXTRACTION

Solvent extraction methods, used as separation methods for other analysis techniques, can often be adapted for use in radiochemistry. They can be quite useful in separating the desired radionuclide from a sample by either a carrier-free or carrier radiochemistry method. Morrison and Freiser(29) have reviewed the applications of ion-association and chelate-complex systems to the determination of most of the elements. Some of these are applicable as separation processes in the radiochemistry of selenium.

Table IV gives a few of the solvent extraction systems that could be used for the separation of selenium. Few specific solvent-extraction methods for selenium have been developed, but many could be adapted.

2.1 Ion-Association Systems

Kitahara(30) 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(31) have shown that only Nb^{+5}, Ta^{+5}, and Re^{+7} were extracted in amounts greater than 50%; 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. These two studies show different extraction values; however, these differences may be due to the manner in which the metal fluorides were prepared. Stevenson and Hicks(32) report that Se^{+6} (as well as Te^{+6}, Fe^{+3}, Ga^{+3}, Sb^{+5}, and As^{+3}) can be quantitatively extracted by diisopropyl ketone from a mineral acid-hydrofluoric acid (6M HCl - 0.4M 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 diisopropyl ketone from a 6M H_2SO_4 - 0.4M HF system.

At least 30% Se^{+4} can be extracted from a mixture of metal bromides

TABLE IV

SOLVENT EXTRACTION SYSTEMS FOR SELENIUM *

Oxidation State	Aqueous Phase	Organic Phase	% Extraction	Reference
IV	4.6M HF	ethyl ether	4.0	30
IV	20M HF	ethyl ether	12.9	31
VI	6M HCl-0.4M HF	diisopropyl ketone	100	32
IV	4-6M HBr	ethyl ether	31	33
IV	1M HNO_3	0.06M-0.6M dibutylphophoric acid	< 5	34
IV	HCl	methyl isobutyl ketone (4-methyl-2-pentanone)	100	35
IV	30-35% HBr	di-isobutyl ketone (2,6-dimethyl-4-heptanone)	90	36
IV	Na-diethyldithio-carbamate	ethyl acetate	100	11,12,13
IV	Piazselenol-complex of 3,3 diaminobenzidine hydrochloride	toluene	100	15
IV	Complex of 2,3 diamino-naphthalene	toluene	100	17
IV	Complex with toluene-3-4-dithiol and 10N HCl	mixture ethylene chloride - CCl_4	100	37

* All of these solvent extraction systems are also applicable to tellurium. The Na-diethyldithiocarbamate system is the only practical method for separating Te from Se. Tellurium can be extracted from this system into carbon tetrachloride at pH 8.5 - 8.7; selenium is not extracted.

(4M to 6M HBr) into ethyl ether(33). 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; Cu^{+2} and Zn^{+2} do not extract.

Scadden and Ballou(34) have shown that less than 5% Se^{+4} (and Te^{+4}) will extract into 0.06M or 0.6M di-n-butyl phosphoric acid (DBPA) from a 1M HNO_3 solution. A 1:1 organic-to-aqueous volume ratio was used in these studies. Yttrium, Sn, Mo, Nb, Ta, Zr, and In are extracted in concentrations varying from 5 to more than 95% 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 HCl(35). This study determined the approximate ranges of extractability for metallic salts of these and other elements.

Kuroda(36) used a HBr-diisobutyl ketone system for the rapid radiochemical separation of Se^{79m}. Selenium (as well as As, Sn, Hg and Au) can be quantitatively extracted into diisobutyl ketone from 30 to 35% HBr. The interfering elements can be stripped by shaking with EDTA and sodium tartrate, or with sodium hydroxide solution.

2.2 Chelate Complex Systems

Selenium can be extracted from an acid solution (pH 3) as the sodium diethyldithiocarbamate salt with ethyl acetate (11,12). Se^{+4} (and Te^{+4}) will also form a complex in an acid solution (pH 5-6) by use of 0.2% solution of sodium diethyldithiocarbamate(13). The complex can be extracted into CCl_4. The addition of a 5% solution of EDTA to the system assists in masking out other extractable elements.

Cheng(15) has shown that a 5% aqueous diaminobenzidine hydrochloride solution will form a piazselenol complex in a formic acid-water system that can be extracted at pH 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. Vanadium (V) oxidizes diaminobenzidine preventing the formation of the complex, but traces of vanadium have little effect. Tellurium is extracted but does not interfere colorimetrically.

Lott, et al.(17) used a similar system for extracting Se. A 1% aqueous (0.1N HCl) solution of 2,3-diaminonaphthalene was used to complex Se; and the complex was extracted, at pH 1.5 to 2.5, into toluene. Masking agents were used to prevent interferences.

Watkinson(37) extracted Se from strong HCl solutions ($<10N$) as the Se (IV) complex with toluene-3,4-dithiol into a mixture of ethylene chloride and carbon tetrachloride. Elements that also react with toluene-3,4-dithiol are Te (IV), Pd, Au, W (VI), and Re (VII).

3. SEPARATION BY VOLATILITY

Selenium (or tellurium) in the selenide (or telluride) form can be separated from metals whose chlorides are nonvolatile by passing Cl_2 gas into a hot aqueous solution(38). Hydrochloric acid gas can be used instead of Cl_2 to separate either Se^{+4} or Se^{+6}. Selenium can be separated from tellurium by a distillation method in which HCl gas is passed into a H_2SO_4 solution(39). The distillate is caught in cold water, and Se^{+6} is precipitated by adding SO_2. Either Se^{+4} or Se^{+6} can be quantitatively separated from tellurium by passing CO_2 gas into a hydrobromic-phosphoric acid solution(40). Selenium oxychloride and $SeOBr_2$ (as well as $TeOCl_2$ and $TeOBr_2$) are volatile from 6N HCl(41) or 6N HBr(42-44) solutions at temperatures above 100°C. Arsenic, antimony, tin and germanium are also volatile under these conditions.

4. ELECTROLYTIC SEPARATION

Electroseparation and electrogravimetry methods for selenium are not extensively reported. Only a few electroanalysis techniques exist for the determination of selenium by amperometry and coulometry; however, a consideration of these might be profitable for use in radiochemistry. For example, Lingane and Niedrach(45) report on the titration of Se^{+4} with cupric copper in an ammonical 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 such that the tetraaminocupric ions and the selenite ions are reducible; its value will increase when excess cupric ion is added. Rowley and Swift(46) have used a coulometric titration of thiosulfate for the determination of Se^{+4}. The back-titration procedures were followed. In one, an excess of iodide is added to a strong selenious acid solution and iodine is liberated and reduced with sodium thiosulfate solution, 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 is determined by coulometric titration with iodine. More accurate results (±0.1% for several hundred micrograms) were obtained by use of the second method.

5. SEPARATION BY ION EXCHANGE RESINS

Kraus and Nelson(47) report that selenite (Se^{+4}) and tellurite show good adsorption on an anion resin column as chloride complexes. 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 0.01M NH_4Cl; Se^{+4} with 0.50M NH_4Cl; and Br with 5.0M NH_4Cl. Attebury, et al.(48), and Aoki(49) report that Se can be separated from Te by adsorption upon an anion resin column from 3M HCl. A mixture of 1M HCl and 1M NH_4CNS was used as the eluant.

Lederer and Kertes(50) used selenite and tellurite ions in a study concerned with the use of a Dowex-resin-impregnated 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(51) have used paper chromatography to separate mixtures of Bi^{210}, Pb^{210}, Po, Se, and Te in HNO_3 solutions. A butanol-propanol mixture was used as the solvent and a good separation of each element was obtained. Crouthamel and Gatrousis(52) also report on a similar separation of Se, Te, Po, and Bi by paper chromatography. Specific separations of Se (as Se^{+4}) from tellurium (as Te^{+4}) in HCl, HNO_3, and HBr have been studied by Burstall, et al.(53), Lederer(54), and Weatherley(55). Solvents such as mixtures of butanol-methanol, butanol-water, and butanol-HCl were used to effect the separation.

VI. DISSOLUTION OF SAMPLES CONTAINING SELENIUM

When dissolving selenium-containing samples, it is necessary to use techniques that will minimize the loss of Se by volatilization(56). Selenium is easily volatilized as $SeO_2 \cdot 2HCl$ from strong HCl solutions by heating. Very little Se is lost by heating dilute HCl solutions at temperatures below 100°C. The presence of alkali salts do not prevent the volatilization of Se. The volatile monochloride of selenium (Se_2Cl_2) can be formed in strong HCl solutions by the action of reducing agents. The reduction of Se should be performed rapidly, with an excess of reducing agent, to reduce the Se to the element. No loss of Se occurs if sulfuric acid or perchloric acid solutions of selenious acid are evaporated to dense fumes(57) unless there are chlorides or bromides present.

Some selenides attack platinum during a fusion process. The fusion can be done with Na_2O_2 or a mixture of Na_2CO_3 and KNO_3 in a nickel or zirconium crucible. Fusion with KCN may cause some loss due to volatilization.

The addition of inactive selenium carrier to the mixture before dissolution begins will assist in achieving an exchange of the radionuclide with the carrier atom. The chemical states of the irradiated selenium and the carrier selenium should be the same during the dissolution procedure so that any losses that occur will be accounted for in the chemical yield determination of the added inactive carrier.

1. METALS AND OXIDES

Acid dissolution is recommended for the assay of metals and oxides. For example, copper metal can be dissolved in nitric acid; iron and steels may be dissolved in HNO_3, HCl and $HClO_4$; lead must be fused with Na_2CO_3 and Na_2NO_3 in a nickel crucible. Insoluble oxides may be fused with Na_2O_2 or sodium carbonate and potassium nitrate in a nickel crucible(58).

2. SALTS

Nitric acid and HCl will decompose most salts. Care should be taken that no selenium is volatilized.

3. ORES

Ore samples can be fused with Na_2O_2 or a mixture of sodium carbonate and sodium nitrate in an iron or nickel crucible(59). Some ores can be decomposed with 1:3 HNO_3 followed by fuming with sulfuric acid to remove HNO_3. Ores containing selenides can be decomposed by heating at dull redness in a current of Cl_2 and catching the volatile chlorides of selenium in 1:1 dilute HCl.

4. BIOCHEMICAL SAMPLES

Biochemical samples can be decomposed by destroying the organic matter with a 1:1 ashing mixture of nitric and perchloric acids(60). Tissues can be decomposed by fusing with Na_2O_2(61). Small amounts of Se in vegetation, grains, and animal matter have been released from these materials by distilling with HBr(62). Organic or biological samples can be decomposed in a Schöniger-type oxygen-combustion flask; the gases are absorbed in a HCl solution containing a selenium carrier. Gorsuch(63), 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 Se from similar materials. The results of these studies showed that Se was lost by volatilization.

5. OTHERS

Glass samples may be taken into solution with hydrofluoric and nitric acids(64). Rubber is decomposed by a fusion with a mixture of Na_2O_2, $NaNO_3$, and sugar.

VII. HAZARDS AND PRECAUTIONS

No matter what method is used to decompose a sample, adequate safety precautions should be followed. The toxicology of most elemental compounds has been reported by Pieters and Creyghton(65), and it should be consulted for information on handling selenium-containing materials safely. Due to the volatile nature of some of the selenium compounds, radiochemical separations requiring heat should be carried out in a well-ventilated hood.

Safety practices are always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in wide-spread radioactive 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 the Oak Ridge National Laboratory's Master Analytical Manual(66). Other similar sources of information exist and should be consulted.

VIII. COUNTING TECHNIQUES

The analysis of sample materials containing selenium radionuclides may be completed either by a direct (non-destructive) measurement of the radioactivity of the particular radionuclide or by obtaining the radionuclide in some form by radiochemically processing the radioactive sample. The choice of technique depends upon the selenium radionuclides being measured, and such characteristics as half-life, type of radiation emitted, and the energy of the radiations. An excellent source for counting techniques is the monograph by O'Kelly entitled, Detection and Measurement of Nuclear Radiation(67).

Table I shows the nuclear characteristics of each of the known radioactive isotopes of selenium. Those usually encountered by the radiochemist are Se^{75} (121 d), Se^{77m} (17.5 sec), Se^{81m} (56.8 m), Se^{81} (18.2 m) and Se^{83} (25 m). These isotopes are produced as a result of a number of nuclear reactions on stable isotopes, either of selenium or other elements. Se^{81m} decays to Se^{81} by isomeric transition; Se^{81} decays further to stable Br^{81} by the emission of 1.38-MeV beta radiation. Se^{81} decays with the half life of Se^{81m} (56.8 m), since the two states are in transient equilibrium. The measurement of Se^{81} must be completed by beta counting, using 4π or 2π Geiger-Mueller or proportional-beta counters.

The other isotopes decay by means of gamma radiations and can be measured with a gamma scintillation counter or gamma scintillation spectrometer. Figures 2 through 6 give gamma-ray spectra of the Se^{73}(87), Se^{75}(87), Se^{77m}(88), Se^{81m}(89 and Se^{83}(90) radioisotopes.

Although a number of radionuclides of selenium are formed by radiative capture in stable selenium isotopes, 121-day Se^{75} and 3.9-minute Se^{79m} have been most extensively used as the analytical indicators for the activation analysis of selenium. However, these are not the most sensitive indicators for a selenium analysis. Table V is a tabulation of the calculated specific-saturation activities of the nuclides formed by radiative thermal-neutron capture in the stable selenium isotopes. Activation cross sections were compiled from information appearing in reports by Hughes and Harvey(69) and by Weigman(70). Kramer, et al.(71) discuss the metastable isomers of selenium, and show that the greatest sensitivity can be obtained by using 17.5-second Se^{77m} as the radioactive indicator.

Selenium^{77m}, a metastable isomer of stable Se^{77}, decays with a half-life of 17.5 seconds with the emission of 0.160-Mev gamma rays. Its short half-life has precluded the use of Se^{77m} in an activation analytical scheme in most laboratories. In fact, there appear to be only two references(61,68) that report quantitative selenium analyses based on this particular nuclide. With rapid pneumatic-tube systems, samples can be transferred from the irradiation facility to the gamma scintillation counter in a few seconds. Okada(68) has recently reported on the use of gamma spectrometry to detect and determine the radioactivity of Se^{77m} (17.5-sec.) in nondestructive analyses of neutron-irradiated sulfur, ammonium compounds, and ores for trace selenium. Putman and Taylor(72,73) have reported a technique for using Se^{75} (121 d), for determining trace selenium in glass. They made measurements of irradiated sample of glass, with and without selenium, simultaneously, with two NaI(Tl) scintillation

TABLE V

CALCULATED SPECIFIC SATURATION ACTIVITIES FOR SELENIUM RADIONUCLIDES PRODUCED BY THERMAL NEUTRON CAPTURE

Stable Nuclide	Isotopic Abundance (%)	Radio-nuclide	Half-Life	Activation Cross-section (barns)	Specific Saturation Activity (a)
Se^{74}	0.87	Se^{75}	121d	26	1.7×10^{10}
Se^{76}	9.02	Se^{77m}	17.5s	22	1.5×10^{11}
Se^{78}	23.52	Se^{79m}	3.9m	0.40	7.2×10^{9}
Se^{80}	49.82	Se^{81m}	56.8m	0.030	1.1×10^{9}
Se^{80}	49.82	Se^{81}	18.2m	0.5	1.9×10^{10}
Se^{82}	9.19	Se^{83m}	70s	0.050	3.5×10^{8}
Se^{82}	9.19	Se^{83}	25m	0.004	2.8×10^{7}

(a) dis/sec.g, based on a thermal flux of 1×10^{13} neutrons/cm^2 · sec.

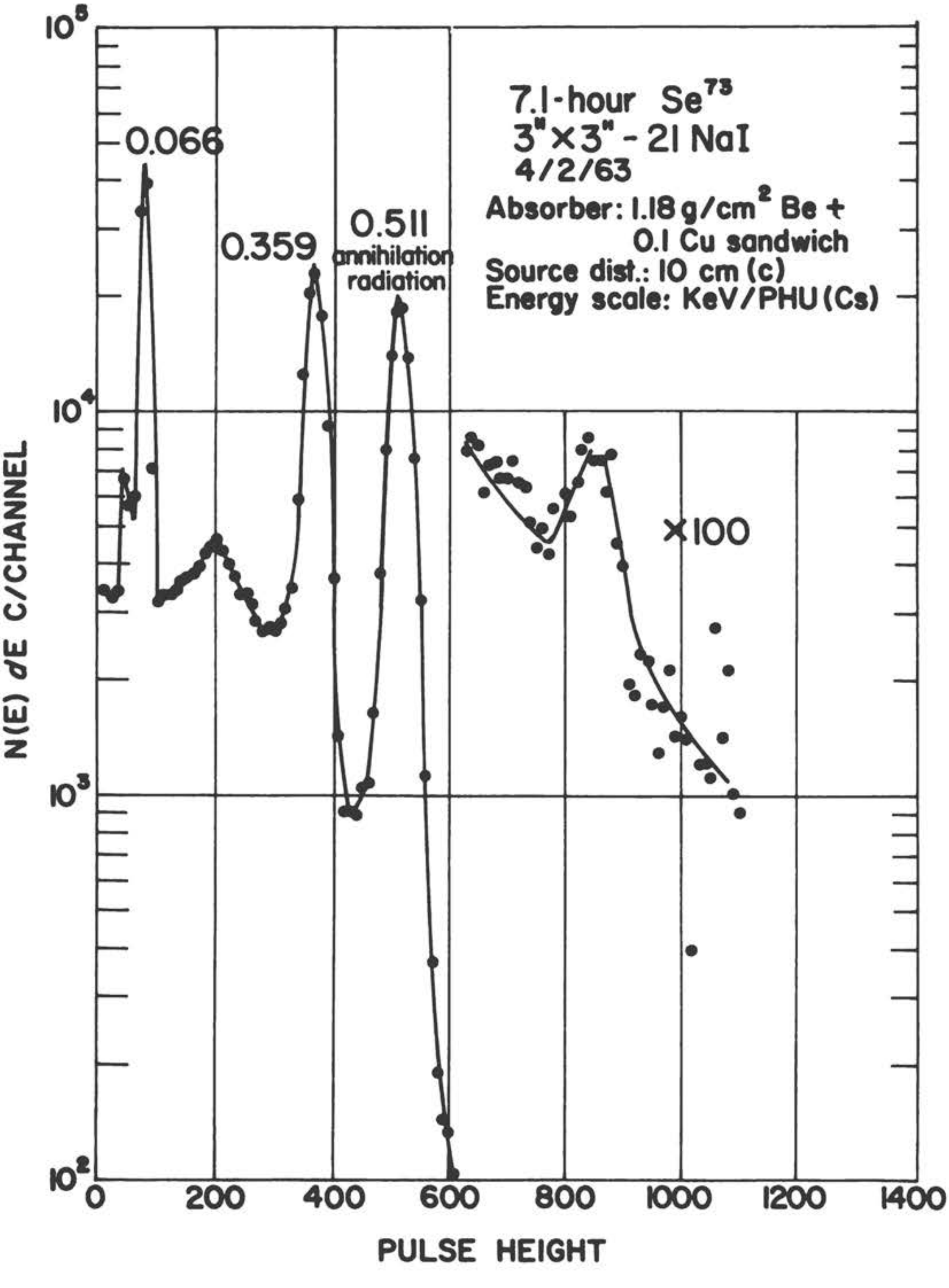

FIGURE 2, Gamma-ray spectrum of 7.1-hour Se^{73}.

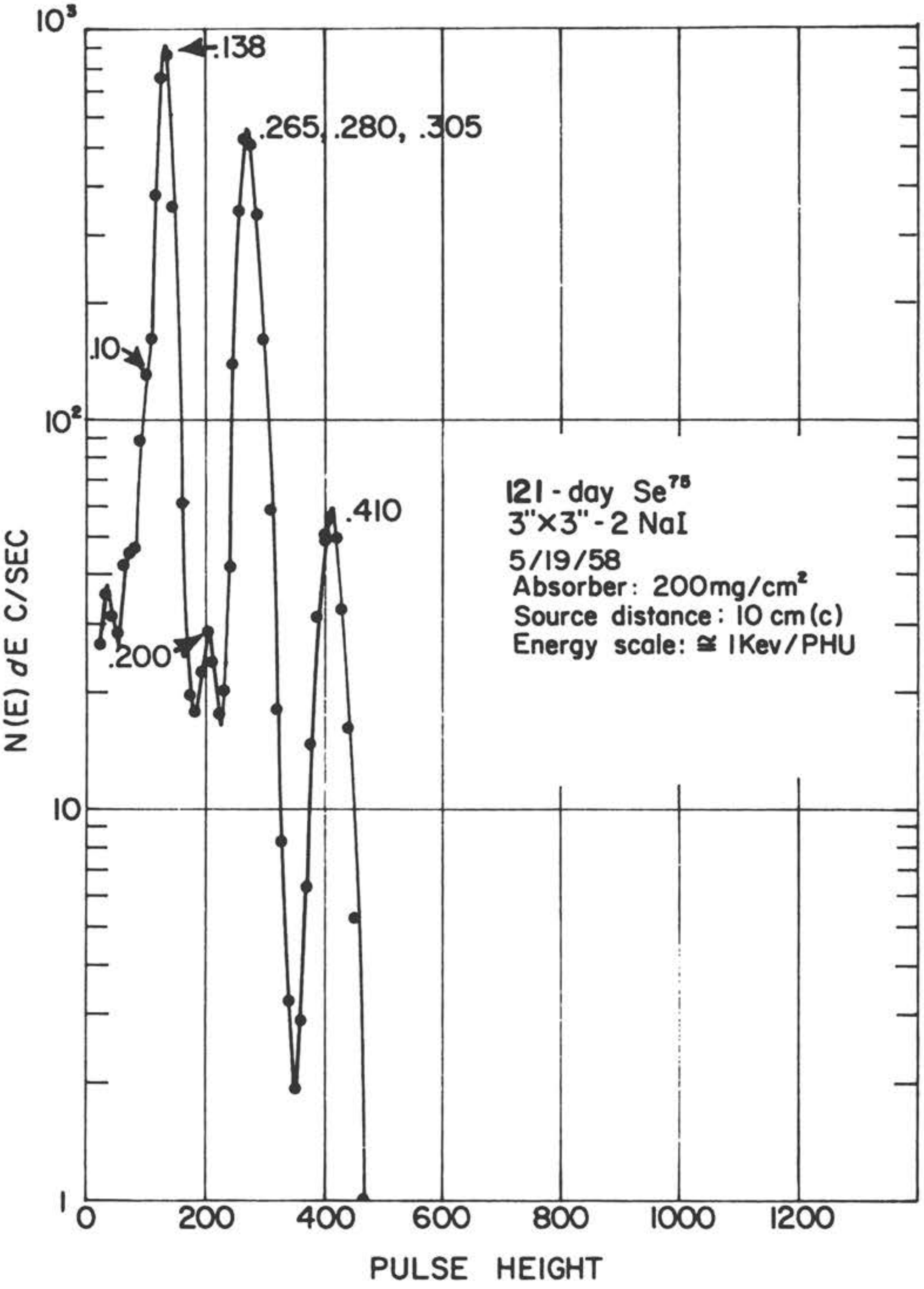

FIGURE 3, Gamma-ray spectrum of 121-day Se^{75}.

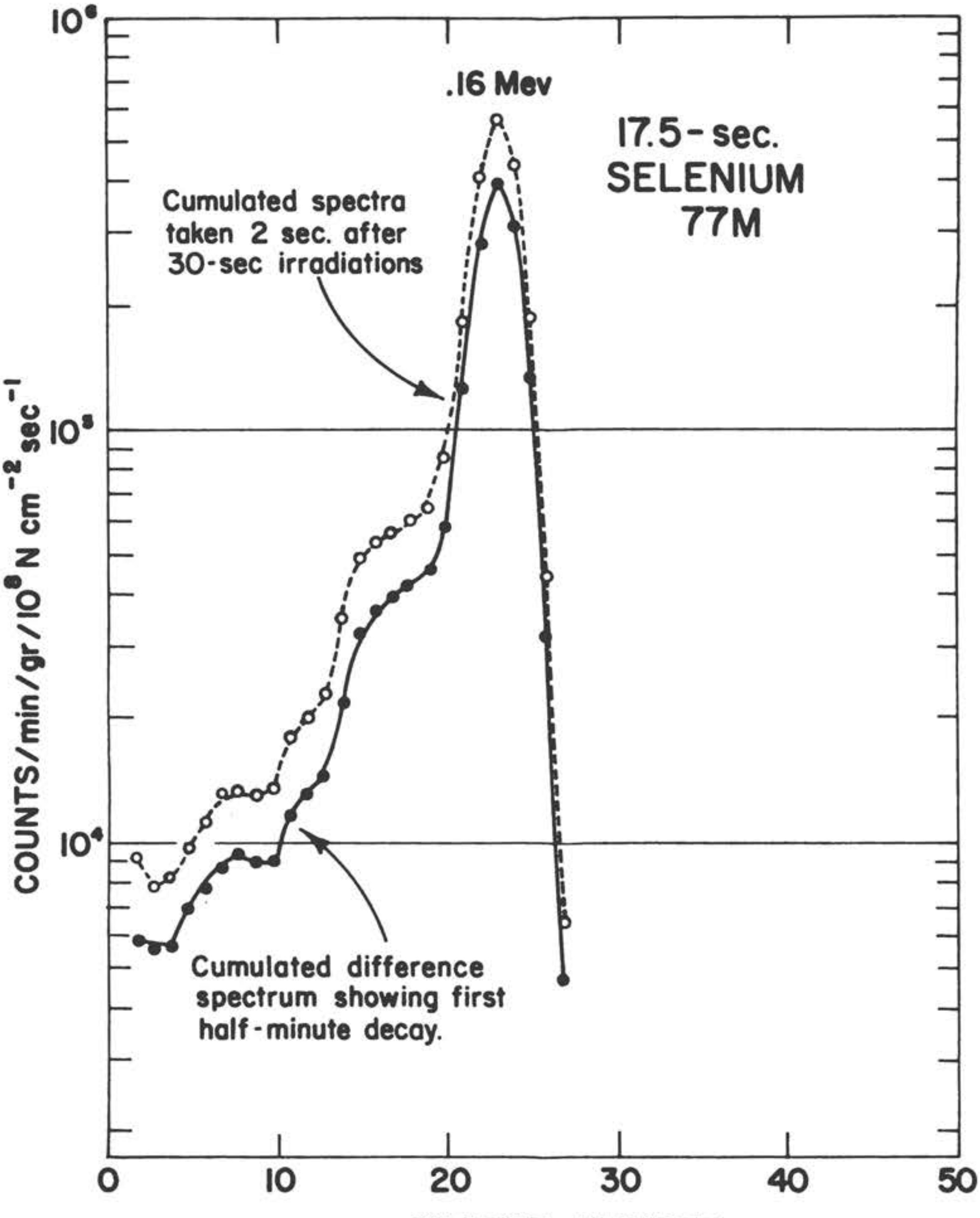

FIGURE 4, Gamma-ray spectrum of 17.5-sec. Se^{77m}.

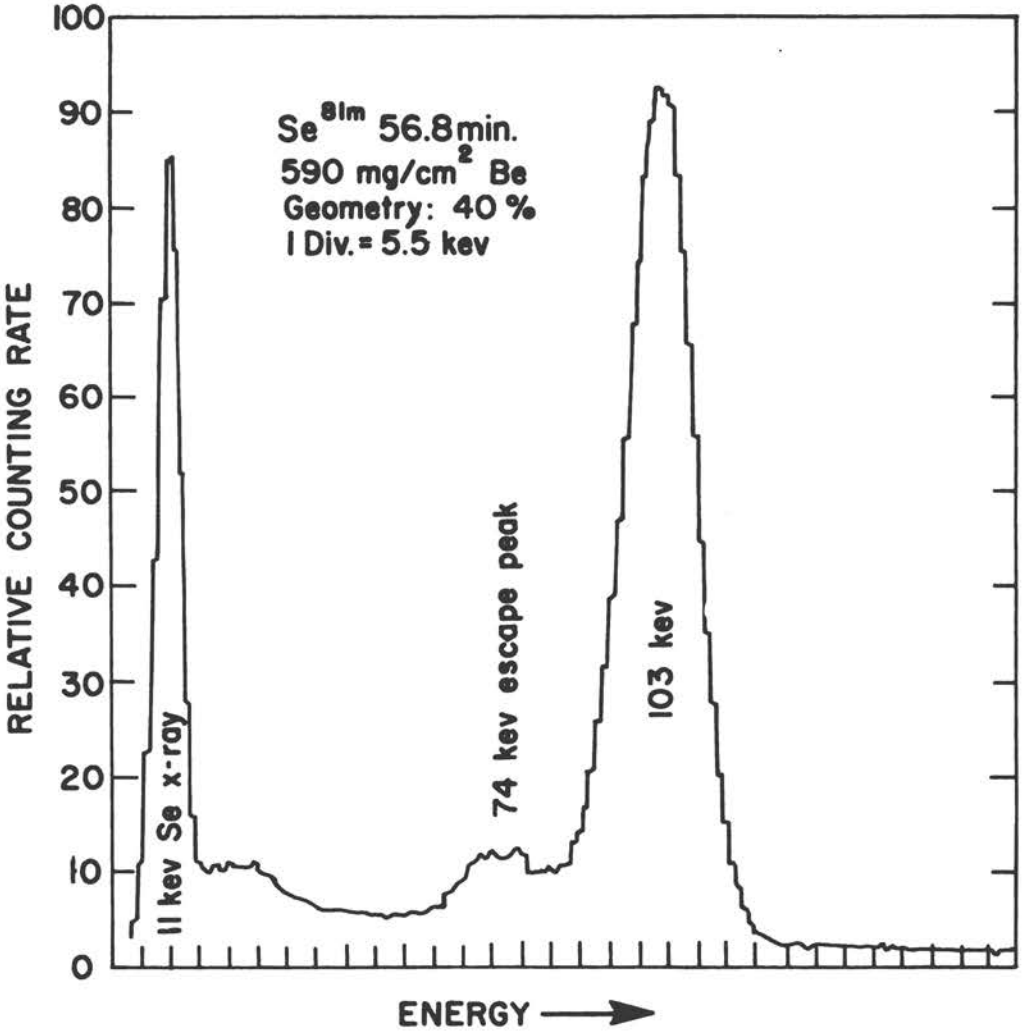

FIGURE 5, Gamma-ray spectrum of 56.8 min. Se^{81m}.

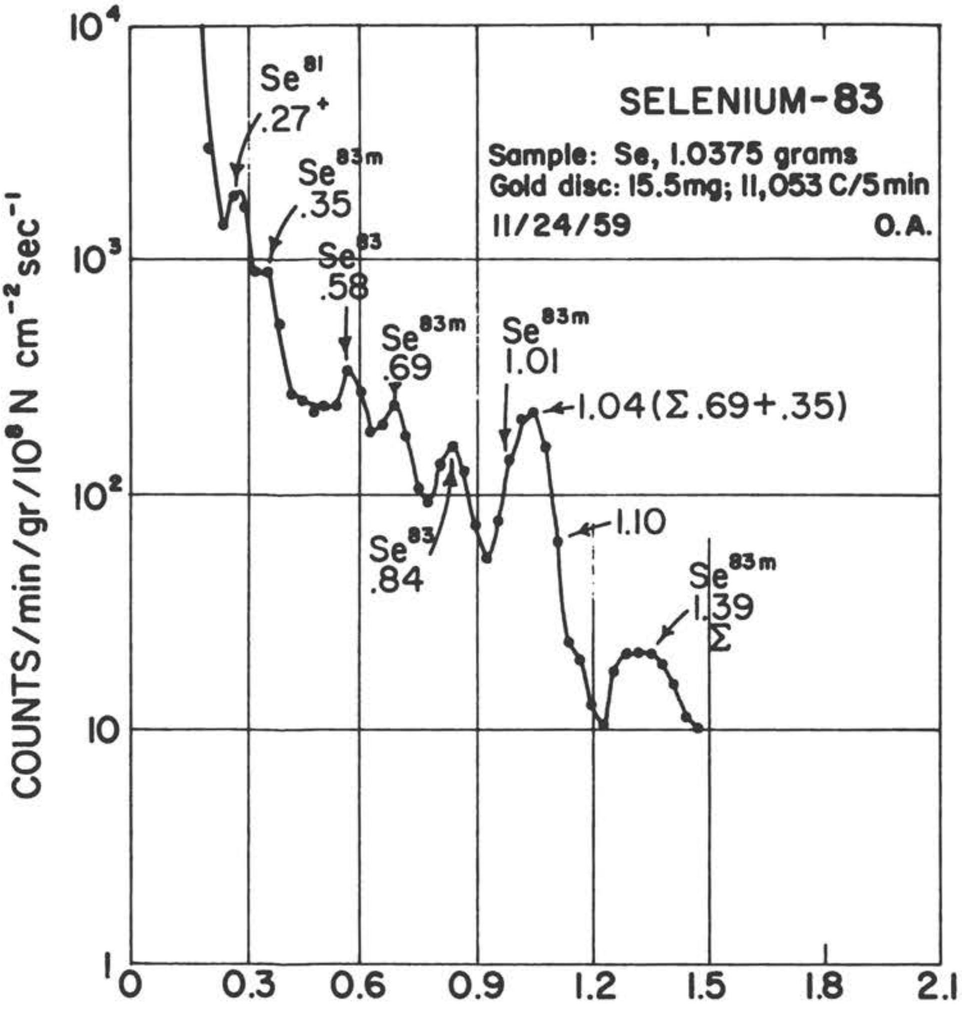

FIGURE 6 , Gamma-ray spectrum of Se^{83}.

counters; the response of the counters can be subtracted to leave only the selenium-75 activity. Erion, et al.(74) and Fineman, et al.(75) have also determined trace selenium in sulfur and ore concentrates by a nondestructive analysis method.

IX. SEPARATION PROCEDURES FOR SELENIUM

The radiochemical procedures described in the following pages have been divided into four categories. In each category, special information regarding the method used, separation time, type of bombardment, etc., appears as part of each procedure. Whenever possible, an evaluation of the procedure is made concerning its use in the decontamination of other radioactive species from the radioactive selenium isotopes.

"Activation-analysis procedures" describe various methods used to determine microgram and submicrogram amounts of selenium in various types of samples. In the activation-analysis procedures cited, a carrier technique was used to separate the radionuclide from the radioactive mixture. In the procedure by Kuroda(36) the carrier was labelled with Se^{75}. The chemical yield can be determined by comparing the peak area of Se^{75} in the final sample with the Se^{75} added with the carrier.

Most procedures describing the preparation of radioactive tracers use carrier techniques to separate the radionuclide from the target material. In the preparation of some radionuclides, however, it is necessary to separate them without any addition of carrier. These procedures appear under a separate classification: carrier-free separation. In addition to the procedures cited, it should be possible to use ion exchange in the carrier-free separation of radioactive selenium isotopes.

Procedures are also included for the anlysis of fission-product activities in plant-process solutions.

X. INDEX OF SEPARATION PROCEDURES

1. ACTIVATION-ANALYSIS PROCEDURES

2. TRACER-PREPARATION PROCEDURES

3. FISSION-PRODUCT PROCEDURES

4. CARRIER-FREE SEPARATION PROCEDURES

1.1 Metals and Alloys, Biological Materials, Waters(76,77-79)

Procedure used in:	Activation analysis
Method:	Volatility and precipitation
Nuclear bombardment:	$Se^{74}(n,\gamma)Se^{75}$ $Se^{80}(n,\gamma)Se^{81m}$ $Se^{80}(n,\gamma)Se^{81}$
Procedure by:	Leddicotte, G. W.(76)
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

1.1.1 Irradiation of Sample Materials

Irradiate known amounts of test (Note 1) and comparator (0.025 to 0.030 g of Se 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.

1.1.2 Preparation of Comparator Samples

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

b. Pipet a 1.00-ml aliquot of this solution into a second 100-ml volumetric flask; dilute to volume with water and mix well.

c. 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 Se concentration (Note 4). Also add 1 ml each of hold-back carriers of As, Cu, Co, Fe, Na, and Sr (Notes 5 and 6). Continue with Part 1.1.4 below.

1.1.3 Preparation of Test Samples

a. 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 standard carrier solution of known Se concentration. Also add 1 ml each of holdback carriers of As, Cu, Co, Fe, Na and Sr (Notes 5 and 6). To this mixture, add dropwise enough concentrated mineral acid to dissolve the sample completely. If necessary, heat the mixture to effect solution. Continue with Part 1.1.4 below.

b. 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 Se concentration. Also add 1 ml each of holdback carriers of As, Cu, Co, Fe, Na, and Sr (Notes 5 and 6). Continue with Part 1.1.4 below.

c. 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 pipet) to the same distillation flask 2.00 ml of a standard carrier solution of known Se concentration. Also add 1 ml each of holdback carriers of As, Cu, Co, Fe, Na and Sr (Notes 5 and 6). To this mixture add 3 ml of H_2O, 1 ml of $6\underline{M}$ 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 to 2 hours. Remove the flask from the hot plate, cool it and continue with Part 1.1.4 below.

1.1.4 Radiochemical Separation of Selenium

a. Add 10 ml of concentrated HCl and 10 ml of 48% HBr 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.

b. 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).

c. Remove the centrifuge tube containing the distillate fraction from the ice bath, then neutralize the solution by adding concentrated NH_4OH dropwise (Note 9).

d. 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 Se. Centrifuge the mixture; discard the supernatant liquid.

e. 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 and stir.

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

g. Dry the precipitate for 30 minutes in a drying oven at 110°C (Note 10). Weigh the Se metal precipitate (Note 11) and filter paper on an analytical balance. Then mount the precipitate for the radioactivity measurements.

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

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

The analyses 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} (18.2m) 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, the major gamma radiations are measured.

b. Following the radioactive measurements, the observed radioactivity is corrected for loss of carrier during the experiment, half-life of the selenium isotope measured, and the 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:

$$\text{Percent stable Se in test sample} = \frac{\text{Corrected Se radioactivity: in test sample}}{\text{Corrected Se radioactivity: in comparator sample}}$$

NOTES:

1. At least 0.10-g portions of solid samples (metals, alloys, tissue, etc.) should be used. Liquid samples (water, body fluids, etc.) should be 1 to 20 ml.

2. Comparator sample may be either Se metal or a solution of a Se compound. If a solution is used, an aliquot of the irradiated solution containing at least 20 micrograms of Se can be pipetted directly into the distillation flask.

3. The sensitivity of the method is such that 2×10^{-8} gm of Se 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 mg/ml.

5. Holdback carriers should be made up to contain 5 mg/ml of desired elemental species.

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

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

8. Tellurium, As, Sb or Ge can follow, wholly or in part, through this distillation procedure. In most of the materials analyzed by this method, the radioactive contaminants were in minor concentrations, or completely eliminated, in the reduction of Se to elemental form.

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

10. If the 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 Se-metal precipitate obtained here with the theoretical yield expected for the amount of Se 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.

1.2 Ore Concentrates, Slags, Waste Gases(75)

Procedure used in:	Activation analysis
Method:	Volatility and precipitation
Type of bombardment:	$Se^{74}(n,\gamma)Se^{75}$
Procedure by:	Fineman, et al.(75)
Chemical yield of carrier:	50-80%
Separation time:	Several hours
Degree of purification:	Excellent from other volatile impurities
Equipment required:	Neutron source and standard laboratory equipment

1.2.1 Procedure:

a. Irradiate samples (0.1 to 1 g) in a nuclear reactor for 14 days at a flux of 4×10^{11} n/cm$^2\cdot$sec.

b. Mix a weighed amount of Se (10-100 mg) thoroughly with irradiated sample and fuse the mixture in a nickel or iron crucible with 25 grams of Na_2O_2 at 900-1000°C.

c. Dissolve cake in 50 ml of water. Cool solution and neutralize with (1:1) H_2SO_4. Add at least 50 ml more of concentrated H_2SO_4 to the solution and evaporate to 100 ml. To separate SiO_2, boil the solution for 15 minutes, then cool to 60 to 70°C. Add 15 ml of 5% gelatin solution and bubble air through the solution for 30 minutes. Add hot water (50 ml) to the solution and filter the SiO_2. Evaporate the filtrate to 100 ml, cool, and then transfer to a distillation flask.

d. Add 100 ml of 48% HBr, containing 7 ml Br_2, to the flask, and distill the mixture into 10 ml of water; collect 40-50 ml distillate.

e. Neutralize distillate with NH_4OH, add 10 ml HCl and 1-2 g hydrazine sulfate. After a 12-hour digestion, filter, wash with water and ethanol, and dry at 105°C; weigh and mount for the radioactivity measurement.

f. Measure the Se^{75} gamma radioactivity by use of a 3" x 3" NaI(Tl) scintillation crystal.

g. Irradiate and process comparator samples in a similar manner to obtain the Se concentration of the materials being analyzed.

1.3 Stony Meteorites(80)

Procedure used in:	Activation analysis
Method:	Fusion, precipitation and ion exchange
Type of nuclear bombardment:	$Se^{74}(n,\gamma)Se^{75}$
Procedure by:	Schindewolf(80)
Chemical yield of carrier:	Quantitative
Separation time:	Several hours
Degree of purification:	Decontamination of $>10^4$ for Ag, Ce, Co, Cs, Hg, Ir, Ru Sb, Sc, Ta, Zn, and Zr.
Equipment required:	Neutron source and standard laboratory equipment

1.3.1 Procedure:

a. Irradiate powdered meteorite samples weighing 0.050 to 0.20 grams.

b. Add 0.020 g each of Se and Te to the irradiated sample and fuse the mixture in a nickel crucible with 1-2 grams of Na_2O_2.

c. After cooling, dissolve the cake in 6N HCl and boil the mixture. Reduce Se and Te to elemental form with SO_2 gas.

d. Dissolve precipitate in aqua regia and make the solution basic with NH_4OH. Scavenge impurities with $Fe(OH)_3$.

e. Acidify the solution with HCl and then adsorb Se and Te on a Dowex-1 (100-200 mesh) anion-exchange resin column. Selenium can be separated from Te by eluting it from the column with 3 to 5-column volumes of 3N HCl.

f. Treat the acid solution with SO_2 gas to reduce Se to the elemental form. Collect precipitate by filtration, weigh, and mount for the radioactivity measurement.

g. Measure the Se^{75} gamma radioactivity with a 3" x 3" NaI(Tl) scintillation crystal.

h. Irradiate and process comparator samples in a similar manner to obtain the Se concentration of the meteorite.

1.4 Fertilizers, Tomato Tissues, Human Blood(60)

Procedure used in:	Activation analysis
Method:	Volatility and precipitation
Type of nuclear bombardment:	$Se^{80}(n,\gamma)Se^{81}$
Procedure by:	Bowen and Cawse(60)
Chemical yield of carrier:	70%
Separation time:	40 minutes
Degree of purification:	Decontamination from arsenic, bromine, manganese, sodium and zinc was found to be satisfactory
Equipment required:	Neutron source and standard laboratory equipment

1.4.1 Procedure:

a. Irradiate samples in a nuclear reactor for 18 minutes at a flux of 10^{12} n/cm$^2\cdot$sec.

b. After irradiation transfer the sample to a beaker containing 10 ml of ashing mixture (1:1 16$\underline{N}$ HNO_3-70% $HClO_4$) and $\sim$ 25 mg each of As, P, Mn, and Te carrier solutions.

c. Heat solution until organic is destroyed and fumes of perchloric acid evolve.

d. Transfer acid solution to distillation flask with 5 ml each of HCl and HBr. Distill for 4 minutes using N_2 as a carrier gas.

e. Collect distillate in 50-ml centrifuge tube containing 5 ml of HCl, 10 ml water, 0.1 ml of Teepol solution (wetting agent, Shell Chemical Company) and 2 drops of Mn carrier.

f. Pass sulfur dioxide through solution for 1 minute and centrifuge the selenium precipitate.

g. Dissolve the precipitate in about 0.25 ml of HNO_3. Add ten ml of hot water, 0.1 ml of H_2O_2 and 5 ml of HCl, and precipitate the Se again with SO_2.

h. After separation by centrifugation, wash the precipitate with water and acetone, and transfer to a weighed aluminum counting tray with acetone.

i. After the sample is dry, count the beta-activity with an end-window Geiger counter. Check radiochemical purity by comparing decay curves of samples and standards over several half-lives.

j. After counting, weigh the selenium to obtain the chemical yield of the carrier.

k. Irradiate comparator samples and process in a similar manner to obtain the Se concentration of the materials being analyzed.

1.5 Silicate Rocks and Sediments(36)

Procedure used in:	Activation analysis
Method:	Solvent extraction
Type of nuclear bombardment:	$Se^{78}(n,\gamma)Se^{79m}$
Procedure by:	Kuroda, R. reported by Meinke(36)
Chemical yield of carrier:	$\sim$ 69%
Separation time:	10 minutes
Degree of purification:	Good except for iodine radioactivity
Equipment required:	Neutron source and standard laboratory equipment

1.5.1 Procedure:

a. Irradiate 1-g sample in nuclear reactor for 10 minutes at a neutron flux of 2×10^{12} n/cm$^2\cdot$sec.

b. Fuse the sample with 6 g of Na_2O_2 containing 30 mg of Se carrier labeled with a known amount of Se^{75} (121 d).

c. Cool the crucible in an ice bath; put the crucible into a beaker; and add successively 10 ml of H_2O, 10 ml of formic acid, 35 ml of HCl and 75 ml of HBr.

d. Filter off the precipitated sodium salts.

e. Add a few grams of hydroxylamine hydrochloride and 15 ml of 2,6-dimethyl-4-heptanone to the filtrate and stir vigorously with a mechanical stirrer.

f. Wash the organic phase with 50 ml of water (Note 1).

g. Wash the organic phase again with 20 ml of 5% tartaric acid and then with 40 ml of 5% EDTA solution containing small amounts of 1N NaOH. Discard washings.

h. Dilute the organic phase to 15 ml with the extractant and measure the Se^{79m} gamma activity.

i. Chemical yield is determined by comparing the peak area of Se^{75} in the organic phase from sample with that of Se^{75} in a known amount of carrier.

NOTE:

1. If the two layers do not separate quickly, add small amounts of formic acid.

1.6 Platinum Metal (84)

Procedure used in:	Activation analysis
Method:	Ion exchange and precipitation
Type of nuclear bombardment:	$Se^{74}(n,\gamma)Se^{75}$
Procedure by:	Morris and Killick (84)
Chemical yield of carrier:	~ 80%
Separation time:	Several hours
Degree of purification:	Separation factor of selenium from tellurium of greater than 10^4.
Equipment needed:	Standard

1.6.1 Procedure:

a. Irradiate sample (0.1 g) in nuclear reactor for 12 days at a flux of 10^{12} n/cm^2·sec.

b. Transfer sample to a flask attached to a water-cooled reflux condenser that contains 10 mg of Te and 15 mg of Se carriers. Wash samples into flask with 6M HNO_3 and add 5 ml of 12M HCl and dissolve the platinum by warming at 60°C on a water bath.

c. Remove HNO_3 by adding 12M HCl and heating. Cool, and transfer to a centrifuge tube. Dilute to 35 ml with water. Place in an ice bath and add 1 g NH_4Cl to precipitate $(NH_4)_2 PtCl_6$. Allow to stand 10 minutes and centrifuge.

d. Separate supernate into clean centrifuge tube. Pass SO_2 rapidly through solution for 2 to 3 minutes. Centrifuge and wash with water.

e. Dissolve Se and Te in minimum amount of 12M HNO_3. Add 2 mg of Pd carrier and dilute to 20 ml with H_2O. Heat to boiling. Neutralize with 6M NaOH and add 1 ml more of the reagent. Add 1 to 2 mg Fe^{+3} carrier dropwise with stirring. Centrifuge and discard the precipitation of $Fe(OH)_3$.

f. Add 1 ml of 6M HNO_3 to supernate and then add, with stirring, 1 ml of 1% solution of dimethylglyoxime in 95% C_2H_5OH. Allow to stand 10 minutes and filter through a Whatman No. 41 paper. Evaporate the filtrate to dryness, adding a few drops of 10% KI during the evaporation; then dissolve with 5 ml of 12M HCl.

g. Pass the solution through a deacidite FF (100-200 mesh, preequilibrated with 12M HCl) anion-exchange column (equivalent to Resin Dowex 1-X8), 5 cm in length and 1 cm in diameter. Elute with 20 ml of 3M HCl into a 50-ml glass centrifuge tube.

h. Add 20 ml of 12M HCl to the eluate in a centrifuge tube. Pass SO_2 through the solution to precipitate the Se and centrifuge. Wash with water and dissolve in minimum quantity of 6M HNO_3. Evaporate to dryness. Add 1 ml of 6M NaOH, then 20 ml of 6M HCl, and boil for 15 minutes. After the addition of 10 ml of 20% solution of hydroxylamine hydrochloride, centrifuge, then discard supernate. Wash the Se with water and then with C_2H_5OH. Transfer the precipitate with a little C_2H_5OH to a weighed aluminum counting tray, and dry at 100°C. Weigh as Se and determine the chemical yield.

2.1 Arsenic(81)

Procedure used in:	Preparation of radioactive tracers
Method:	Volatility and precipitation
Type of nuclear bombardment:	194-Mev deuterons
Procedure by:	H. Hopkins, Jr., reported by Meinke(81)
Separation time:	45 minutes
Chemical yield of carrier:	$> 90\%$
Decontamination:	Radiochemically pure by a factor of ~ 100
Equipment needed:	Standard

2.1.1 Procedure:

a. Dissolve As metal in minimum 10N HNO_3.

b. Add 5 mg Se carrier, evaporate to near dryness to remove excess HNO_3.

c. Make up to 3 ml with 1N HCl, add $NH_2OH \cdot HCl$ until Se **starts** to precipitate from hot solution.

d. Add 1 ml 1N KI, heat 5 minutes, centrifuge off mixture of Se and I_2.

e. Dissolve with a minimum amount of fuming HNO_3, repeat precipitation.

2.2 Bismuth Metal(81)

Procedure used in:	Preparation of radioactive tracers
Method:	Volatility and precipitation
Type of nuclear bombardment:	184" cyclotron (388-Mev alphas; 348-Mev protons; 194-Mev deuterons)
Procedure by:	Goeckerman, reported by Meinke(81)
Separation time:	1 hour
Chemical yield of carrier:	$\sim 90\%$
Decontamination:	$\sim 10^4$ from fission and spallation products
Equipment needed:	Standard

2.2.1 Procedure:

a. To aliquot of HNO_3 solution of target, add 10 mg Se and Te, 10 ml concentrated HBr, and 0.5 ml liquid Br_2 in a glass still. Using an air stream, distill into a centrifuge tube containing 5 ml saturated Br_2 water, which is cooled in an ice bath, distill until only a 3-ml residue remains.

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

c. Dissolve Se in a few drops of concentrated HNO_3, add 10 ml concentrated HCl and reduce with SO_2 in an ice bath. Centrifuge with aerosol.

d. Repeat $SeBr_4$ distillation and Se precipitations as often as necessary for desired purity.

e. Precipitate Se, filter, wash three times with 5 ml H_2O, three times with 5 ml ethyl alcohol, three times with 5 ml ether, dry 10 minutes at 110°C. Weigh as Se.

2.3 Uranyl Nitrate(36)

Procedure used in:	Preparation of radioactive tracers
Method:	Solvent extraction
Type of nuclear bombardment:	Neutron - 5 min. at power level of 1000 Kw.
Procedure by:	Kuroda, reported by Meinke(36)
Separation time:	19 min.
Chemical yield of carrier:	70%
Decontamination:	Radiochemically pure by gamma spectroscopy
Equipment needed:	Neutron source and standard laboratory equipment

2.3.1 Procedure:

a. Dissolve 30-50 mg irradiated uranyl nitrate in 20 ml of concentrated HBr containing $\sim$ 1 mg of Te and 30 mg of Se carriers. Pass air stream through the solution for 5 minutes to expel fission gases.

b. Extract Se with 5 ml of 2,6-dimethyl-4-heptanone for 40 sec. and discard aqueous phase.

c. Shake the organic phase for 30 seconds with 10 ml 10% tartaric acid; repeat with 10 ml of 1N NaOH. Discard aqueous phases.

d. Wash the organic phase by shaking for 30 seconds with 30 ml of a solution 5% in EDTA and 5% in sodium tartrate. Then shake with 20 ml of water.

e. Strip Se from the organic phase by shaking for 20 seconds each with three 10-ml portions of Cl_2-saturated water.

f. To the aqueous phase add a few mg of iodide carrier and 6 ml of 1N NaOH and shake.

g. Add 20 drops of conc. HNO_3 to acidify the solution.

h. Add dropwise a 20% solution of hydroxylamine hydrochloride until brown color of iodine appears.

i. Extract iodine with successive 5-ml portions of carbon tetrachloride until the color of the organic phase disappears.

j. The organic phase is discarded each time and the radiochemical purity of the aqueous phase is tested by gamma spectroscopy.

3.1 Fission-Product Solutions(82)

Procedure used in:	Determination of fission-product activities in plant process solutions.
Method:	Volatility and precipitation
Type of nuclear bombardment:	Uranium fission
Procedure by:	Glendenin and Winsberg(83)
Chemical yield of carrier:	80%
Separation time:	1 hour
Degree of purification:	Excellent
Equipment required:	Standard laboratory equipment

3.1.1 Procedure:

a. 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 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 to 3 ml of solution remains in the distillation flask (Note 2).

b. 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).

c. Dissolve the Se by heating with 5 to 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 b.

d. Repeat step c.

e. Transfer the Se with 5 to 10 ml of water onto a weighed paper (Note 5) in a small Hirsch funnel and filter with suction. Wash three times with 5 ml of ethanol, and three times with 5 ml of ether. Dry at 110°C for ten 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.

3.2 Irradiated Polyphenyls(85)

Procedure used in:	Determination of fission product activities in irradiated polyphenyls
Method:	Volatility and precipitation

Type of nuclear bombardment:	Uranium fission
Procedure by:	Felber and Koch(85)
Chemical yield of carrier:	50-90%
Degree of purification:	Good
Equipment required:	Standard laboratory equipment

3.2.1 Procedure:

a. Aliquots of samples (not exceeding 15 grams) and carriers are dissolved in conc. HNO_3, and perchloric acid is added to decompose the organic material. Sample is taken to fumes of $HClO_4$.

b. Sulfur is separated from the solution by precipitation of $BaSO_4$.

c. Selenium is separated by reduction with SO_2. The Se precipitate is dissolved in conc. HBr containing sulfuric and nitric acids. $SeBr_4$ is distilled in the presence of air into water. Selenium metal is precipitated by reduction with SO_2.

d. Selenium is distilled a second time and the metal is repeatedly precipitated, and then weighed as the metal and the Se^{75} is counted.

4.1 Szilard-Chalmers Reaction

Procedure used in:	Carrier-free separation of Selenium radioactivity
Radioelement(s) separated:	Se^{83}(25m), Se^{81m}(59m), Se^{81}(17m), and Se^{75}(121d)
Procedure by:	Gest and Edwards(86)

4.1.1 Procedure:

a. One gram of ammonium selenite (Note 1) irradiated for 30 minutes.

b. After irradiation dissolve selenite in 3N HCl and extract with CS_2 (Notes 2 and 3).

c. Evaporate CS_2 fraction to dryness and the take up Se in conc. HNO_3.

NOTES:

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

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

3. In a second method, a 6N 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.

4.2 Deuteron Bombardment of an Arsenic Target

Procedure used in:	Preparation of carrier-free selenium
Method:	Bombardment of arsenic target
Type of bombardment:	19-Mev deuteron bombardment with 60" cyclotron
Time of separation:	3-4 hours
Chemical yield:	80-95%
Procedure by:	Garrison, Maxwell and Hamilton(8)
Degree of purification:	At least factor of 10^3
Equipment required:	Standard laboratory equipment

4.2.1 Procedure:

a. Dissolve arsenic-powder target in aqua regia.

b. Add 12N HCl to destroy excess HNO_3 and adjust acidity to 3N.

c. Add 10 mg of tellurous acid and precipitate Te with SO_2; approximately 95% of Se carries.

d. Dissolve the Te precipitate in conc. HNO_3 and reprecipitate from 3N HCl in presence of As holdback carrier.

e. Repeat Step d two more times.

f. Wash the Te precipitate, dissolve in minimum volume of 16N HNO_3, and transfer to distilling flask.

g. Add 14% HBr dropwise while a stream of N_2 carrier gas is bubbled through the solution at 200°C. Collect the distillate in a water trap cooled with ice.

h. Remove the HBr with HNO_3 and evaporate to dryness on 40 mg of NaCl in the presence of excess HCl. The activity, presumably as selenate, is quantitatively soluble in 5 ml of water.

4.3 Uranium Fission

Procedure used in:	Preparation of carrier-free selenium radioactivities
Type of bombardment:	Neutron source
Radioelement(s) separated:	Se^{77m}(17.5 s), Se^{79m}(3.9 m), Se^{81m}(57.5 s), Se^{81}(18.2 m).
Procedure by:	Kuroda, reported by Meinke(36)
Degree of purification:	Radiochemically pure by gamma spectroscopy
Equipment required:	Standard

4.3.1 Procedure:

a. Put irradiated uranyl nitrate (40-50 mg) into a centrifuge tube. Add 2 or 3 drops of concentrated nitric acid and 4 ml of water. Pass air stream through solution for 5 minutes.

b. Add $\sim$ 1 mg of Te carrier and 20 ml of conc. HBr.

c. Extract selenium with 5 ml of 2,6-dimethyl-4-heptanone for 40 seconds and discard aqueous phase.

d. Shake the organic phase for 30 seconds with 10 ml 10% tartaric acid; repeat with 10 ml of 1N NaOH. Discard aqueous phases.

e. Wash the organic phase by shaking for 30 seconds with 30 ml of a solution 5% in EDTA and 5% in sodium tartrate, then shake with 20 ml of water.

f. Strip selenium from the organic phase by shaking for 20 seconds each with three 10 ml portions of Cl_2 - saturated water.

g. To the aqueous phase add a few mg of iodide carrier and 6 ml of 1N NaOH and shake.

h. Add 20 drops of conc. HNO_3 to acidify the solution.

i. Add dropwise a 20% solution of hydroxylamine hydrochloride until brown color of iodine appears.

j. Extract iodine with successive 5-ml portions of carbon tetrachloride until the color of the organic phase disappears.

k. The organic phase is discarded each time, and the radiochemical purity of the aqueous phase is tested by gamma spectroscopy.

5. CARRIER PREPARATION AND STANDARDIZATION

1. Preparation

Dissolve 16.4 grams of selenious acid in water and dilute to one liter (1 ml = ~ 10mg Se).

2. Standardization

Pipet 5 ml of carrier solution into a beaker. Add 100 ml of 5N HCl. Add 10 ml of a 25% hydroxylamine hydrochloride solution. Heat for 1-2 hours at 90°C. Filter through a pretreated sintered glass crucible, wash with water, and then with alcohol. Dry in an oven at 105-110°C for 20 minutes. Cool and weigh as selenium metal.

$$\text{Mg Se/ml} = \frac{\text{wt. of Se metal}}{5 \text{ ml}}$$

NOTES:

1. If the red selenium is overheated it may convert to the crystalline grey-black variety. This may result in high results due to the occlusion of water and oxidation.

2. To prevent oxidation the precipitate can be dried in an atmosphere of carbon dioxide.

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