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NUCLEAR SCIENCE SERIES

The Radiochemistry
of Antimony

U.S.
Atomic
Energy
Commission

COMMITTEE ON NUCLEAR SCIENCE

The Radiochemistry of Antimony

WILLIAM J. MAECK

Phillips Petroleum Company
Atomic Energy Division
Idaho Falls, Idaho

February 1961

Subcommittee on Radiochemistry
National Academy of Sciences — National Research Council

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 antimony 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 antimony which might be included in a revised version of the monograph.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to James E. Rein for reviewing the manuscript and to Deanna Shawneen Anderson for typing and preparing the manuscript for publication.

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WILLIAM J. MAECK

Phillips Petroleum Company
Atomic Energy Division
Idaho Falls, Idaho

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6. Wagner, W., Hull, C. J., Markle, G. E., "Advanced Analytical Chemistry", Reinhold, New York (1956).

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II.   GENERAL REVIEWS OF THE RADIOCHEMISTRY OF ANTIMONY

1. Coryell, C. D., Sugarman, N., eds. "Radiochemical Studios: The Fission Products", Book 3, National Nuclear Energy Series, McGraw-Hill, New York (1951).

2. Finston, H. L., Miskel, I., Ann. Rev. Nucl. Sci., $\underline{5}$, 269-296 (1955).

III.   TABLE OF ANTIMONY ISOTOPES

Isotope	Half-Life	Type Of Decay	Energy Of Radiation in Mev	Assignment
Sb^{115}	60 m	β^+	0.75, 1.10	mass assignment
		γ	0.060, 0.090	uncertain
Sb^{116}	15 m	β^+	1.5, 2.4	In^{115} (26-Mev α, 3n) ?
		γ	0.90, 1.31, 2.22	Sn^{116} (>5-Mev p, n) ?
Sb^{116m}	60 m	β^+	1.45	In^{115} (α, 3n) ?
		γ	0.41, 0.95, 1.31	In^{113} (20-Mev α, n) ?
Sb^{117}	2.8 h	β^+ (2.5%)	0.6	In^{115} (α, 2n) ?
		EC (97.5%)		Sn^{116} (5-Mev d,n) ?
		γ	0.161	Sn^{117} (5-Mev p,n) ?
$Sb^{118\,m}$	3.5 m	IT (?)		In^{115} (11-Mev α,n) ?
		β^+	3.10	In^{115} (16-Mev α,n) ?
		γ	1.24	
Sb^{118}	5.1 h	No β^+ (<0.4%)		In^{115} (20-Mev α,n) ?
		EC		Sn^{117} (10-Mev d,n) ?
		γ	0.040, 0.255, 1.03, 1.22	

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III. TABLE OF ANTIMONY ISOTOPES - cont'd

Isotope	Half-Life	Type Of Decay	Energy Of Radiation in Mev	Assignment
Sb^{119}	38.0 h	EC	0.53 bremstrahlung endpoint	d 16^h Te^{119}
		γ	0.024	Sn^{119} (5-Mev p,n) ?
				Sn^{118} (10-Mev d,n) ?
Sb^{120m}	5.8 d	No IT		Sn^{119} (18-Mev d,n)
		No β^+		Sn^{120} (18-Mev d,2n)
		γ	0.090, 0.200, 1.040, 1.170	Sb^{121} ($\leq$ 50-Mev γ,n) ?
Sb^{120}	16.4 m	β^+	1.70	Sb^{121} (17-Mev α,n) ?
		γ	1.18	Sn^{119} (5-Mev d,n) ?
				Sb^{121} (15-Mev n,2n) ?
$\underline{Sb^{121}}$	57.25%			
$Sb^{122\,m}$	3.5 m	IT		Sb^{121} (th n, γ)
		γ	0.061, 0.075	
Sb^{122}	2.80 d	β^+(0.01%)	0.565	Sb^{121} (th n, γ)
		β^-(97%)	0.74, 0.90, 1.40, 1.97	Sn^{122} (5-Mev d,2n) ?
		EC(3%)		

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III.   TABLE OF ANTIMONY ISOTOPES - cont'd

Isotope	Half-Life	Type Of Decay	Energy of Radiation in Mev	Assignment
Sb^{123}	42.75%			
$Sb^{124\ m2}$	21 m	IT		Sb^{123} (th n, γ)
		γ	0.0185	
		β^- (W)	$\sim$ 2.5	
$Sb^{124\ m1}$	1.3 m	IT		Sb^{123} (th n, γ)
		γ	0.012	
		β^-	3.2	
Sb^{124}	60.4 d	β^-	0.202, 0.36, 0.608, 0.745 0.871, 0.930, 1.590, 1.658	Sb^{123} (th n, γ) I^{127} (fast n, γ)
		γ	0.603, 0.632, 0.645, 0.713, 0.722, 0.967, 1.05, 1.33, 1.37, 1.45, 1.70, 2.09, 2.3	
Sb^{125}	2.0 y	β^-	0.125, 0.300, 0.444, 0.612	U (n,f)
		γ	0.113, 0.175, 0.205, 0.214 0.320, 0.377, 0.427, 0.463 0.595, 0.637	Sn^{124} (pile n, $\gamma\beta$) ? d 9.4^d Sn^{125} p $Te^{125\ m}$

III. TABLE OF ANTIMONY ISOTOPES - cont'd

Isotope	Half-Life	Type Of Decay	Energy of Radiation in Mev	Assignment
Sb^{126}*	18.8 m	β^-	?	U (n,f)
		γ	0.42, 0.65	Te^{126} (fast n,p)
Sb^{126}*	6.2 d	β^-	0.86	U (n,f)
		γ	0.417, 0.685, 0.90	Te^{128} ($\leq$ 70-Mev γ,p,n) ?
			1.10, 1.35	U (26-Mev d,f)
Sb^{127}	3.66 d	β^-	1.11, 1.50	U (n,f)
		γ	0.60, 0.248, 0.310	U (26-Mev d,f)
			0.463, 0.772	p 9.3^h Te^{127} (78%)
				p 105^d Te^{127} (22%)
Sb^{128}*	10.7 m	β^-	2.9	U (n,f)
		γ	0.32, 0.75	Te^{128} (n,p)
				Te^{130} (28-Mev d, α) ?
Sb^{128}*	9.9 h	β^-	1.0	U (n,f)
		γ	0.32, $\sim$0.4, 0.75, 0.90 ?	Te^{128} (n,p)
				Te^{130} (28-Mev d, α) ?

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III. TABLE OF ANTIMONY ISOTOPES - cont'd

Isotope	Half-Life	Type Of Decay	Energy of Radiation in Mev	Assignment
Sb^{129}	4.6 h	β^-	1.87 (20%) others	U (n,f)
		γ	0.165, 0.308, 0.534, 0.788	p67^m Te^{129} (76%)
				p33^d Te^{129} (24%)
Sb^{130}	33 m	β^-		U (n,f)
				Te^{130} (n,p)
Sb^{130}	7.1 m	β^-		U (n,f)
				Te^{130} (n,p)
Sb^{131}	23.1 m	β^-		U (n,f)
				p 25m Te^{131} (85%)
				p 1.2^d Te^{131} (15%)
Sb^{132}	2.1 m	β^-		U (n,f)
				p 78^h Te^{132}
Sb^{133}	4.1 m	β^-		U (n,f)
				p 53^m Te^{133} (92%)
				p 2^m Te^{133} (8%)

III. TABLE OF ANTIMONY ISOTOPES - cont'd

Isotope	Half-Life	Type Of Decay	Energy of Radiation in Mev	Assignment
Sb^{134}	45 s	β^-		U (n,f) ? assignment uncertain

*Mass and half-life assignments are uncertain. See National Research Council Nuclear Data Sheets

Sb-128-1 NRC 58-8-11 for discussion of assignments.

Sources of data used in this compilation and to be referred to for additional information are as

follows:

1. Nuclear Data Sheets, National Academy of Sciences- National Research Council,

   2101 Constitution Avenue, Washington 25, D.C.

2. Strominger, D., Hollander, J. M., Seaborg, G. T., Rev. Mod. Physics 30, 585 (1958).

3. Sullivan, W. H., Trilinear Chart of Nuclides (1958 and revisions), Supt. of Documents,

   U. S. Government Printing Office, Washington 25, D.C.

IV-1 OXIDATION STATES

Other than the metal, the common oxidation states of antimony are

-3 in SbH_3, +3 in Sb_2O_3, and +5 in Sb_2O_5. Claims made for the existence

of $H_2Sb_2O_5$ and the stability of Sb_2O_4 indicate a +4 crystalline state

also. Latimer[2] summarizes the oxidation-reduction potentials of the

couples as:

$$SbH_3 \xrightarrow{0.51} Sb \xrightarrow{-0.212} SbO^+ \xrightarrow{-0.68} Sb_2O_4 \xrightarrow{0.48} Sb_2O_5 \quad \text{(Acid)}$$
$$\text{(from SbO}^+\text{ to Sb}_2O_5\text{) } -0.581$$

$$SbH_3 \xrightarrow{(1.34)} Sb \xrightarrow{0.66} SbO_2^- \xrightarrow{(0.40)} H_3SbO_6^{-4} \quad \text{(Base)}$$
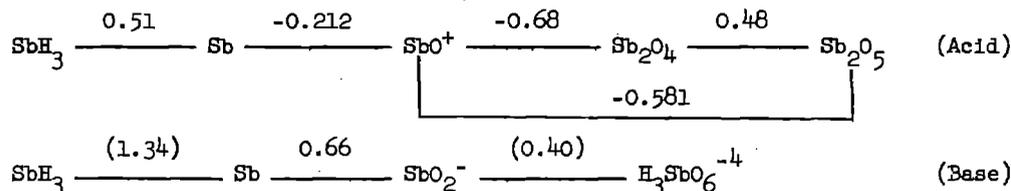
Reduction to the metal is easily performed with Pb, Sn, Bi, Cu, Cd,

Fe, Zn, and Mg. In some cases where the metals evolve hydrogen from

dilute acid, partial reduction to SbH_3 may occur[3]. Kjelbert and Pappas[4]

used chromous ion for reduction in a radiochemical procedure (see

Antimony Procedure No. 5, Section VIII). Robinson and Milton[5] separated

antimony from irradiated $SnCl_2$ by depositing it as the metal on copper

from an acid halide solution without the use of external current. Under

the best conditions a yield of 71% is reported.

In the analytical laboratory, antimony is commonly found as the +3

or +5 salt. Metallic antimony is easily oxidized to Sb(III) and to as

high as +5 by HNO_3, Cl_2, Br_2, Cr(VI), Mn(VII), and other strong oxidants,

depending on the amount of reagent and temperature. Iodine oxidizes Sb^0

to Sb(III) and in alkaline solution Sb(V) may form.

Antimonic compounds are reduced to the +3 state by $SnCl_2$ (distinc-

tion from As) and NaH_2PO_2.

IV-2 ELEMENTAL ANTIMONY

According to Sidgwick[1], there are four solid forms of antimony

metal.

IV-2.1 _Yellow Antimony._ This form is transparent and soluble in carbon

disulfide. It is evidently covalent and corresponds to white phosphorous and yellow arsenic.

IV-2.2 _Black_ _Antimony_. The action of oxygen on stibine at low temperatures or the rapid cooling of antimony vapor gives this form. It is formed from the yellow species and is more chemically active than the ordinary form.

IV-2.3 _Metallic_ or _Ordinary_ _Antimony_. This form is truly metallic, melting at 630°C. and boiling at 1325°C.

IV-2.4 _Explosive_ _Antimony_. The electrolysis of antimony trichloride, tribromide, or triiodide with high current density produces this form. On heating to 200°C. or scratching, it changes explosively to the ordinary form.

IV-3 OXIDES OF ANTIMONY

Three oxides of the element exist, Sb_2O_3, Sb_2O_4, and Sb_2O_5. The trioxide along with some tetroxide is formed when the metal is burned in air. Heating the trioxide in air to $300\text{-}400^\circ$C. forms the tetroxide; however, at higher temperatures (i.e. 900°C.) it decomposes back to the trioxide. The trioxide is amphoteric, it dissolves in concentrated acids and basic salts are crystallized from solution. The basic antimonyl (SbO^+) salts are hydrolyzed in hot water. The trioxide also dissolves in alkalies forming salts of antimonous acid such as $NaSbO_2 \cdot 3H_2O$.

The tetroxide is acidic in character dissolving only in basic solutions.

The pentavalent state of antimony may be prepared by the action of HNO_3 on the trioxide. The oxide and corresponding acid, $HSb(OH)_6$, are only slightly soluble in water but readily soluble in alkali.

IV-4. HYDRIDE OF ANTIMONY

Only one hydride, SbH_3, is known. It is easily prepared by cathodic reduction or by reduction of antimony compounds in acid solution by strong metal reductants. The generation of stibine as a means of separating antimony from fission product solutions is presented in Sections V-3 and VIII, Procedures 3 and 4.

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IV-5. SOLUBLE COMPOUNDS

The soluble compounds of antimony [22,23,24] are given in

Table 1.

TABLE 1. SOLUBLE ANTIMONY SALTS

Salts	Solubility in g/100 ml.		Other
	Cold H_2O	Hot H_2O	
$SbBr_3$	d.	d.	S. HCl, HBr, CS_2, NH_3, al., acet.
$SbCl_3$	601.6^o	80	S. al., HCl, tart. a., CS_2
$SbCl_5$	d.	d.	S. HCl, tart. a.
SbF_3	384.7^o	563.6^{30}	i. NH_3
SbF_5	s		S. KF
SbI_3	d.	d.	S. HI, HCl, KI, al., CS_2, acet.
SbH_3	20 cm^3	4 cm^3	1500 cm^3 al. 2500 cm^3 CS_2
$Na_3SbS_4 \cdot 9H_2O$	27.1^{30}	57.1^{80}	S. NaOH
$K_3SbS_4 \cdot 5H_2O$	75.1^{30}	79.2^{80}	S. KOH
$Li_3SbS_4 \cdot 10H_2O$	50.1^{30}		S. alc.
$(NH_4)_3SbS_4 \cdot 4H_2O$	54.5^{30}		
$(SbO)KC_4H_4O_6 \cdot \frac{1}{2}H_2O$	5.3^9	35.7^{100}	S. gly
$Sb(C_2H_4NOS)_3$	200		i. eth.
$Sb_2(C_4H_4O_6)_3 \cdot 6H_2O$	s.		

IV-6. INSOLUBLE COMPOUNDS

Of the many insoluble salts of antimony several have been used
for gravimetric determinations and to establish yields in radiochemical
procedures.

IV-6.1 Hydrolysis Products. Except for the fluoride and some organic
compounds (e.g. tartrates and citrates), all the salts of +3 Sb are
hydrolyzed, which is often overlooked by the analyst. The chloride
hydrolyzes to insoluble white oxychloride, the composition being
dependent upon the amount of water. The precipitate is soluble in

solutions of tartaric acid, strong HCl, or excess alkali halide due to complex formation. Washing the precipitate with water slowly converts it to the oxide. With $SbCl_5$, the basic salt is thought to be $SbOCl_3$, but the formula has been questioned[3].

IV-6.2 Oxides. The alkali hydroxides and carbonates precipitate white, bulky Sb_2O_3 from acid solutions of antimonous salts. The precipitate is soluble in hot solutions of excess alkali but insoluble in NH_4OH. If an alkaline solution of Sb(III) is carefully neutralized with acid (not HF, citric or tartaric) the oxide is precipitated and at once dissolved by further addition of the acid. Freshly precipitated Sb_2O_3 is soluble is oxalic acid but a precipitate soon forms unless excess alkali oxalate is present to form the soluble double oxalate[3]. The oxide or hydrated oxides are precipitated from solutions of fixed antimonites or antimonates upon neutralization with HNO_3 or other mineral acids but the freshly formed precipitate will readily dissolve in excess acid. A gravimetric procedure of weighing the tetroxide resulting from ignition of the sulfide is discussed by Hillebrand and Lundell[26].

IV-6.3 Sulfides. Hydrogen sulfide precipitates the orange-red sulfide, Sb_2S_3, from dilute acidic solutions of Sb(III). In neutral solutions (tartrate present), precipitation is incomplete. No precipitate forms in fixed alkali solutions. The sulfide is slowly decomposed by boiling water; insoluble in $(NH_4)_2CO_3$ (distinction from As); slowly soluble in boiling solutions of fixed alkali carbonates; soluble in cold concentrated and hot 1:1 HCl (distinction from As). The orange antimonic sulfide, Sb_2S_5, is precipitated under similar conditions. This sulfide has the same solubilities as the trisulfide except that it is soluble in NH_4OH[3]. All salts of antimony when boiled with $Na_2S_2O_3$ precipitate as the sulfide.

IV-6.4 Complex Sulfide. A solution of ethylenediamine and chromous chloride yields the complex $CrNH_2(CH_2)_2NH_2SbS_4$ which has been used for the microgravimetric determination of antimony[27].

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IV-6.5 <u>Silver Antimonate</u>. Antimonates precipitate with $AgNO_3$ to give white $AgSbO_3$ which is soluble in NH_4OH. A silver salt also forms when SbH_3 is bubbled through a silver nitrate solution. The silver reduces and the antimony coverts to the oxide (or acid) which is only slightly soluble in H_2O (distinction from As)[3].

IV-6.6 <u>Thioanalide</u>. Antimony(III) can be separated by precipitating $Sb(C_{12}H_{10}ONS)_3$ from either acidic or basic solutions. Chloride and sulfate interfere by causing the formation of basic salts. Arsenic, Bi, Cd, Au, Pb, Hg, Th, Sn, and the alkaline earths also precipitate[28].

IV-6.7 <u>8-Hydroxyquinoline</u>. The yellow complex $Sb(C_9H_6ON)_3$ quantitatively precipitates from acidic solution as the pH is increased toward 6. This complex is stable at $105-110°C$. and may be used for the gravimetric determination of antimony[28]. Since many other ions also react with this reagent, a preseparation is required.

IV-6.8 <u>Triphenylmethylarsonium Chloride</u>. Dwyer[29] and Figgis[30] recommend arsonium halides, especially triphenylmethylarsonium chloride and iodide, for the determination of Sb as well as for Bi and Cd. A simple ion association compound triphenylmethylarsonium tetrachloroantimonate(III) is formed. As little as 10 μg can be determined by nephelometry and larger amounts gravimetrically.

IV-6.9 <u>Pyrogallol</u>. Feigel[31] discusses the precipitation of antimony with pyrogallol. A large excess of pyrogallol in air-free water is added to a dilute acidic solution for analysis. Welcher[33] lists 18 other elements which can be determined by this reagent.

IV-6.10 <u>9-Methyl-2,3,7-Trihydroxy-6-Fluorone</u>. Feigel[32] discusses briefly the work of Wenger[33] who recommends 9-methyl-2,3,7-trihydroxyl-6-fluorone as a specific reagent for antimony. The compound is soluble in alcohol. A red compound with antimony salts forms in strongly acid solutions. It is probable that the complex can be extracted.

IV-6.11 <u>Cupferron</u>. Several elements are precipitated with cupferron from strongly acid solutions[32]. The only antimony oxidation state that

completely precipitates is +3. The pentavalent state does not precipitate. For specificity, a preseparation is required.

IV-6.12 α-Aminopyridine. An orange-yellow precipitate of antimony is formed with α-aminopyridine[33]. As little as 0.12 ug. is detected. Bismuth, Co, Cu, Au, and Zn interfere.

IV-6.13 Phenylthiohydantoic Acid. Several metals, including Pb, Ag, Cd, Cu, Co, and Sb are quantitatively precipitated with this reagent. The precipitate forms in dilute acetic acid after boiling for about 5 minutes. Welcher[33] gives a detailed procedure for the determination of antimony but it appears to offer little advantage over other methods.

IV-6.14 Methyl Violet. Antimony(V) is precipitated with methyl violet[44]. Poper[45] reports similar findings. Goto and Kakita[46] have extracted the precipitated complex into amyl acetate.

Several other organic reagents have been proposed for the detection of antimony. The reader is referred to Welcher[33] and Feigel[44] for more complete listings.

IV-7. VOLATILE COMPOUNDS AND DISTILLATION OF ANTIMONY

The volatilization of elements as bromides and chlorides has been extensively studied by Hoffman and Lundell[81]. Both Sb(III) and Sb(V) are quantitatively distilled as the bromide from $HClO_4$ or H_2SO_4. Antimony does not significantly distill as the chloride from $HClO_4$, differentiating it from Sn(II) and Sn(IV)[81]. Arsenic(III) and As(V), Re, and Ru also distill from an HBr-H_2SO_4 solution.

The volatile hydride, SbH_3 is discussed in Section IV-4. Use of the volatile halides and stibine in analytical separations is discussed in Section V-3.

IV-8. COMPLEX IONS AND CHELATES

Antimony(III) halide complexes $\left[SbX_4\right]^-$ and $\left[SbX_5\right]^=$ with X = Cl^- or F^-, have been reported. Hexahalo complexes, corresponding to $\left[SbF_6\right]^-$, $\left[SbCl_6\right]^-$, and $\left[SbBr_6\right]^-$ are also known[35]. The bromide complex differs from the chloride and fluoride by being highly colored and easily

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hydrolyzed. A heptafluoroantimony ion of unknown structure is reported[1] for the salt $K_2SbF_7 \cdot H_2O$.

Both Sb(III) and Sb(IV) form chelates with catechol. Undoubtably many of the organo compounds described in Section IV-6 are also chelates.

Little use has been made of complex ions and chelates in radio-chemical procedures for antimony. Both simple ion-association compounds and chelates are easily extracted in organic solvents and can form the basis for selective separations.

IV-9. ISOTOPIC EXCHANGE REACTIONS AND HOT-ATOM CHEMISTRY

Barker and Kahn[99] studied the rate of exchange of Sb between $SbCl_3$ and $SbCl_5$ in CCl_4. The rate of exchange is both time and light dependent. At $50^\circ C$. and $81^\circ C$. the half time of the reaction was 235 hours and 19.5 hours respectively. The rate of exchange of Sb(III) and Sb(IV) in HCl solutions according to Bonner[100] is a function of HCl concentration. The half time of the reaction is 1400 hours in $\underline{3M}$ HCl, 60 hours in $\underline{6M}$ HCl, and 36 minutes in $\underline{12M}$ HCl.

Melander[101] studied the Szilard-Chalmers reaction with both phenylstibinic acid and triphenylstibine. No concentration of Sb activity was obtained from the irradiated phenylstibinic acid. A concentration factor of 100 is obtainable by irradiating $(C_6H_5)_3$ Sb in benzene and extracting with aqueous 2% tartaric acid, 0.05% KSbO tartrate. Concentration factors up to 6000 are reported[102] for the slow neutron irradiation of $(C_6H_5)_3$ Sb in benzene followed by extraction with $2.5\underline{M}$ HCl. Large concentration factors have also been obtained by irradiating solid triphenyl antimony compounds, dissolving the target in chloroform and extracting with an aqueous KNa tartrate solution[103]. The reader is referred to Wahl and Bonner[103] for a more detailed discussion of hot-atom chemistry.

V. ANALYTICAL CHEMISTRY OF ANTIMONY APPLICABLE
TO SEPARATIONS AND YIELD DETERMINATIONS

V-1. SOLVENT EXTRACTION

Solvent extraction provides radiochemists with a rapid and simple technique for the selective separation of an element from complex mixtures. Through the judicious use of various scrubbing agents and strippants, high degrees of separation are attainable. The simplicity of the operation renders this technique easily adaptable to remote operation.

In many instances the entire separation may be performed on a carrier free basis thereby eliminating the inherent errors, such as coprecipitation and non-stoichiometric relationships, associated with gravimetric yield determinations. Because many extractable complexes are colored, the yield, if required, can in many cases be determined by a simple spectrophotometric measurement. The use of deep well crystals and gamma spectrometry combined with solvent extraction separations and spectrophotometric yields is gaining popularity in radiochemistry.

V-1.1 Ion-Association Systems

V-1.1.1 Fluoride System. Extraction studies of fluoride systems are relatively few. Kitahara[36] studied the extraction of several elements from HF solutions into ethyl ether. The extraction of Sb(III) from 3.5$\underline{M}$ HF is reported[36] to be less than 1% as is the extraction of Sb(V) from 20$\underline{M}$ HF[37]. Large quantities of Sb(V) can be extracted with diethyl ether from an aqueous phase 6$\underline{M}$ in HCl and 0.4$\underline{M}$ in HF with the extracted species probably being the chloride rather than the fluoride complex.

V-1.1.2 Chloride System. Extensive reviews of the extraction of the chloride complexes of Sb are available[38,39,40]. Edwards and Voigt[41] have shown that the extraction of antimony into isopropyl ether is superior to that of diethyl ether. The distribution coefficient is greater than 200 for Sb(V) from 6.5 to 8.5$\underline{M}$ HCl. Excellent separation

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of Sb(V) from Sb(III) is achieved. Schweitzer and Storms[43] confirm these

findings. Complete extraction of Sb(V) and 68% extraction of Sb(III)

from HCl solutions with methylisobutyl ketone has been reported[42]. The

extraction, and separation of Sb(V) from several elements, from 1 to

2$\underline{M}$ HCl containing oxalate and citrate into ethyl acetate has been

reported by White and Rose[47]. Iron, Sn, Cu, Cd, Pb, Ge, and Te are

not extracted; As, Bi, and Mo extract in trace amounts; Ag and Hg

partially extract; and Au completely extracts.

The separation of Sb from Sn, oftentimes desired in radiochemical

separations, can be attained by extraction of Sb(V) into ethyl acetate

from 6$\underline{M}$ HCl[49]. Tin(IV) remains in the aqueous phase. The separation,

by extraction into isopropyl ether, is reported by Coombe[50]. The

procedure of White and Rose[47] mentioned above is also applicable.

Tri-n-octylphosphine oxide in cyclohexane extracts antimony(III)

from 7$\underline{M}$ HCl[48] with reasonable separation from several other elements.

The extraction of Sb in chloride systems, though simple, is a

poor system because a large number of chloride complexes of other

elements also extract. The use of sequestering agents, both in the

original aqueous phase and subsequent scrubs, contributes to a cleaner

separation. Passas[64] developed a rapid (~5-min.) procedure for the

separation of short lived antimony isotopes from freshly irradiated

uranium by extraction of the chloro complex into isopropyl ether.

Molybdenum which also extracts is retained in the organic phase by

formation of the highly soluble thiocyanate complex.

V-1.1.3 Bromide Systems. Bock, Kusche, and Bock[51] extensively

studied the extraction of various elements from HBr. Ninty-five

per cent extraction of Sb(V) from 5$\underline{M}$ HBr into ethyl ether is reported,

the extraction of Sb(III) is considerably less. Gold, Ga, In, As(III),

Tl, Sn(II and IV), Mo(VI), and Fe(III) extract to greater than 50%

from 4 to 6$\underline{M}$ HBr. The same general comments given for the chloride

system regarding specificity apply to the bromide system.

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V-1.1.4 _Iodide System_. Iodide extraction systems have been more

extensively studied than bromide. Antimony(III) quantitatively

extracts from 6.9M HI into ethyl ether as do As(III), Cd(II), Au(III),

In(III), Hg(II), Tl(I), Tl(III), and Sn(II). With 1.5M KI in 0.75M

H_2SO_4, less than 50% of the antimony extracts into ethyl ether[52]. West[53]

states that small amounts of the tetraiodoantimonate(III) ion extract

into benzene from a H_2SO_4-KI aqueous phase.

V-1.1.5 _Thiocyanate System_. Slight or no extraction of Sb(III) into

ethyl ether from 0.5M HCl containing up to 5M NH_4CNS has been observed[54].

Tin(IV) quantitatively extracts from a similar media suggesting a

possible separation.

V-1.1.6 _Alkylphosphoric Acids_. Less than 5% extraction of Sb(III) and

Sb(V) with 0.6M dibutylphosphoric acid with greater than 95% extraction

of Sn(IV), Zr, Nb, Y, and In is reported[39].

V-1.1.7 _Trialkylphosphine Oxides_. With tri-n-octylphosphine oxide,

Sb(III) partially extracts from 1M HCl[48]. Complete extraction of

Sb(III) is realized by increasing the HCl concentration to 7M.

V-1.1.8 _Methyldioctylamine_. Extraction of antimony from greater

than 6M HCl is quantitative with 2 to 3 volume percent solutions of

methyldioctylamine in xylene[50]. The extraction decreases with lower

HCl concentrations.

V-1.1.9 _Quaternary Amines_. Work in progress in the author's labora-

tory pertaining to the quaternary amine extraction of the elements shows

that both Sb(III) and Sb(V) are completely extracted from 5M HCl as the

tetrabutylammonium chloro antimony complex into hexone. Little or no

extraction was observed in HNO_3, H_2SO_4, HF, or NaOH systems.

V-1.1.10 _Rhodamine B_. The chloro complex of Sb(V) forms an ion-

association complex with rhodamine B readily extractable into benzene

or ethyl acetate from 3 to 6M HCl[39]. Several investigators[55,56,57]

describe modified determinations of antimony. Recently VanAman et. al.[66]

described a colorimetric rhodamine B procedure which eliminates hydrolysis

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problems encountered in other methods. A relative standard deviation of 1.2% is reported for the range of 2-20 ug of Sb.

V-1.1.11 Methyl Violet. Antimony(V) forms a precipitate with methyl violet in HCl which is soluble in amyl acetate[46]. The sensitivity of this system is 0.1 ug./ml. Jean[58] describes the extraction of the violet blue complex from 6M HCl into benzene.

V-1.1.12 Azo Dyes. Morrison and Freiser[39] list several azo dyes which form ion-association complexes with Sb(V) in strong HCl - saturated ethanol media extractable into benzene. Generally the reactions are quite sensitive (1-8 ug./ml. of Sb).

V-1.2 Chelate Systems

V-1.2.1 Cupferron. Cupferron has been used for the separation and determination of several elements. The insoluble precipitates formed with cupferron are soluble in organic reagents such as ether and chloroform. Antimony(III) is quantitatively extracted into chloroform from 10% H_2SO_4[62]. Several other elements also extract[39].

V-1.2.2 Sodium Diethyldithiocarbamate. A 2% aqueous solution of this reagent will extract about 20 elements[39]. Between pH 4 to 9.5, Sb(III) extracts into carbon tetrachloride. Of radiochemical interest, As(III) and Sn(IV) also extract. Use of masking agents such as EDTA and cyanide have greatly increased the selectivity of this reagent.

V-1.2.3 Morin. Antimony(III), in addition to Al, Be, Ce(III), Ga, In, Sc, Sn, Th, Ti, and Zr, form complexes with morin, extractable into butyl, amyl, and cyclohexyl alcohol from acidic media[39].

V-1.2.4 8-Quinolinol. The precipitation of antimony with 8-quinolinol has been discussed in Section IV-6.7. It seems reasonable to assume that the complex is organic soluble and extractable. The reagent also reacts with about 40 other metals[39].

V-1.2.5 Potassium Xanthate. Islein and Vorbes[65] report the extraction of Sb from acidic solutions into carbon tetrachloride with potassium xanthate. Less metals are reported[39] to react with this compound

compared to the other chelates. Further investigation of this system appears warranted as an extraction procedure for the separation of Sb in fission product mixtures.

V-1.2.6 Antipyrine. The separation of Sb from Bi, Hg, Sn(IV), As(III), Zn, Co, Ni, and Cr has been reported for a chloroform system[65].

V-2 CHROMATOGRAPHY OF ANTIMONY

V-2.1 Ion-Exchange

V-2.1.1 Cation-Exchange. According to Lure and Filippora[68], antimony is separable from arsenic and tin by passage of a dilute HCl solution through the sulfonic acid cation exchanger Wofatit-P in the hydrogen form. Arsenic passes through with Sb and Sn remaining tightly bound. Bismuth is separable from Sb as the thiocyanate[68]; the separation being made with a 6% solution of NH_4CNS 0.5$\underline{M}$ in H_2SO_4. Antimony(III) can be separated from Sn(II) on Amberlite IR-120 by elution with 0.1$\underline{M}$ HCl containing 2% tartaric acid[69]. Antimony(III) elutes, and Sn(II) remains on the column. Antimony(III) and Sb(V) can be separated by eluting Sb(III) with dilute oxalic acid[70]. The unexpected adsorption of negatively charged chloride complexes, including Sb(V), on a cation exchanger has been reported[67].

V-2.1.2 Anion Exchange

V-2.1.2.1 Chloride System. Kraus and Nelson[71] extensively studied the anion exchange properties of the elements in HCl with Dowex-1. The distribution coefficient of Sb(III) is greater than 10^3 in 1$\underline{M}$ HCl while that of Sb(V) is less than 10. Separation of Sb(III) and Sb(V) is difficult due to the slow rate of desorption of Sb(V) with dilute HCl elutriant and the hydrolytic properties of Sb(III) in dilute HCl. Trace amounts (Sb^{124}) indicate that Sb(V) is not adsorbed on Dowex-1 in dilute HCl whereas Sb(III), formed by reduction of Sb(V) with H_2SO_3, is strongly adsorbed[70]. The separation of Sb(V), Te(IV), and Sn(IV) using a Dowex-1-X4 column has been reported[72]. For other possible separations the reader is referred to the summary paper of Kraus and

Nelson[71] for a table of the distribution coefficient of the elements.

V-2.1.2.2 <u>Fluoride System</u>. Faris[73] has studied the fluoride-anion exchange properties of the elements similar to that described above for chloride. Antimony(III) is strongly adsorbed in dilute HF; Sb(V) appears strongly adsorbed at all concentrations. Arsenic(V) as well as Sn(IV) are also strongly held. Arsenic(III) is not adsorbed offering some possibility for the separation of As and Sb.

V-2.1.2.3 <u>Nitrate System</u>. Faris[80] has also studied the anion exchange properties of the elements in nitric acid on Dowex 1. Antimony(V) and As(V) are not adsorbed and Sn(IV) is slightly adsorbed. This system appears to offer little advantage for the separation of Sb from other elements.

V-2.1.2.4 <u>Oxalate System</u>. Mixtures of Sn(IV), Sb(V), and Te(IV) are separable on a Dowex 1 column[74]. The sample in $3\underline{M}$ HCl - $0.1\underline{M}$ oxalic acid is placed on the column. Tellurium(IV) is eluted first with $0.1\underline{M}$ oxalic acid, then antimony is separated with $0.1\underline{M}$ pH 4.8 sodium oxalate, finally tin is removed with $1\underline{M}$ H$_2$SO$_4$.

V-2.1.2.5 <u>Malonate System</u>. The separation of tracer Sb(V) and Sn(IV) using ammonium malonate as the elutriant on an Amberlite IRA-400 column has been described[75]. The Sn(IV) malonate is retained on the column while the antimony is eluted with a 3% malonate solution at a pH of 4.8. Tin is removed with $4.5\underline{M}$ H$_2$SO$_4$.

V-2.1.2.6 <u>Sulfide</u>. The separation of Sn, As, and Sb as sulfide complexes in basic solution on Dowex 2 columns has been studied. A 3% sodium polysulfide solution is placed on a Dowex 2 column in the hydroxide form. Tin is removed with $0.5\underline{M}$ KOH, arsenic with $1.2\underline{M}$ KOH, and antimony with $3.5\underline{M}$ KOH.

V-2.2 <u>Inorganic Alumina Exchangers</u>

Numerous procedures have been developed for the separation of elements with an alumina column. Generally, washing with selected solvents separates the elements into bands which are identified by

adding reagents to form colored complexes. Arsenic(III) can be separated from Sb(III) by washing with dilute HCl and developing the color with H_2S saturated water. The upper (As) band is yellow and the lower Sb(III) band is orange-red[77]. Antimony can be removed from the elements of the tin group by addition as a Na_2S solution and washing with dilute HCl[77]. Arsenic is eluted with a Na_2S saturated solution and moves down the column as a lemon yellow band. Following the desorption of arsenic, antimony is removed with concentrated NH_4OH. Tin, Te, and Mo are partially eluted. Selenium, Sn, Te, and Mo are completely removed by washing with a solution of $(NH_4)_2S$. Arsenic and Sb are separated; Sn and Sb separation is poor. The reader is referred to Lederer and Lederer[79] for a more complete discussion of inorganic exchangers.

V-2.3 Paper Chromatography

Generally, this technique consists of dipping the end of a filter paper strip into the sample solution. The ions migrate up the paper with characteristic rates dependent on such variables as the solvent media, pH, and type of paper. In many cases, papers impregnated with $Al(OH)_3$ or an ion-exchanger have been used to increase the degree of separation. The paper may be sprayed with color forming reagents or sections cut out for subsequent quantitative analysis.

Many useful separations of As(III) and Sb(III) have been reported contrasted to few for Sb and Sn[79]. In a butanol-HCl media, As is separated from Sb and Sn. The separation of As(III) and Sb(III) has been accomplished with the lower alcohols[79]. Separation of As(III), Sb(III), and Sn(IV) has been obtained with collidine saturated with $0.4\underline{M}$ HNO_3.

V-3 DISTILLATION AND VOLATILIZATION

The volatile antimony compounds have been described in Section IV-7. Scherrer[82] describes a distillation procedure for the separation of arsenic, antimony, and tin. The sample is placed in the distillation

flask and made 6$\underline{M}$ in HCl and 0.5 to 1$\underline{M}$ in H$_2$SO$_4$. Arsenic is distilled

at 111-112°C. The receiver is removed, phosphoric acid is added to the

distilling flask, and antimony is distilled at 155-165°C. After

cooling, the receiver is changed and the distillation is continued

at 140°C. with a 3 to 1 mixture of concentrated HCl and concentrated

HBr dropping into the distilling flask. Molybdenum, Re, Se, Te, and

Hg partially distill.

Radioantimony is separated by distillation in Procedure 2, de-

scribed in detail in Section VIII. Heuss[83] describes a simplified

distillation procedure for Sb, As, and Sn, and Maxwell et. al.[84]

describe the distillation of Sb from HClO$_4$-HBr. The easily accomplish-

ed electrolytic formation of stibine, SbH$_3$, has been used as the basis

for the separation of radioantimony. Cook[13] separates antimony from

fission product mixtures by generating stibine at a lead cathode in

an atmosphere of hydrogen. The stibine, swept out of the cell by the

hydrogen stream, passes through a slightly acid silver nitrate solution,

forming a mirror when heated or remaining as insoluble silver antimonide.

The latter technique is more convenient. Love[93], using this technique,

recently described a 10-second procedure (Section VIII, Procedure 4) for

separating short-lived antimony from fission product mixtures with

greater than 10^7 decontamination. Other methods based on generation

of stibine have been reported[14,15,16,17,18].

V-4 ELECTROCHEMISTRY OF ANTIMONY

V-4.1 Electrodeposition

One important advantage of electrodeposition compared to

precipitation is that extraneous ions are not added which can interfere

in subsequent analytical steps. Controlled potential techniques pro-

vide specificity, with completeness and speed of separation primarily

dependent upon the differences in the reduction potentials of the ion-

metal reactions. The technique is particularly advantageous for

radiochemical application because thin and evenly deposited films on

counting plates are obtainable. Details of instrumentation, cells, and general methodology are fully described by Lingane[8].

Reynolds[6] extensively studied the controlled cathode potential separation of antimony, tin, and bismuth. Quantitative recovery was obtained from a sulfuric acid - hydrazine sulfate solution at -0.3 V. Jovanovic[9] studied the cathodic deposition of bismuth and antimony from H_2SO_4 media and gives procedures for their separation from tin. Norwitz[25] also discusses the electrolytic determination of antimony. Several comprehensive studies of controlled - potential electrodeposition have been reported recently. Tanka[10] describes the electrodeposition behavior of antimony in HCl, H_2SO_4, HNO_3, NH_4OH, and cyanide media. The controlled potential separation and determination of antimony, copper, lead, and tin in nonferrous alloys is discussed by Hayakawa[11].

Electrodeposition has been used in several radiochemical separations. A method for the separation and mounting of antimony as well as several other elements is described by Lee and Cook[7]. Excellent beta counting plates, suitable for decay scheme studies, were obtained. Herr[12] isolated the separated antimony from a Szilard-Chalmers reaction by electrodeposition on a platinum electrode.

Hydrogen can be liberated in an electrodeposition technique and care must be taken to prevent the loss of antimony as SbH_3.

V-4.2 Polarography

Polarography has not been used for the radiochemical determination of antimony. Kolthoff and Lingane[19] discuss several polarographic methods for the determination of antimony in complex mixtures. Excellent waves are obtained in 1M HNO_3 with gelatin as a maximum suppressor with a half wave potential of -0.3 V. vs. S.C.E.

Love[20] has been pioneering the applications of polarography to radiochemistry. Antimony has not been investigated; however, the technique may be applicable to the separation of antimony from fission product mixtures.

V-4.3 __Amalgams__

Isotopic exchange with mercury amalgams has been proposed by Meinke[21] as a technique for the separation of radioelements from complex mixtures. Attempts to prepare an antimony-amalgam were unsuccessful.

V-5 GRAVIMETRY

Volumetric methods for the non-radiochemical determination of antimony are accurate and rapid, hence the more tedious gravimetric methods are seldom used.

Precipitation as the sulfide has been used almost to the exclusion of other methods. (See Section IV-6 for a compilation of precipitants). However, disagreement exists concerning its use. Hillebrand and Lundell[26] state that weighing of the trisulfide is satisfactory if it is dried and heated in an atmosphere of CO_2 at 280-300°C. Norwitz[25] claims that errors inherent in depositing the sulfide from acidic solution include adhering deposits and incomplete precipitation. Results can be 1 to 1.5% high due to occlusion of oxygen and sulfur compounds.

Although sulfide precipitation as a means of determing antimony requires precise conditions for accurate macro analysis, the errors involved do not appear to be of such consequence to seriously affect yield determinations in routine radiochemical analyses. Yield determinations for many elements are subject to similar conditions of occlusion and non-stoichiometric precipitation. The author believes that other more precise analytical techniques, such as titrimetry or spectrophotometry, are better suited for yield determinations. The increasing use of gamma spectrometry and especially deep well counting encourages investigation along these lines.

V-6 SPECTROPHOTOMETRY

This proven technique can substitute for gravimetric yield determination in many radiochemical methods and circumvert such errors as coprecipitation, occlusion, and questionable formula of ignited

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products. It is a simple matter to develop the color by addition of a chromogenic agent, make to volume, remove an aliquot for the absorbance measurement, and count the remainder. An example of this, using rhodamine B as the chromogenic agent, is given in Section VIII, Procedure 4.

Rhodamine B is the most widely used reagent for Sb. Sandell[85] discusses the merits and shortcomings of the method. For quantitative recovery, the crucial step in the rhodamine B method is conversion of Sb(III) to $SbCl_6^-$. The HCl concentration must be greater than 6$\underline{M}$ and Ce(IV) appears to be one of the few suitable oxidizing agents. Because $SbCl_6^-$ slowly hydrolyzes, the rhodamine B is added immediately after oxidation. The precipitate (bright red) is easily extracted into organic solvents, providing additional decontamination. Luke[88] and VanAman[66] report slight modifications in the procedure.

In acid solution, strongly, yellow colored iodoantimonite is formed by addition of excess iodide to either Sb(III) or (V)[86]. Beer's law is followed for the range of 5 to 50 ppm of antimony. Nitrite, hypochlorite, and sulfite interfere and close control of iodide and acidity must be maintained. A pyridine-iodide method for antimony has been described by Clarke[87]. In this procedure, pyridine forms a slightly soluble, colored iodoantimonite complex, which is kept in suspension by gum arabic. Sulfuric acid concentration for maximum color intensity is 3 to 4$\underline{M}$ and iodide and pyridine concentrations must be closely controlled.

Methyl violet, brilliant green, and anthraquinone-1-azo-dimethyl aniline react with antimony(V) in a manner similar to rhodamine B[85].

V-7 TITRIMETRY

Titrimetric methods also offer convenience for determining the yield in a radiochemical method. The entire separated sample can be titrated, then counted in a well crystal. Usually antimony is determined by oxidimetric titration of Sb(III) with permanganate, iodine, or bromate.

Cerium(IV) and dichromate can also be used.

Titration with bromine is usually carried out at an elevated temperature with methyl orange or indigo sulfonic acid as the indicator. Antimony(III) can be titrated with iodine in concentrated bicarbonate solution. Tartrate is added to hold the antimony in solution. The reaction is slow near the equivalence point and offers no advantages over the bromate titration[89]. In the presence of HCl, Sb(III) is oxidized to Sb(V) by permanganate. Acidity is critical. Hydrolysis may occur if too little acid is present while strong acid gives high results due to oxidation of chloride. Willard and Young[90] have titrated Sb(III) in HCl with ceric sulfate with iodine monochloride as catalyst. The titration is carried out at 50°C. using ferroin indicator. The solution should contain 15 ml. of concentrated HCl per 100 ml. of solution. Titration with dichromate has also been reported[91]; however, the method is unattractive because 2 to 3 hours are required for the oxidation and the endpoint is not very sharp.

Antimony(V) has been determined by titration with titanous sulfate[92]. After oxidation, with bromine, the solution is boiled to remove excess oxidant. The titration is made in an inert atmosphere (i.e. CO_2) above 60°C. using indigo carmine indicator. This approach does not seem practical for a radiochemical yield determination.

VI. DISSOLUTION OF ANTIMONY CONTAINING COMPOUNDS

Because antimony is easily lost by volatilization from hydrochloric acid media, dissolution with this reagent should be carried out under total reflux. Dissolution with sulfuric acid and a reducing agent or an alkali fusion prevents the loss of antimony and is preferred.

The metal is soluble in hot sulfuric acid. Bisulfite fusion in a porcelain or silica crucible dissolves the metal and lead alloy. The cooled melt is soluble in a dilute hydrochloric - sulfuric acid media.

The Sb(III) sulfide is soluble in hot sulfuric acid; the Sb(V)

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sulfide in alkali sulfate solution containing free sulfur or in sulfurous acid.

Fusion methods are recommended for samples containing oxidized material that may not readily dissolve with sulfuric acid. Sodium hydroxide in an iron crucible, dehydrated sodium thiosulfate, and a mixture of sodium carbonate and sulfur in a porcelain crucible are used.

VII. COUNTING TECHNIQUES

The common fission product antimony isotopes encountered in analysis are 2.4y Sb^{125}, 28d Sb^{126}, and 93 hr. Sb^{127}. Some 9 hr. Sb^{126m} and 4.6 hr. Sb^{129} may be observed in short cooled material. Of these isotopes, all may be gamma counted except the 28d Sb^{126} which is a pure beta emitter. Gross beta or gamma counting can be confusing due to the grow in of the tellurium daughter products. Gamma counting using a multichannel analyzer is recommended. Characteristic gamma spectra are given by Heath[104] and Crouthamel[105].

VIII. COLLECTED RADIOCHEMICAL PROCEDURES FOR ANTIMONY

In preparation of this monograph the author requested from the other monograph authors radiochemical methods for antimony used in their laboratories. These methods are included in the following compilation which is believed to be representative of the methods now in use.

PROCEDURE 1

(ION-EXCHANGE)

W. E. Nervick[94]

Note: This procedure has been used to obtain pure Sb fractions from U,
Th, and Cf fission product mixtures but should be applicable to almost
any mixture of activities. Chemical yields are approximately 60% and
it usually takes about five hours to run four samples. (W. E. N.)

- -

1. Add 30 mg Sb carrier plus 1 mg Mo, Te, Sn carriers. (Solution at
this point should be free of oxidizing agents----if it is not, ppt Sb
with pH 6-7 acetate buffer, wash once with dilute acetate buffer, dis-
solve in 8 ml 6$\underline{M}$ HCl).

2. Adjust to 2$\underline{M}$ HCl (25-30 ml vol) - $\underline{ice}$ $\underline{cool}$ - add 10 ml $CrCl_2$
("Oxsorbent", made by Burrell Corp.) - digest $\underline{cold}$ 5 min. - bubble in
O_2 1 min. - cent - wash twice with H_2O. (If Sb° does not centrifuge,
filter it, wash with H_2O, and dissolve it off the filter as in Step 3).

3. Dissolve Sb° in 4 ml conc. HCl + $\underline{liquid}$ Br_2 - add 1 mg each of Sn
and Mo carrier - add $NH_2OH\cdot HCl$ to reduce Br_2 - dilute to 30 ml - add 1
ml 5$\underline{M}$ NaI - digest hot 15 min.

4. Add $\underline{2\ ml}$ 6$\underline{M}$ $NH_4F\cdot HF$ - ice cool - saturate with H_2S - digest hot
15 min. (no longer) (saturate with H_2S every 5 min.) - cent - wash once
with (1$\underline{M}$ HCl + H_2S + dilute $NH_4F\cdot HF$).

5. a) Dissolve Sb_2S_3 in 15 ml hot 6$\underline{M}$ HCl - add 1 mg Te - pass in H_2S -
cent.

   b) Add 1 mg As^{+3} - digest - filter As_2S_3.

6. a) Adsorb Sb on Dowex A-1 anion exchange column (6 mm x 10 cm;
Dowex 1 x 8, 50-100 mesh, pre-equilibrated with 6$\underline{M}$ HCl).

   b) Wash column with 5 ml 6$\underline{M}$ HCl

                        15 ml 1$\underline{M}$ HCl

                        10 ml 9$\underline{M}$ H_2SO_4

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c) Elute Sb with 2 ml H_2O

15 ml boiling $2\underline{M}$ NaOH

7. Adjust to $m\underline{M}$ in HCl - filter (Whatman No. 44 paper) - ice cool -
add 10 ml $CrCl_2$ - digest cold 10 min. - pass in O_2 1 min. - cent - wash
twice with $0.5\underline{M}$ HCl, once with acetone, dry at 110' - weigh as Sb^O.

PROCEDURE 2

(BROMIDE DISTILLATION)

J. W. Barnes[95]

1. Introduction

Antimony is separated from most of the fission products by distil-
lation of the tribromide from acid solution. Among the substances which
also appear in the distillate are volatile compounds (probably the bro-
mides) of germanium(IV), arsenic(III), tellurium(IV), and tin(IV).
Tin(IV) is the main contaminant of the distillate under the conditions
employed. Germanium tetrabromide boils at a considerably lower tempera-
ture than antimony tribromide and is largely removed by discarding an
appropriate low boiling fraction. Tin is removed by an acid hydrogen
sulfide precipitation in the presence of fluoride ion, the latter
forming a stable complex with the tin and preventing its precipitation.
Remaining germanium, as well as arsenic and tellurium, which have pre-
cipitated along with antimony, are separated by concentrated hydrochloric
acid extraction of the sulfide precipitate. Antimony(III) sulfide dis-
solves, whereas the others are unaffected by the acid treatment. Antimony
is finally converted to the metal by reduction with chromous chloride
and is weighed and counted in this form. The chemical yield is 70 to
90%.

2. Reagents

Sb carrier: 10 mg Sb/ml (added as $SbCl_3$ in $\underline{6M}$ HCl)--standardized

Mo carrier: 10 mg Mo/ml (added as Na_2MoO_4 in H_2O)

Sn carrier: 10 mg Sn/ml (added as $SnCl_2 \cdot 2H_2O$ in $\underline{6M}$ HCl)

Te carrier: 10 mg Te/ml (added as Na_2TeO_3 in H_2O)

As carrier: 10 mg As/ml (added as $NaAsO_2$ in H_2O)

HCl: Conc.

H_2SO_4: $\underline{3M}$

H_2SO_4: Conc.

H_3PO_4: 85%

HBr: Conc.

HF: Conc

NH_4OH: Conc.

$N_2H_4 \cdot H_2O$: 85% aqueous solution

$CrCl_2$ solution (Oxsorbent, Burrell Corp.)

S: Solid

Aerosol: 1% in H_2O

Methanol: absolute

H_2S: gas

3. Equipment

Fisher burner

Drying oven

Centrifuge

Block for holding centrifuge tubes

Mounting plates

Forceps

Pipets: assorted sizes

100-ml, 3-neck distilling flask (with ground glass joints)

360° thermometer (with adapter; to fit into ground glass joint in flask above)

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Spray trap (to fit into ground glass joint in flask above)--consists of

a 2" long section of glass helices in a 16-mm tube. This should be

jacketed and heated to prevent condensation of $SbBr_3$. The very

simple method of heating used is to lead the hot gases from a

Fisher burner under the 3-neck flask up through a large diameter

glass tube to the jacket. The spray trap leads to a condenser.

Condenser

125-ml Erlenmeyer flask (receiver for distillate)--outlet tube from the

condenser touches the bottom of the flask

Dropping funnel (fits into ground glass joint in flask above)--see Pro-

cedure for diagram

N_2-tank

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)

Filter flasks (one per sample)

No. 40 Whatman filter circles: 7/8" diameter--weighed

40-ml conical centrifuge tubes: Pyrex 8320 (four per sample)

Filter beaker containing 15-ml sintered glass crucible of fine porosity

(one per standardization)--see Preparation and Standardization of

Carrier

100-ml beakers (one per standardization)

60-ml sintered glass crucibles: fine porosity (two per sample)

Wash bottle

Stirring rods

4. Preparation and Standardization of Carrier

Dissolve 18.7 gm of $SbCl_3$ in 6$\underline{M}$ HCl and make the solution to a
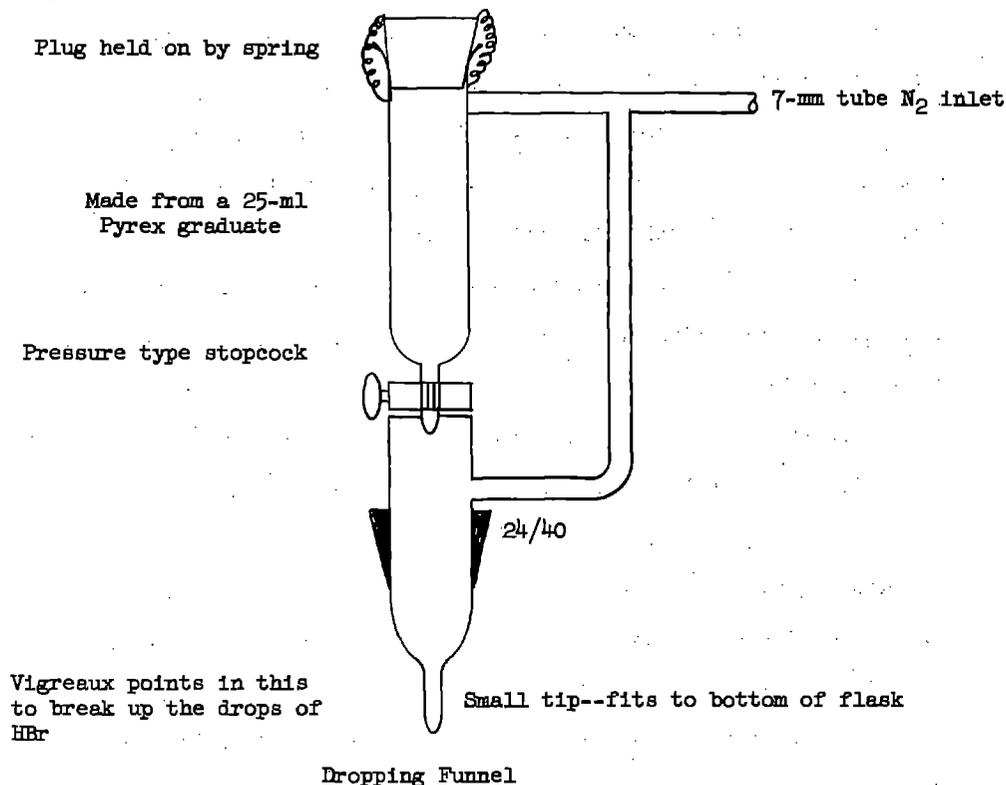
volume of 1 liter with the acid.

Pipet 5 ml of the above carrier solution into a weighed filter

beaker. (This beaker has a 15-ml, fine porosity sintered glass crucible

sealed into the side near the top so that the operations which follow--

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reduction, filtration, drying, and weighing--may be carried out in this one vessel.) Add 5 to 10 ml of $CrCl_2$ solution (Oxsorbent). After conversion to Sb metal is complete, filter, and wash the precipitate with small portions of H_2O and absolute CH_3OH. Dry the filter beaker containing the Sb at 100° for 1 hour. Cool and weigh.

5. Procedure

1. To the sample in a 100-ml, 3-neck distilling flask, add the following reagents: exactly 2 ml. of standard Sb carrier; 1 ml of Mo carrier; 2 ml of Sn carrier; 1 to 3 ml of 85% H_3PO_4; approximately 0.1 gm of S (Note 1); 20 ml of conc. H_2SO_4 (slowly). Place a 360° thermometer, a short spray trap leading to a condenser, and a dropping funnel (see diagram) in the three ground joints of the flask.

Plug held on by spring

7-mm tube N_2 inlet

Made from a 25-ml Pyrex graduate

Pressure type stopcock

24/40

Vigreaux points in this to break up the drops of HBr

Small tip--fits to bottom of flask

Dropping Funnel

2. Bubble N_2 through the solution in the flask while 15 to 20 ml of conc. HBr is added dropwise from the dropping funnel. The temperature

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of the liquid in the flask is maintained at 180 to 230° (Note 2) by means of a Fisher burner during the 15 to 20 min. required for the addition of HBr. The distillate which comes over below 180° is discarded and the addition of HBr is begun only after a temperature of 210° is reached (Note 3).

3. To the distillate (180 to 230°) in the 125-ml Erlenmeyer receiver add 1 ml of Te carrier, 0.5 ml of As carrier, and 2 ml of $N_2H_4 \cdot H_2O$ (Note 4). Neutralize the solution with conc. NH_4OH. Make the neutral solution slightly acid with conc. HCl and add a few drops of aerosol solution and 0.5 to 0.7 ml of conc. HF. Saturate with H_2S until the sulfide precipitate begins to settle, leaving a clear supernate. This should be done as rapidly as possible because SnS and SnS_2 will also precipitate after a short time; also the precipitation should be carried out at room temperature or below to aid in the rapid formation and coagulation of Sb_2S_3. Transfer the mixture to a 4-ml conical tube and centrifuge. Wash the precipitate with 15 ml of 3M H_2SO_4 containing aerosol. Discard both the supernate and the washings.

4. Boil the precipitate with 2 to 4 ml of conc. HCl, dilute to 20 ml with H_2O, and centrifuge (Note 5). Transfer the supernate to another 40-ml centrifuge tube.

5. To the supernate, add a few drops of aerosol solution, 0.1 ml of Sn carrier, 1 ml of Te carrier, and 0.5 to 0.7 ml of conc. HF. Precipitate and wash sulfides as in Step 3.

6. Dissolve the precipitate in 4 ml of conc. HCl, boil off the H_2S formed, and filter the solution through a 60-ml fine sintered glass crucible into a 40-ml centrifuge tube.

7. Add a few drops of aerosol solution and 0.5 to 0.7 ml of conc. HF and precipitate and wash Sb_2S_3 as in Step 3.

8. Dissolve the precipitate in 5 to 10 ml of conc. HCl and boil off the H_2S. Make the solution 3 to 5M in HCl and filter through a 60-ml

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fine sintered glass crucible into a 40-ml centrifuge tube.

9. Add sufficient $CrCl_2$ solution (Oxsorbent) to completely precipitate Sb as the metal. Start filtering through a weighed No. 40 Whatman filter circle, 7/8" diameter, within 1 min. or less, using a ground-off Hirsch funnel and a chimney. Wash the metal with 5-ml portions of H_2O and absolute CH_3OH. Dry at 100° for 15 min. Cool, weigh, and mount (Note 6).

Notes

1. Sulfur is added to the distilling flask to prevent the formation of Br_2 from HBr.

2. All temperatures noted are at about 590 mm of Hg pressure.

3. Much of the Ge in the fission-product solution is removed when the fraction coming over below 180° is discarded.

4. Hydrazine hydrate reduces any Sb(V) in the distillate to Sb(III).

5. Any Ge, As, or Te which is precipitated along with Sb as sulfide is insoluble in conc. HCl, whereas Sb_2S_3 is soluble.

6. The procedure described is designed for the determination of Sb^{127}. Counting is started after 4 days, in which time 9.3h Te^{127} has grown into equilibrium with Sb^{127}. The half-lives obtained for Sb^{127} resulting from thermal neutron fission of U^{235} average about 94.3h. Half-lives from fast neutron fission (14 Mev neutrons) average 97 to 98h. The cause of this discrepancy is probably the existence of another Sb isotope having a shorter half-life than 2.7y Sb^{125}.

PROCEDURE 3

(SbH₃ VOLATILIZATION, 8-HYDROXYQUINOLINE PRECIPITATION)

K. F. Flynn, L. E. Glendenin, and E. P. Steinberg[96]

Introduction

This procedure was developed for the radiochemical determination of Sb in fission product mixtures. Samples of U^{233}, U^{235}, and Pu^{239} which had undergone about 10^{13} fissions were analyzed for both Sb^{127} and Sb^{129}. The decay curves of these isotopes showed less than 0.5% of any long lived contaminant to be present. Accurate decontamination factors from specific elements have not been determined, but a separation of inactive Sb from a solution containing As^{77} tracer showed no activity in the final Sb sample, indicating a decontamination factor of greater than 10^3. Chemical yields are about 25% and the analysis can be performed in about 40 minutes or less.

Procedure

1. Add to the sample (free of nitrate) in a distillation flask 4 ml of Sb standardized carrier (10 mg Sb^{+5}/ml) and 4 ml of 6N H_2SO_4. Boil with a drop of Br_2 to insure exchange. Add 5 grams of granulated zinc and pass the SbH_3 into 20 ml of 6N HCl containing a few drops of liquid bromine using an air stream to sweep the gas through the system. (1 cc/sec flow rate for 5 min.)

2. Add 10 mg Te and 1 gram hydrazine-HCl to the solution. Heat to boiling and gas with H_2S. Centrifuge and discard ppt. (This is zero time for Te removal).

3. Add 5 ml of conc. NH_4OH, dilute to 30 ml, and gas with H_2S. Centrifuge the Sb_2S_3 ppt and wash. Dissolve in 2 ml conc. HCl, add 1/2 gram $NaHSO_3$, dilute to 10 ml, and boil. Add 3 ml of 8-hydroxy-quinoline (3% solution in 2N HCl) and boil. Add 1 ml conc. NH_4OH, and 3M NH_4Ac until pptn. is complete (pH=5). Wash with H_2O, alcohol, ether, and dry at 110°C. for 15 min.

Carrier Standardization: Take 5 ml of Sb carrier solution (in 3N HCl). Add 1 ml of 6N HCl, 1/2 gram NaHSO$_3$, and boil. Add 4 ml of 8-hydroxy-quinoline (3% solution in 2N HCl). Add 1 ml of conc. NH$_4$OH and 3M NH$_4$Ac until pptn. is complete (pH=5). Wash with H$_2$O, alcohol, and ether. Dry at 110°C. for 15 min. Weigh. Gravimetric Factor = 3.8.

PROCEDURE 4

(SbH$_3$ VOLATILIZATION, SPECTROPHOTOMETRIC YIELD)

D. L. Love

Rapid Separation of Antimony from Fission Product Mixtures

Decontamination Factor: 10^7 for gross fission products

Chemical Yield: 80%

Time: 10 seconds

Basis of Method: Formation of SbH$_3$ and its conversion to Sb metal

Zinc metal (40 mesh) is placed in a distilling flask and warmed to 100°C. Antimony(III) carrier plus fission products plus 30% H$_2$SO$_4$ are dropped onto the Zn and SbH$_3$ is immediately formed before the Zn has had a chance to convert the Sb(III) to Sb metal. The SbH$_3$ (plus the H$_2$ formed) passes through a CaCl$_2$ drying tube and then through a heated small diameter quartz tube (Pyrex is acceptable but it does not keep its shape when warmed with a burner). The SbH$_3$ is converted to Sb metal, part of which collects as a mirror on the cool portion of the quartz tube and the rest (~50%) on a fine fritted glass filter. The metal is rapidly dissolved with warm H$_2$SO$_4$. If it is desirable to study the I decay products of Sb, the metal may be dissolved in tartaric acid. The chemical yield may be determined either by using Sb^{124} tracer or a spectrophotometric determination of the Sb-rhodamine B complex.

Arsenic is expected to follow the antimony; however, most of it

collects on a different position of the tube. The arsenic can be removed from the Sb metal by leaching with sodium hypochlorite.

Complete exchange is obtained even if some of the fission product Sb is Sb(V).

PROCEDURE 5

(BROMIDE EXTRACTION, METAL PRECIPITATION)

A. Kjelberg and A. C. Pappas[4]

(Rapid separation of Sb from irradiated enriched Te-128 and Te-130)

Recommended for decay scheme studies where yield is not important.

Time of Separation: less than 5 minutes

Decontamination: 5×10^4 for Te

10^5 for Sn

50-100 for I

Chemical Yield: 60-70%

Reagents:

1. Isopropyl ether - washed repeatedly with a solution of $FeSO_4$ and distilled from solid $FeSO_4$ and NaOH and equilibrated with 9N HCl.

2. Antimony carrier - 10 mg/ml as $SbCl_3$ in 9N HCl. Before use, it is oxidized by shaking with 2 drops Br_2 in 10 ml benzene and washed with 10 ml benzene.

3. $SnCl_2$ Solution - 100 mg/ml Sn as $SnCl_2$ in 9N HCl. The solution should be fresh when used.

4. Cr^{++} Solution - 1M $CrCl_3$ solution, 1N in HCl, is reduced by boiling with amalgamated, granulated metallic Zn.

5. HCl - Conc. and 9N

6. HNO_3 - Conc.

7. Br_2

8. Benzene

9. $N_2H_4 \cdot H_2O$, 50%

Equipment:

1. 30-ml beaker

2. Glass rod

3. Sintered glass gooch crucible

4. 100-ml suction flask

5. 50-ml separatory funnels

Procedure:

1. Dissolve the target in 5 ml $9\underline{N}$ HCl to which is added 2 mg Sb(V) carrier. Add under vigorous stirring 2.5 ml $SnCl_2$ solution per 100 mg target. After about 1/2 minute, filter with suction through a gooch, and wash twice with 2 ml $9\underline{N}$ HCl.

2. Transfer the filtrate to a separatory funnel containing 10 ml C_6H_6, 1.0 ml. isopropyl ether and 0.1 ml Br_2 per 100 mg target. Shake the funnel for about 10 sec. (Distinct brown color of Br_2 should remain in the organic phase, showing complete oxidation). Discard the water phase and wash with 1 ml $9\underline{N}$ HCl.

3. Transfer the organic phase to a separatory funnel containing 5 ml $9\underline{N}$ HCl and 1.0 ml $SnCl_2$ solution and shake. (The organic phase should be colorless after extraction, showing complete reduction).

4. Transfer the water phase to a separatory funnel containing 10 ml of C_6H_6, 1.0 ml isopropyl ether and 0.05 ml Br_2 (or as little as possible) and shake for 10 sec. (permanent brown color). Discard the water phase and wash with 1 ml $9\underline{N}$ HCl.

5. Transfer the oragnic phase to a separatory funnel containing 5 ml $9\underline{N}$ HCl and add dropwise a minimum amount of $SnCl_2$ solution (0.5 to 1.0 ml). Shake, eventually add SnCl to just discolor the organic phase.

This solution can either be used for liquid beta counting; or:

6. Add 2-3 mg $SbCl_3$ carrier, heat the solution, and add approximately 15 ml boiling hot Cr^{++} solution. Filter the solution and wash the precipitate carefully in boiling hot $9\underline{N}$ HCl, then with H_2O, alcohol and ether. (Some metallic Sn is also pptd.)

PROCEDURE 6

(SULFIDE PRECIPITATION)

A. S. Newton and W. R. McDonell

Element Separated: Antimony

Parent Material: Tin

Milking Procedure (Sb from low energy p, d, or n produced Sn

activity fractions)

Yield: 60-80%

Degree of Purification: At least a factor of 10^4 from Sn

Procedure:

1. To a 3-$4\underline{N}$ HCl solution of the Sn, add 10 mg Sb^{+++} carrier (Note 1). Add iron powder to excess (hydrogen evolution), heat with stirring, ppt. Sb metal (black). Filter by vacuum through a sintered glass filtering crucible.

2. Dissolve the Sb in aqua regia, dilute to $1\underline{N}$ acid, pass in H_2S and ppt. Sb_2S_3 + S. Dissolve the sulfide out of the sulfur with concentrated HCl (warming and stirring).

3. Add 10 mg Sn^{+4} carrier to filtrate. Heat in boiling water bath, pass in H_2S to saturate, ppt. orange Sb_2S_3. Centrifuge hot, decant. Dissolve Sb_2S_3 in concentrated HCl. Dilute to $3\underline{N}$ HCl.

4. Repeat Step 3 twice.

5. Filter the Sb_2S_3 on filter paper and wash with water. Heat gently (Note 2).

PROCEDURE 6 (Continued)

Notes:

1. Indium may be scavenged out of this milking by adding 10 mg In carrier to initial Sn solution (Step 1), repeating the Fe reduction if the amount of In activity present warrants it.

2. The sulfide should not be relied upon for accurate yield determination.

PROCEDURE 7

(SULFIDE-PHENYLARSONIC PRECIPITATION)

H. L. Finston[98]

(Separation of Sb from Sn)

1. Dissolve the Sn in 48% HF plus a few drops of HNO_3 and evaporate the solution to about 1 ml. Add 1 mg of Sb carrier and dilute the solution to 20 ml and bubble hydrogen sulfide into each solution for 5 minutes.

2. Centrifuge and dissolve the precipitate in concentrated HNO_3. Add 10 mg of Sn^{++} carrier and evaporate the solution nearly to dryness.

3. Add 2 ml. of HNO_3 and dilute the solution to 20 ml. Add 3 drops of concentrated HCl and heat the solution to near boiling.

4. Add with stirring, 4 ml of phenylarsonic acid.

5. Centrifuge and discard ppt.

6. Bubble H_2S into the supernate to again ppt. the Sb.

7. Filter, mount, and count.

PROCEDURE 8

(ANTIMONY, NEUTRON ACTIVATION ANALYSIS (ISOTOPIC CARRIER) METHOD)

G. W. Leddicotte[119]

SCOPE

This method of neutron activation analysis can be used to determine microgram and submicrogram amounts of antimony in a variety of materials. Under the conditions of neutron irradiation that are specified, the limit of measurement of the method is about 1×10^{-8} or 1×10^{-7} g. depending upon which nuclear reaction is used. The sensitivity may be increased by the use of a higher neutron flux.

PRINCIPLE

Antimony can be determined quantitatively by measuring the radio-activity induced into its stable isotopes, Sb^{121} and Sb^{123}, by the slow neutron reactions, $Sb^{121}(n, \gamma)Sb^{122}$ and $Sb^{123}(n, \gamma)Sb^{124}$. The isotopic activation cross sections of these reactions are 6.8 ± 1.5 and 2.5 ± 0.5 barns, respectively. Antimony-121 is 57.25% abundant; Sb^{122} has a half life of 60 d. and emits both beta and gamma rediations in its decay. Other products of these neutron reactions, i.e., $Sb^{122m}(3.5 \text{ m})$, $Sb^{124m1}(1.3 \text{ m})$, and $Sb^{124m2}(21 \text{ m})$, will not interfere in the determination described herein.

Test portions of the test sample and of a comparator sample (in this case, antimony metal) are irradiated simultaneously in one of the ORNL reactors for an appropriate length of time. The irradiated test portions are dissolved, and a known amount of inactive antimony, as antimony chloride, is added to each as a "carrier" for the radioactive antimony. Holdback ("scavenging") carriers, which are arsenic, tin, copper, iron, sodium, and cobalt in solution, are also added to the solutions of the test portions in order to decontaminate the Sb^{122} (and/or Sb^{124}) radioactivity from contaminant radioactive species in the samples. The arsenic and tin carriers are separated by distillation.

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The antimony carrier and the antimony radioactivities are precipitated as antimony trisulfide, Sb_2S_3, in order to remove them from the other holdback carriers and radioelements. Additional scavenging steps are used to further decontaminate the antimony trisulfide.

As an alternate procedure to the precipitation of antimony tri-sulfide, the antimony can be converted to antimony metal by reduction with chromous chloride. The antimony trisulfide, or the antimony metal is weighed and is then assayed for either beta or gamma radioactivity. The quantity of antimony in the original sample is obtained by comparing the Sb^{122} (and/or Sb^{124}) radioactivity found in the test sample with the Sb^{122} (and/or Sb^{124}) radioactivity in the comparator sample that was analyzed in the same manner as the test sample.

STATUS

This method was developed and is used in the ORNL Nuclear Analyses Laboratory to determine antimony in metals and alloys. It can be adapted for the determination of microgram and submicrogram amounts of antimony in other materials.

For the procedure which uses the $Sb^{121}(n, \gamma)Sb^{122}$ reaction, the limit of measurement is about 1×10^{-8} g; this quantity is the smallest weight of antimony that can be determined quantitatively when the test portion is irradiated at a neutron flux of 5.0×10^{11} neutrons/cm^2/sec for 62 hr. The limit of measurement by the $Sb^{123}(n, \gamma)Sb^{124}$ reaction, for which a one-week irradiation at the same neutron flux is used, is about 1.0×10^{-7} g. These limits of measurement can be extended downward by the use of higher neutron flux. The choice of the neutron reaction to be used is governed by the time available for the analysis and by the nature of the test sample. Known interferences can result if the sample contains iodine as I^{127} and tin as Sn^{124}. The fast-neutron reaction (n, α) on I^{127} produces Sb^{124} (60 d). The slow-neutron reaction on Sn^{124} will produce Sb^{125} (2.7 y); the reaction is $Sn^{124}(n, \gamma)$

$Sn^{125} \xrightarrow{9.4\ d} Sb^{125}$ (2.7 y). If U^{233} or U^{235} is present in a sample, a number of radioactive isotopes of antimony will be produced by fission.

The use of the comparator sample eliminates the necessity of controlling rigidly such factors as neutron flux, position of the sample in the reactor, duration of irradiation, and efficiency of the radioactivity measurements. The radiochemical separation procedure has been shown to be reproducible, and it gives adequate decontamination of the antimony from other radioactive components in the sample. It is advisable to scavenge at least twice for contaminant radioelements. The chemical yield should be at least 70% of the added inactive antimony carrier; a recovery of less than 50% is regarded as unsatisfactory and requires that the analyses be repeated. It is assumed that negligible amounts of sulfur and antimony pentasulfide, Sb_2S_5, are formed in the final precipitation step in which the antimony carrier and radioactive antimony are precipitated as antimony trisulfide.

SAMPLING

If the sample is a solid, weigh out to the nearest 0.001 g, a test portion that weighs 0.10 to 0.20 g; if the sample is a liquid, use a 5- to 25-ml portion. In each instance, prepare at least duplicate portions for analysis. As a comparator sample use spectrographically pure antimony metal; weigh out to the nearest 0.0001 g duplicate test portions that weigh 0.025 to 0.030 g. These suggested sizes of the test portions are those arbitrarily established for use by the ORNL Nuclear Analyses Group and are usually governed by the type of container and the facilities used for the irradiation.

PROCEDURE

Make all analyses for antimony on at least duplicate portions of the test and comparator samples.

A. Preparation of Test Portions for Irradiation

1. Weigh out test portions of the comparator sample and of the test sample as instructed in Sampling, above.

2. Place test portions of solid materials in cork stoppered, quartz tubes or wrap them in aluminum foil.

3. Place portions of liquid samples in polyethylene bottles equipped with polyethylene caps (sealed quartz ampoules may be substituted for the polyethylene bottles).

B. Irradiation of Test Portions

1. Irradiate comparator and test samples simultaneously under identical conditions.

C. Preparation of Irradiated Test Portions for Analysis

1. By whichever of the following procedures applies, prepare the portions for analysis:

a. Antimony Comparator Sample

(1) Quantitatively transfer the irradiated test portion of the comparator sample from the quartz tube or aluminum wrap to a 50-ml volumetric flask. Dissolve the test portion in a small, measured volume of aqua regia; then dilute the solution to 50 ml with water. Mix the solution well by shaking it carefully.

(2) By means of a volumetric pipet, pipet a 1.00-ml aliquot of this solution into a second 50-ml volumetric flask; then dilute the aliquot to 50 ml with distilled water.

(3) Shake the solution thoroughly; then pipet a 1.00-ml aliquot of it into a 100-ml distillation flask. By means of a volumetric pipet, add to the same distillation flask 2.00 ml of a standard carrier solution of known antimony concentration and 1 ml each of holdback carrier solutions of the ions of arsenic, cobalt, copper, iron, sodium, strontium, and tin (Note a). Evaporate the solution to a volume of approximately 3 ml. Continue with Part D below.

PROCEDURE 8 (Continued)

b. Solid Test Samples

(1) If the sample is a metal or alloy, quantitatively transfer the irradiated test portion from the quartz tube or aluminum wrap to a 100-ml 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 antimony concentration. Also add 1 ml each of holdback carriers of arsenic, cobalt, copper, iron, sodium, strontium, and tin (Note a). To this mixture, add dropwise enough concentrated mineral acid to completely dissolve the sample. Evaporate the solution to a volume of approximately 3 ml. Continue with Part D below.

c. Liquid Test Samples

(1) Pipet an aliquot of the irradiated portion into a 100-ml distillation flask. By means of a volumetric pipet, add to the same distillation flask 2.00 ml of a standard carrier solution of known antimony concentration and also add 1 ml each of holdback carriers of arsenic, cobalt, copper, iron, sodium, strontium, and tin (Note a). Evaporate the solution to a volume of approximately 3 ml; then continue with Part D below.

D. Radiochemical Separation of Antimony

1. To the mixture in the distillation flask, add 2 ml of conc. HCl and 3 ml of HBr.

2. Attach a water-cooled condenser to the distillation flask. Place the delivery tube of the condenser in a distillate collection vessel that is set in an ice bath. By means of a hose, apply a gentle stream of air to the flask in order to minimize bumping.

3. Distill the mixture in the flask until the temperature of the mixture reaches 110°C. or until only approximately 5 ml of the solution remains in the flask. Add an additional 3 ml of HBr to the distillation flask, and then continue the distillation until only

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approximately 5 ml of the solution remains.

4. Discard the distillate and quantitatively transfer the contents of the distillation flask to a 50-ml centrifuge tube. Add 25 ml of a saturated solution of oxalic acid; then heat the mixture to near boiling. Saturate the solution with H_2S in order to precipitate the antimony as antimony trisulfide, Sb_2S_3. Centrifuge the mixture and discard the supernatant liquid.

5. Dissolve the Sb_2S_3 by warming it in a mixture of 2 ml of conc. HCl and 2 drops of conc. HNO_3. Add 1 ml each of holdback carrier solutions of iron, copper, strontium, and sodium; precipitate Sb_2S_3 by adding 10 ml of conc. HNO_3 and then boiling the solution. Centrifuge the mixture and discard the supernatant liquid. Wash the precipitate with three 10-ml portions of hot, conc. HNO_3. After each washing, centrifuge the mixture and discard the supernatant liquid.

6. Dissolve the Sb_2S_3 precipitate in 2 ml of conc. HCl. Add to the solution 30 ml of a saturated solution of oxalic acid and 1 ml of tin holdback carrier solution. Heat the solution to boiling (the boiling helps to coagulate the precipitate); then precipitate Sb_2S_3 by saturating the solution with H_2S.

7. Filter off the Sb_2S_3 through a tared filter paper that is held in a Hirsch funnel; wash the precipitate once with 3- to 5-ml portions each of H_2O, ethyl alcohol, CS_2, and ethyl ether in that order. Dry the precipitate for one minute. Weigh the Sb_2S_3 precipitate and filter paper on an analytical balance. Mount the precipitate and count its activity.

IX. NEUTRON ACTIVATION ANALYSIS

With a thermal neutron flux of 5×10^{11} n/cm.^{2}/sec., the theoretical sensitivity of this technique for antimony is reported[106] as 0.004 ug based on 2.8d Sb^{122} and 0.03 ug based on 60d Sb^{124} for an induced activity of 40d/s at saturation. Because of the long irradiation time required for saturation, the practical limit is about an order of magnitude greater. On the other hand, an advantage of a relatively long lived activation product is that samples may be allowed to age for short lived activity to decay. Gamma spectra of neutron activation isotopes are given by Heath[104], Crouthamel[105], and Brooksbank[107]. For spectra that cannot be resolved due to other activities the methods described in Section VIII are recommended for chemical separation.

Table 2 is a partial list of materials which have been analyzed for antimony by thermal neutron activation analysis. A typical method is described in Procedure 8, Section VIII.

TABLE II. ACTIVATION ANALYSIS OF ANTIMONY

Sample	Remarks	Reference
ZrO_2	sens. 0.5 ppm	108
Al		109, 113
Si	sens. 1×10^{-4} ppm f = 3×10^{12}	110
	sens. 2×10^{-4} f = 2×10^{14}	111
Ge	sens. 10^{-5} ppm f = 3×10^{12}	109, 115
Liquid Metals	1×10^{-3} ppm	112
Biological Materials		114
Pb		116
Mg		117
Water	0.04 ppm determined	118

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