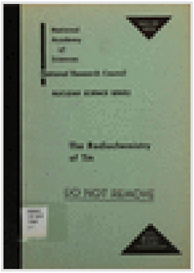

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The Radiochemistry of Tin

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Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

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

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

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The Radiochemistry of Tin

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF TIN

1. W. W. Scott (N. H. Furman, Ed.); "Standard Methods of Chemical Analysis," 5th Edition; D. Van Nostrand Co., Inc., New York, 1939, Vol. 1, pp. 954-74.

2. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman; "Applied Inorganic Analysis," 2nd Edition; John Wiley & Sons, Inc., New York, 1953, pp. 285-96.

3. H. Remy; "Treatise on Inorganic Chemistry;" Elsevier Publishing Co., Houston, 1956, Vol. 1, pp. 524-38.

4. Fritz Ephraim (P. C. L. Thorne and E. R. Roberts, Eds.); "Inorganic Chemistry," 5th Edition; Interscience Publishers, Inc., New York, 1949.

5. M. C. Sneed and R. C. Brasted; "Comprehensive Inorganic Chemistry;" D. Van Nostrand Co., Inc., New York, 1958; Vol. 7, pp. 212-27.

6. E. B. Sandell; "Colorimetric Determination of Traces of Metals," 3rd Edition; Interscience Publishers, Inc., New York, 1959.

7. F. J. Welcher; "Organic Analytical Reagents;" D. Van Nostrand Co., Inc., New York, 1948.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF TIN

1. C. D. Coryell and N. Sugarman, Eds.; "Radiochemical Studies: The Fission Products;" McGraw-Hill Book Co., Inc., New York, 1951; Book 3, Parts V, VI, VII, VIII (National Nuclear Energy Series).

III. TABLE OF ISOTOPES

Data in Figs. 1 and 2 are reproduced from the G. E. Chart of the Nuclides (KAPL), 5th Edition, Revised to April 1956. For more detailed information consult: "Table of Isotopes;" D. Strominger, J. M. Hollander, and G. T. Seaborg; Revs. Modern Phys. 30, No. 2, Pt. 2, 585-904 (1958).

IV. CHEMISTRY OF TIN

IV. 1. OXIDATION STATES

IV. 1. A. METALS

Tin is a relatively common element which may exist either as the metal or in the +2 or +4 oxidation states. According to Latimer,[98] the potentials between states are:

$$\mathrm{Sn}\overset{0.136}{\text{----------}}\mathrm{Sn}^{+2}\overset{-0.15}{\text{----------}}\mathrm{Sn}^{+4}.$$

The metal is not very electropositive and therefore may be obtained relatively easily by reduction with a fairly wide variety of reducing agents (Al, Zn, etc.). For small scale reductions, such as those most often carried out in radiochemical separations, chromous chloride ("Oxsorbent," manufactured by Burrell Corp., Pittsburgh, Pa.) is a very effective reducing agent since it works rapidly and no extraneous metal need be introduced into the tin solution. Tin metal has many interesting properties,[144] one of the most frustrating of which is its softness. Freshly precipitated metallic tin (reduced by $CrCl_2$, for instance) has a tendency to coalesce into a single inhomogeneous globule which can be neither washed effectively nor spread out in a thin uniform layer for counting, characteristics which make the precipitation of metallic tin somewhat undesirable in most radiochemical separations.

IV. 1. B. ELECTROCHEMISTRY

Electrodeposition has proven to be a useful method for obtaining tin from a solution. Precautions must be taken that small amounts of tin are not lost: (1) by formation of gaseous hydride (SnH_4) at the cathode, (2) by volatilization of stannic chloride or bromide during the preparation of the solution, (3) by re-solution of the metallic tin deposit during washing, and (4) by mechanical loss of tin crystals from deposits of poor quality. But with the proper techniques essentially quantitative electrodeposition of tin may be obtained.[87, 132]

Since tin lies in an intermediate position on the EMF table of potentials, special methods are required if it is to be separated from a mixture of more electropositive or more electronegative elements.

Essentially, this "controlled potential electrolysis" technique involves the application of a known potential (usually measured against a standard calo-

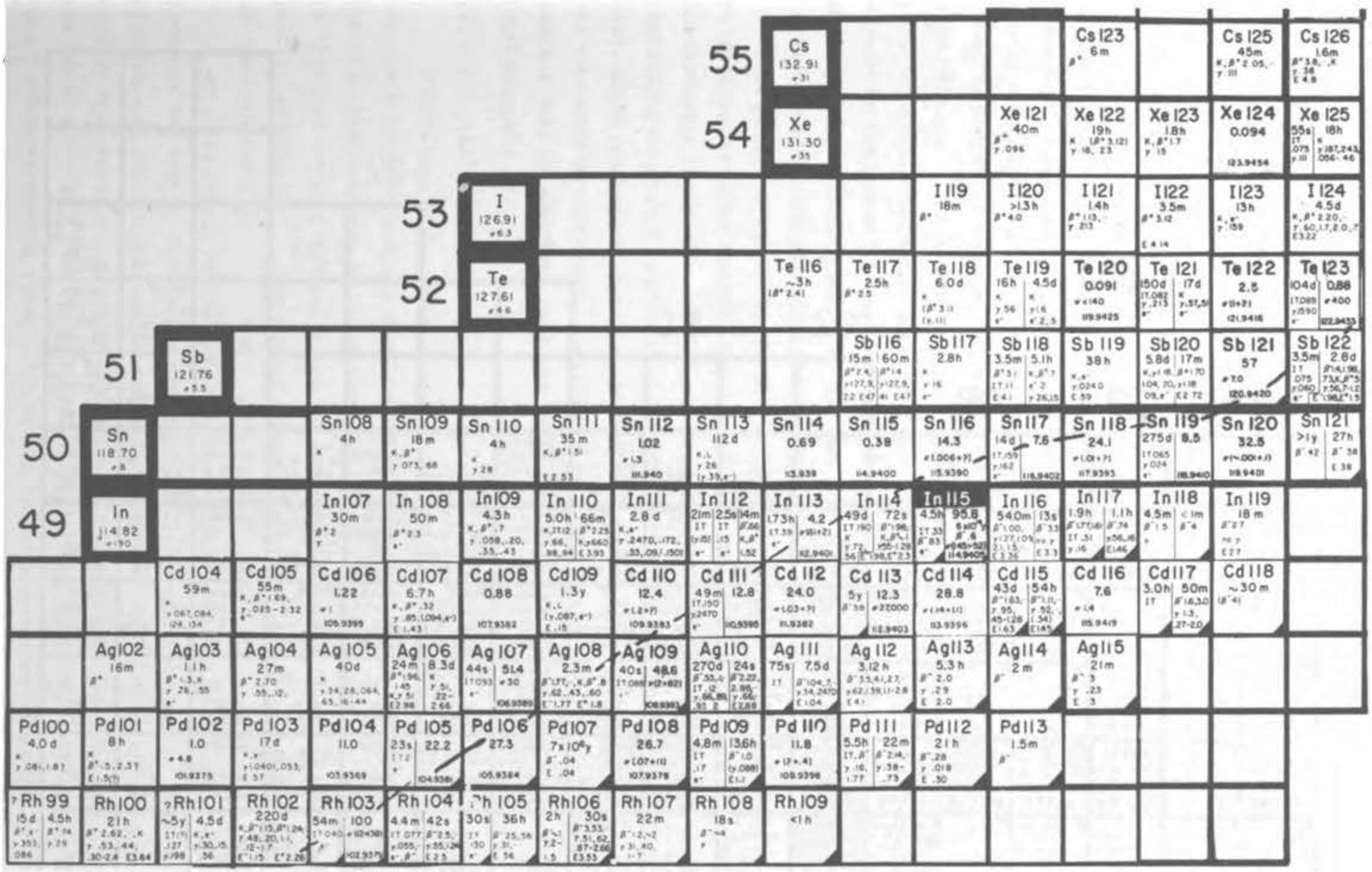
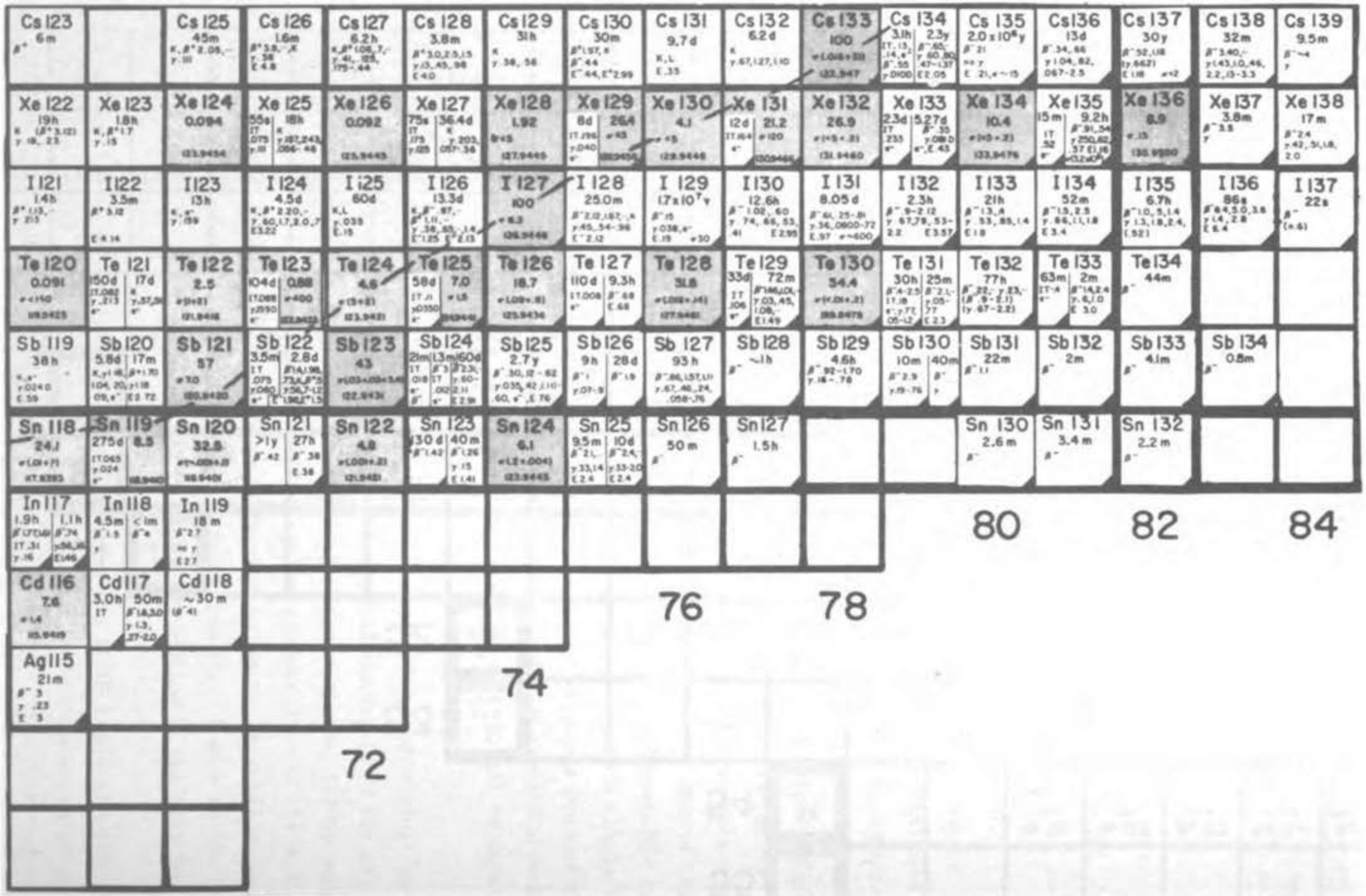

55
Cs 132.91
Cs 123 6m
Cs 125 45m
Cs 126 1.6m
54
Xe 131.30
Xe 121 40m
Xe 122 19h
Xe 123 1.8h
Xe 124 0.094
Xe 125 55s 18h
53
I 126.91
I 119 18m
I 120 >1.3h
I 121 1.4h
I 122 3.5m
I 123 13h
I 124 4.5d
52
Te 127.61
Te 116 ~3h
Te 117 2.5h
Te 118 6.0d
Te 119 16h 4.5d
Te 120 0.091
Te 121 150d 17d
Te 122 2.5
Te 123 104d 0.88
51
Sb 121.76
Sb 116 15m 60m
Sb 117 2.8h
Sb 118 3.5m 5.1h
Sb 119 38h
Sb 120 5.8d 17m
Sb 121 57
Sb 122 3.5m 2.8d
50
Sn 118.70
Sn 108 4h
Sn 109 18m
Sn 110 4h
Sn 111 35m
Sn 112 1.02
Sn 113 112d
Sn 114 0.69
Sn 115 0.38
Sn 116 14.3
Sn 117 14d 7.6
Sn 118 24.1
Sn 119 275d 8.5
Sn 120 32.5
Sn 121 >1y 27h
49
In 114.82
In 107 30m
In 108 50m
In 109 4.3h
In 110 5.0h 66m
In 111 2.8d
In 112 21m 2.5s 14m
In 113 1.73h 4.2
In 114 49d 72s
In 115 4.5h 95.8
In 116 54.0m 13s
In 117 1.9h 1.1h
In 118 4.5m <1m
In 119 18m
Cd 104 59m
Cd 105 55m
Cd 106 1.22
Cd 107 6.7h
Cd 108 0.88
Cd 109 1.3y
Cd 110 12.4
Cd 111 49m 12.8
Cd 112 24.0
Cd 113 5y 12.3
Cd 114 28.8
Cd 115 43d 54h
Cd 116 7.6
Cd 117 3.0h 50m
Cd 118 ~30m
Ag 102 16m
Ag 103 1.1h
Ag 104 27m
Ag 105 40d
Ag 106 24m 8.3d
Ag 107 44s 51.4
Ag 108 2.3m
Ag 109 40s 48.6
Ag 110 270d 24s
Ag 111 75s 7.5d
Ag 112 3.12h
Ag 113 5.3h
Ag 114 2m
Ag 115 21m
Pd 100 4.0d
Pd 101 8h
Pd 102 1.0
Pd 103 17d
Pd 104 11.0
Pd 105 23s 22.2
Pd 106 27.3
Pd 107 7x10^6y
Pd 108 26.7
Pd 109 4.8m 13.6h
Pd 110 11.8
Pd 111 5.5h 22m
Pd 112 21h
Pd 113 1.5m
Rh 99 15d 4.5h
Rh 100 21h
Rh 101 ~5y 4.5d
Rh 102 220d
Rh 103 54m 100
Rh 104 4.4m 42s
Rh 105 30s 36h
Rh 106 2h 30s
Rh 107 22m
Rh 108 18s
Rh 109 <1h

Fig. 1.


Cs 123 6m
Cs 125 45m
Cs 126 1.6m
Cs 127 6.2h
Cs 128 3.8m
Cs 129 31h
Cs 130 30m
Cs 131 9.7d
Cs 132 6.2d
Cs 133 100
Cs 134 3.1h 2.3y
Cs 135 2.0x10⁶y
Cs 136 13d
Cs 137 30y
Cs 138 32m
Cs 139 9.5m
Xe 122 19h
Xe 123 1.8h
Xe 124 0.094
Xe 125 55s 18h
Xe 126 0.092
Xe 127 75s 36.4d
Xe 128 1.92
Xe 129 8d 26.4
Xe 130 4.1
Xe 131 12d 21.2
Xe 132 26.9
Xe 133 2.3d 5.27d
Xe 134 10.4
Xe 135 15m 9.2h
Xe 136 8.9
Xe 137 3.8m
Xe 138 17m
I 121 1.4h
I 122 3.5m
I 123 13h
I 124 4.5d
I 125 60d
I 126 13.3d
I 127 100
I 128 25.0m
I 129 1.7x10⁷y
I 130 12.6h
I 131 8.05d
I 132 2.3h
I 133 21h
I 134 52m
I 135 6.7h
I 136 86s
I 137 22s
Te 120 0.091
Te 121 150d 17d
Te 122 2.5
Te 123 104d 0.88
Te 124 4.6
Te 125 58d 7.0
Te 126 18.7
Te 127 110d 9.3h
Te 128 31.8
Te 129 33d 72m
Te 130 34.4
Te 131 30h 25m
Te 132 77h
Te 133 63m 2m
Te 134 44m
Sb 119 38h
Sb 120 5.8d 17m
Sb 121 57
Sb 122 3.5m 2.8d
Sb 123 43
Sb 124 21m 1.3m 60d
Sb 125 2.7y
Sb 126 9h 28d
Sb 127 93h
Sb 128 ~1h
Sb 129 4.6h
Sb 130 10m 40m
Sb 131 22m
Sb 132 2m
Sb 133 4.1m
Sb 134 0.8m
Sn 118 24.1
Sn 119 275d 8.5
Sn 120 32.5
Sn 121 >1y 27h
Sn 122 4.8
Sn 123 130d 40m
Sn 124 6.1
Sn 125 9.5m 10d
Sn 126 50m
Sn 127 1.5h
Sn 130 2.6m
Sn 131 3.4m
Sn 132 2.2m
In 117 1.9h 1.1h
In 118 4.5m <1m
In 119 18m
Cd 116 7.6
Cd 117 3.0h 50m
Cd 118 ~30m
Ag 115 21m
72
74
76
78
80
82
84

mel electrode) to a solution containing tin plus other elements. The potential is first maintained at a point just short of reducing tin until all metals more easily reduced than tin are deposited, at which point the cathode is replaced and the potential increased slightly until all the tin has been removed. The method requires fairly elaborate apparatus for precise control of the potential and, if many elements are to be removed before tin is deposited, can take as much as 3 or 4 hours before tin is separated. These may be serious restrictions on the use of the method in certain applications, but for those cases where time and equipment limitations are not severe, several excellent articles may be consulted for details of the technique. Dean and Reynolds[36] have used "controlled cathode electroanalysis" to determine bismuth, antimony, and tin in their mixtures; Lingane and Jones[107] have separated mixtures of copper, bismuth, lead, and tin; and Subramanian and Janardhanan[172] have reviewed the quantitative electrodeposition of tin, copper, bismuth, antimony, and lead. Of particular interest to radiochemists should be the paper by Lee and Cook,[103] who give a detailed description of a method for separating Ag, Rh, Sn, Sb, Te, and Cd from fission product mixtures by controlled potential electrodeposition.

In general, restrictions on electrolyte composition are not severe and each of the articles quoted contains recipes which seem to work satisfactorily. Electrolysis is usually carried out in a slightly acid solution of HCl or H_2SO_4 containing an anodic depolarizer (hydrazine sulfate or hydrochloride are the best, although hydroxylamine hydrochloride may also be used). If hydrolyzable elements are present, complexing agents such as citrate, tartrate, or oxalate may be added to keep the solution clear and improve the nature of the final deposits.

IV.1.C. AMALGAMS

Tin is one of the many metals soluble in mercury, and tin amalgams may be formed relatively easily either by electrolysis or by dissolving the metal in hot mercury in the absence of oxygen.[63] Although the amalgam may be obtained without difficulty and tin may be recovered from the amalgam quickly and easily,[104] the author knows of no application of tin amalgam to tin radiochemistry.

An interesting radiochemical separation technique developed recently involves the use of "amalgam exchange."[38] Certain elements, present in aqueous solution, apparently have the property of exchanging atoms quite rapidly with their amalgams. Essentially carrier-free Cd, Pb, and Zn, for example, exchange 90% or more of their activity with their amalgams in less than 5 minutes mixing time. According to the preliminary data of DeVoe et al.,[38] tin does not exchange with its amalgam in either 0.5$\underline{M}$ $NaNO_3$ or saturated NaCl solutions. In certain applications, therefore, it might be advantageous to scavenge contaminating elements (Pb, for instance) away from Sn merely by stirring the solution in contact with the appropriate amalgam.

IV.1.D. POLAROGRAPHY

In the great majority of cases polarographic techniques are of little value to the radiochemist. Since tin may be determined polarographically, however, and it is conceivable that circumstances might arise in which this technique would be useful, several references which deal specifically with the polarography of tin are included: Cooper[30] has studied the anodic behavior of tin in acid, neutral, and alkaline solution, while Lingane[105] has studied the polarographic behavior of chloro and bromo complexes of stannic tin. Sara[148] has used polarography to determine tin in a dichromic acid medium, and Stricos and Porter[171] have used this technique to determine cadmium, indium, and tin in silver-base alloys.

IV.1.E. VARIOUS OXIDATION STATES

Solutions of stannous (+2) tin are common in any inorganic analytical laboratory. Stannous chloride, for example, is a very effective reducing agent for a large number of species. Stannous tin may be prepared quite easily, and the reduction of Sn^{+4} to Sn^{+2} with iron or nickel metal is a usual preliminary step in the most common analytical method for quantitative determination of tin: volumetric titration with a standard iodine solution.

Unfortunately, stannous tin solutions are quite unstable and, if left in contact with air for any appreciable length of time, are oxidized to stannic tin.[99, 100] This "autooxidation" may be inhibited by a number of organic reagents, the most efficient of which are the complex quinonoid compounds: Bandrowski's base and Barsilowski's compound.[5] Under normal conditions, however, oxidation of stannous solutions is prevented either by excluding all oxidizing agents (including air) or by storing the solution over a reducing agent (usually tin metal).

Since the $Sn^{+2} - Sn^{+4}$ potential is only -0.15 v, tin is easily oxidized to its highest oxidation state and most radiochemical tin procedures deal almost exclusively with stannic tin. With a single oxidation state predominating, one would expect the chemistry of tin to be relatively simple. Tin salts may be fairly easily volatilized, however, and stannic tin in aqueous solution has a notable tendency to hydrolyze at the slightest provocation. This behavior, plus the fact that there are very few chemical separation steps which are at all selective for tin, makes tin one of the more difficult elements to obtain radiochemically pure. A more detailed description of the chemical behavior of stannic tin will be presented in subsequent sections.

Stannane (SnH_4) may be produced by a number of different methods, of which those of chief interest to radiochemists are: cathodic reduction of tin solutions at high overvoltages, particularly with lead electrodes, and reduction of tin in acid solution with strong reducing agents such as Mg or Zn metal.[71] For those who wish to persevere, it may be produced more efficiently by reduction with $LiAlH_4$[71, 51] or $NaBH_4$.[154] It is an unstable gas which decomposes fairly rapidly in air at room temperature, and decomposes immediately at 150°C. Of chief interest to the radiochemist is the fact that stannane can be formed in reduction processes in which hydrogen is evolved and that it may be swept out of solution by the hydrogen gas. The amount of stannane formed by this technique is usually quite low, but for those who are unaware of this phenomenon the inadvertent disappearance of their tin samples in a tin reduction step could prove most embarrassing.

IV.2. SOLUBLE SALTS

Few data are available on the solubility of the soluble tin salts. Such data as are given in the Handbook of Chemistry and Physics,[66] the Handbook of Chemistry,[97] and Seidell's "Solubilities of Inorganic and Metal Organic Compounds"[160] are reproduced in Table 1.

IV.3. VOLATILE COMPOUNDS

IV.3.A. CHLORIDE

Tin forms volatile chlorides and bromides easily enough to make distillation a valuable procedure for separating tin from a large number of other elements.

Hoffman and Lundell[67] have shown that in the temperature range 200-220°C Sn^{+2} and Sn^{+4} may be distilled essentially quantitatively from HCl-$HClO_4$ solution but that no tin is distilled when H_3PO_4 is present. In an HCl-H_2SO_4 solution only a small percentage of either Sn^{+2} or Sn^{+4} can be distilled. In contrast to these data, however, Hoffman and Brandt[68] prefer to distill $SnCl_4$ by heating an aqua regia solution to dryness, and state that if either sulfuric acid or perchloric acid is added before the volatilization process is completed, considerable quantities of tin are retained in the distilling flask. In the Hoffman and Brandt procedure the $SnCl_4$ is heated at about 300°C for 5 minutes after the aqua regia has been evaporated, and the distillation is repeated twice to effect removal of all of the tin. The essential part of this procedure is the high temperature distillation after removal of the aqueous phase. Atkinson, Steigman, and Hiskey[3] have found distillation of anhydrous chlorides to be an effective method for separating tin from niobium and tantalum, and Hudswell and Nairn[70] have used the distillation of anhydrous $SnCl_4$ as an essential step in the preparation of extremely pure tin samples; but in general the distillation of tin chloride is less attractive as a separation step than is the distillation of tin bromide.

Table 1. Solubilities of tin salts.

Tin	Formula	Solubility in g/100 ml		
		Cold H_2O	Hot H_2O	Other
acetate(ous)	$Sn(C_2H_3O_2)_2$	d.		s. dil. HCl
bromide(ous)	$SnBr_2$	85.2(0°)	222.5(100°)	
(ic)	$SnBr_4$	s. d.	d.	s. acet., $AsBr_3$, PCl_3, act.
chloride(ous)	$SnCl_2$	83.9(0°)d.	269.8(15°)d.	s. al., eth., acet., pyr., ethyl acetate, methyl acetate.
	$SnCl_2.2H_2O$	118.7 d.	∞d.	
(ic)	$SnCl_4$	s.	d.	s. eth.
	$SnCl_4(3,4,5H_2O)$	s.	-	
chromate (ic)	$Sn(CrO_4)_2$	s.		
fluoride(ous)	SnF_2	s.		
(ic)	SnF_4	v. s.	d. to SnO_2	
iodide(ous)	SnI_2	1.32(20.8°)	3.55(98.5°)	d. KOH, HCl s. HF, CS_2
(ic)	SnI_4	d.	d.(to SnO_2)	145(15°C)CS_2, s. al., eth., chl., bz.
nitrate(ous)	$Sn(NO_3)_2.20H_2O$	d.	d.	
(ic)	$Sn(NO_3)_4$	d.	d.	
sulfate(ous)	$SnSO_4$	33(25°)	18(100°)	s. H_2SO_4
(ic)	$Sn(SO_4)_2.2H_2O$	v. s.	d.	s. eth., dil. H_2SO_4; reacts with HCl.

IV.3.B. BROMIDE

At 200-220°C tin may be distilled essentially quantitatively from HBr-$HClO_4$, HBr-H_3PO_4-$HClO_4$, and HBr-H_2SO_4 solutions.[67] A number of other elements, notably arsenic and antimony, also distill from these solutions; but by proper control of the experimental conditions, arsenic and antimony may be removed from the solution before tin is distilled.

A number of authors have published articles describing the bromide distillation of tin but the definitive work in this field is probably the article by Scherrer,[156] who used distillation techniques to separate arsenic, antimony, and tin from their mixtures. An all-glass apparatus such as is shown in the

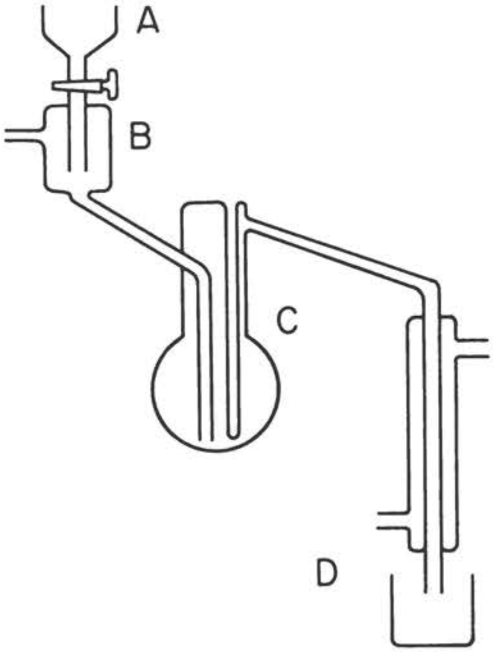


Fig. 3. Distillation apparatus.

schematic diagram of Fig. 3 was used for the distillation. In Fig. 3, A is a funnel for holding the acid which is added in the course of the distillation.

B is an arrangement for gaging the rate of flow of the acid and is provided with a side tube for the purpose of introducing a stream of CO_2. C is a distilling flask provided with a delivery tube, thermometer well, and side tube connected to a water condenser. D is the distillate-receiving flask.

In a distillation separation of As^{+3}, Sb^{+3}, and Sn^{+4} the initial solution in distilling flask C should be an $HCl\text{-}H_2SO_4$ mixture, > 6M HCl, 0.5-1M H_2SO_4. (Note: As^{+5} and Sb^{+5} may easily be reduced to their trivalent states by boiling a concentrated H_2SO_4 solution containing hydrazine sulfate. Sn^{+4} is unaffected.[65]) With a continuous stream of CO_2 bubbling through the solution, distillation will remove the arsenic and result in a final distilling temperature of 110-111°C. At this point the receiver flask is replaced, concentrated H_3PO_4 is added to the distilling flask, and Sb is distilled at 155-165°C, with concentrated HCl being added slowly but continuously through funnel A. When all the antimony has been distilled the apparatus is cooled, the receiver flask is again replaced, and distillation is resumed at 140°C with a 3-to 1-mixture of conc. HCl and conc. HBr flowing slowly into the distilling flask. The volumes of liquid required for a given distillation will depend on the size of the equipment and the amount of material being distilled, of course. As a rough indication of what is needed, Scherrer uses a 200-ml distillation flask and recommends that 25-50 ml of HCl be used to distill milligram amounts of arsenic; 100 mg of antimony requires 150-175 ml of HCl, and 100 mg of tin requires about 125 ml of mixed HCl-HBr. All distillates are collected in an initial volume of 50-100 ml of H_2O.

While this distillation procedure separates tin from a large number of elements, it is not completely selective, and Mo, Re, Se, Te, and Hg may be expected to come over in part with the tin fraction.[67, 65]

Other articles which deal with the distillation of $SnBr_4$ use essentially the same procedure as described by Scherrer, but in each paper there are experimental details which may be of value to those who have problems in this field. Heuss[64] describes a simplified procedure for separating As, Sb, and Sn in their mixtures, while Blyum and Zyryanova[12] determined small amounts of tin in ores by distilling $SnBr_4$ and determining the tin polarographically. Farnsworth and Pekola,[50] Jantsch, Hummer-Kroupa, and Gansinger,[72] and Schwaibald, Borchers, and Nagel[158] all use distillation as a preliminary step to the colorimetric determination of microgram amounts of tin. Wilkinson and Grummitt[188] have published a procedure for separating tin from fission products which includes an $SnBr_4$ distillation step, and, finally, Maxwell, Haymond, Bomberger, Garrison, and Hamilton[119] have used distillation techniques to separate carrier-free tin activities from cadmium cyclotron targets.

IV.3.C. FLUORIDE

Chapman, Marvin, and Tyree[23] have shown that when HF-$HClO_4$ solutions containing tin are evaporated to strong fumes of $HClO_4$ no tin is lost through volatilization.

IV.3.D. IODIDE

Caley and Burford[21] have described a procedure by which stannic oxide may be separated from various oxides by ignition with ammonium iodide at 400-500°C. Stannic iodide is volatilized while the oxides or iodides of iron, silica, tungsten, copper, lead, and nickel remain in the crucible.

IV.4. INSOLUBLE SALTS

IV.4.A. INSOLUBLE SALTS AND GRAVIMETRIC COMPOUNDS

IV.4.A.1. Hydrolysis

The disconcerting ease with which tin ions can combine with water to form hydrolysis products of varying degrees of solubility complicates all phases of tin chemistry. As Thorne and Roberts[178] put it: "The chemistry of the hydrated oxides of the less electropositive metals forms one of the most difficult chapters of inorganic chemistry. Their properties, structure, formation and ageing place them outside the general lines of method and theory of pure chemistry or even of colloid chemistry and involve all sorts of questions of thermo-chemistry, thermodynamics, and of optics." Therefore it should be emphasized at the outset that the dehydrated species of tin are extremely difficult to study in any detail since their structure and properties depend to such a large degree on their age as well as the exact way in which they were formed. In spite of these limitations on detailed knowledge, however, a general understanding of the hydrolytic behavior of tin is essential for anyone doing radiochemical separations of this element.

Many stannic salts dissolve in strong base to give a perfectly clear solution. The exact nature of the Sn^{+4}-OH^--H_2O species in this medium has not been determined to everyone's satisfaction; its formula weight corresponds to SnO_3^{-2}, but the consensus seems to be that the most probable formula is $[Sn(OH)_6]^{-2}$. The only difference between these two formulae, of course, is in three waters of hydration, but the preference for $[Sn(OH)_6]^{-2}$ is based to a considerable degree on the existence of well-defined salts of definite composition, such as $K_2[Sn(OH)_6]$, $Sr[Sn(OH)_6]$, $Pb[Sn(OH)_6]$, etc.[145] X-ray determination of structures also confirms the view that the $[Sn(OH)_6]^{-2}$ radical underlies the stannates obtained from aqueous solutions.[145]

The acid corresponding to this radical, $H_2[Sn(OH)_6]$, cannot be obtained in the free state. Neutralization of stannate solutions with strong acids yields voluminous white precipitates which are soluble both in an excess of strong acid and in alkali. The precipitates, ordinarily called stannic acids, have the appearance of gels, and it is not certain whether they contain chemically bound water or whether they are merely SnO_2 gels. Freshly formed precipitates possess no crystalline structure detectable by x rays, but through aging, either by heating or by prolonged standing in contact with the solution, they develop a crystal structure characteristic of SnO_2. The freshly formed, gelatinous precipitate is markedly different in chemical behavior from the aged, crystalline precipitate, and the two forms are distinguished as α- and β-stannic acid respectively, or as "ordinary stannic acid" and "metastannic acid." α-Stannic acid is characterized by the relative ease with which it may be dissolved in acids, alkali carbonate, or caustic solutions. β-Stannic acid is noted chiefly for its intractability; in acids or bases it does not dissolve but peptizes to form collodial solutions.[145]

It has been suggested that these behavioral differences between α- and β-stannic acid can be explained by the assumption that the two substances are different collodial varieties of insoluble tin dioxide or its hydrates, differing from one another only by their particle size. Another point of view is that α-stannic acid, initially present as $SnO_2 \cdot xH_2O$, condenses under the influence of higher temperature or prolonged time to more thermodynamically stable crystalline forms by eliminating water. The latter hypothesis is supported by evidence for the existence of the transient condensation products $SnO_2 \cdot 3H_2O$, $2SnO_2 \cdot 3H_2O$, $4SnO_2 \cdot 5H_2O$, and $SnO_2 \cdot H_2O$ but it seems probable that both polymerization and condensation take part in the change from α- into β-stannic acid.[145, 26]

Whatever the mechanism of formation, however, it is essential to recognize the existence of two forms of stannic acid, and to realize that if the acid has been precipitated under conditions where metastannic acid is the predominant form, subsequent dissolution and treatment of the tin sample might be fairly difficult.

In acid solution it may be assumed, as a general rule, that stannic tin will hydrolyze unless a complexing agent is present which will keep it in solution. The rate of hydrolysis is a function of temperature and tin concentration as well as the kind of acid that is present, however, and it may be possible for cold, dilute solutions of tin to stand for some time before the characteristic cloudiness appears. Practically complete precipitation of tin as metastannic acid may be obtained fairly quickly by digesting tin in 3<u>M</u> HNO_3 at 80-100° C, although excessive amounts of iron interfere and cause incomplete precipitation.[65] Hot solutions of $HClO_4$ and H_2SO_4 also precipitate metastannic acid at a reasonable rate and Krokowski[93] reports that a precipitate having many of the properties of metastannic acid is formed when an excess of Br_2 is added to a dilute caustic stannate solution.

It should be emphasized once again, however, that conditions under which metastannic acid is formed are usually avoided like the plague in radiochemical separation procedures. If it is formed in a carrier-free solution before tin carrier is added, the isotopic exchange problem can be formidable. If it is used for quantitative precipitation of tin, care must be taken that all complexing and interfering ions are absent, or precipitation will not be complete. If its precipitation is intended as a separation step, Sb, Te, Nb, and the other acid-insoluble elements must be expected to coprecipitate with the tin. If it is once precipitated, it is difficult to wash because of its marked tendency to peptize. And if it is washed effectively without peptizing, it is difficult to redissolve. It is possible to dissolve metastannic acid by boiling in concentrated sulfurous acid for a few minutes, adding concentrated HCl, and boiling again for a few minutes,[65] but the generally intractable and antisocial behavior of metastannic acid eminently qualifies it for ostracism from the ranks of well-behaved chemical compounds.

Stable acid solutions of Sn^{+4} in hydrochloric acid can be prepared, presumably due to the formation of the $SnCl_6^{-2}$ complex ion, provided that a sufficient excess of HCl is present. Johnson and Kraus[75] have shown that in solutions where the HCl concentration is greater than 0.7$\underline{M}$, tin solutions remain apparently stable for periods of years. Below 0.7$\underline{M}$ HCl, the solutions are not stable, and polymerization and precipitation occur, although in the borderline region around 0.5-0.7$\underline{M}$ HCl the precipitation rate can be extremely slow (months or years).[75, 94]

Stannous tin (Sn^{+2}) behaves very much like Sn^{+4} in its aqueous hydrolytic reactions. When Sn^{+2} solutions are neutralized with alkali carbonate or hydroxide a very insoluble white precipitate of $Sn(OH)_2$ is obtained (solubility product = 8×10^{-29} at 22° C).[90] On aging in contact with the solution or by heating, $Sn(OH)_2$ decomposes to form the brown anhydrous stannous oxide, SnO.[145] The white stannous hydroxide dissolves in strong bases to form the hydroxostannite complex, $Sn(OH)_3^-$, and crystalline compounds having the composition $Na[Sn(OH)_3]$, $Ba[Sn(OH)_3]_2$, and $Sn\,[Sn(OH)_3]_2 \cdot 2H_2O$ have been prepared.[157] Little has been reported on the hydrolysis of Sn^{+2} in acid solution, but Tobias, in a masterful study of this phenomenon,[179] reports that the main product of hydrolysis in a 3$\underline{M}$ ClO_4^- medium is $Sn_3(OH)_4^{+2}$, although $Sn_2(OH)_2^{+2}$ and $SnOH^+$ are formed to a lesser extent. Stannous tin is a powerful reducing agent in all aqueous media, and the problem of keeping Sn^{+2} solutions free of Sn^{+4} has undoubtedly complicated the unequivocal measurement of the hydrolysis reactions of Sn^{+2}.

IV.4.A.2. Sulfide

Stannic sulfide (SnS_2) may be precipitated essentially quantitatively by addition of H_2S to acid solutions of stannic salts. The acid concentration range in which complete precipitation may be achieved is fairly broad, provided that no strong tin complexes are formed with the acid. In H_2SO_4, for example, stannic sulfide may be precipitated completely from acid concentrations as high as 6$\underline{N}$,[113] but in HCl, acid concentrations greater than 1$\underline{N}$ result in significant losses of tin. Sorum and Wolf[168] have studied the solubility of SnS_2 in HCl solutions in some detail and, since this is the medium in which radiochemical stannic sulfide precipitations are most often performed, their data are reproduced in Fig. 4. As is apparent from Fig. 4, stannic sulfide has an appreciably greater solubility than either antimony sulfide or arsenic sulfide in all concentrations of HCl. Its solubility is fairly strongly dependent on temperature, also, so that cold solutions having an HCl concentration less than 1$\underline{M}$ should be used if tin losses are to be kept to a minimum. It should be pointed out, however, that the data in Fig. 4 were obtained in HCl solutions which were initially sulfide-free; i.e., preprecipitated and washed sulfides were equilibrated with fresh HCl solutions of various concentrations and measurements were made of the amount of cation that went into solution. In cases where the supernatant solution is saturated with

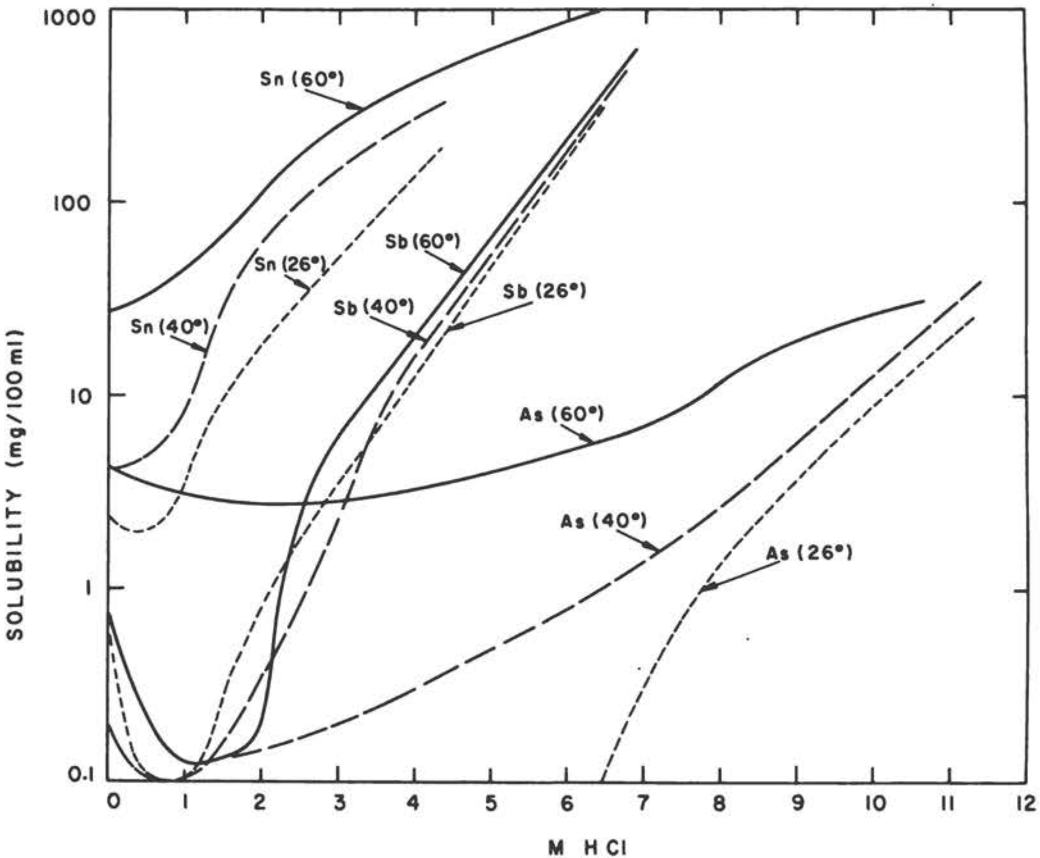


Fig. 4. The solubilities of the sulfides of arsenic (As_2S_5), antimony (Sb_2S_5), and tin (SnS_2) in hydrochloric acid at 26°, 40°, and 60° C.

H_2S it is to be expected that the absolute solubilities of these sulfides would be lower than is shown in Fig. 4, but the relative solubilities of the sulfides of Sn, Sb, and As should remain approximately as they are shown by the curves.

Stannic sulfide dissolves readily in alkali sulfide solutions due to the formation of thiostannate ions. Combination of one S^{-2} ion with SnS_2 gives the "metathiostannate" $(SnS_3)^{-2}$, while two S^{-2} ions give the "orthothiostannate" $(SnS_4)^{-4}$ complex. Stannic sulfide also dissolves in alkali hydroxide solutions, forming both thiostannate and hydroxostannate ions:[145]

$$3\ SnS_2 + 6OH^- = 2(SnS_3)^{-2} + [Sn(OH)_6]^{-2}.$$

Formation of these complexes is reversible, and acidification of the basic solution results in the precipitation of SnS_2. Indeed, Taimni and Agarwal have applied this technique for precipitating stannic sulfide to the quantitative gravimetric determination of tin.[177]

Tin sulfide is usually precipitated by passing a stream of H_2S gas through a dilute acid solution containing tin. Thioacetamide may also be used,[52, 53] although thioformamide seems to be somewhat more effective.[128]

In a great majority of radiochemical procedures, precipitation of stannic sulfide is used as a purification step to separate tin from other elements of the periodic table. Precipitation of the sulfide is certainly not selective for tin, and the fact that it is used so often reflects more on the paucity of good separation steps for tin than on its effectiveness in getting tin away from other elements. Normally, however, an attempt is made to improve the separation factor by precipitating sulfides from a solution in which a complexing agent prevents precipitation of stannic sulfide. After these sulfide scavenges are completed, the tin complex is destroyed and SnS_2 is precipitated.

Thus, Sarudi[150] has separated antimony from tin by precipitating Sb_2S_3 from 2.5-3<u>M</u> HCl with phosphoric acid present as the complexing agent. The separation seems to work satisfactorily, but subsequent chemistry on the tin fraction is often complicated by the presence of occluded phosphate in the SnS_2 precipitate.[128]

Tartrate has also been used as a complexing agent to inhibit precipitation of stannic sulfide. The data of Dey,[40] who studied the degree of inhibition as a function of time and tartrate concentration, are shown in Table 2. The effectiveness of inhibition is almost certainly pH dependent (see next paragraph), and, since Dey made no attempt to keep the pH constant, the quantitative data of Table 2 as a function of tartrate concentration are open to serious question.

Table 2. Percentage inhibition of the precipitation of stannic sulfide by sodium tartrate in dilute HCl. (40)

$Sn^{+4}:C_4H_2O_6^{-2}$	Time after filtration (hours) 0	1/2	4	8	96
1:0	2.35%	2.35%	1.90%	--	--
1:0.665	11.78	11.50	11.28	10.42%	9.28%
1:1.33	15.24	13.34	12.08	11.29	10.36
1:2.66	18.50	15.32	14.12	13.75	12.03
1:5.32	33.71	26.21	25.28	23.62	22.51
1:10.64	43.31	33.59	30.65	28.01	26.28
1:15.96	56.01	42.21	38.73	32.58	29.36
1:21.28	69.28	48.73	40.38	36.71	33.05

At a constant tartrate concentration, and presumably a constant pH, the data should be valid, and indicate that short digestion periods are desirable if tin is to be kept in solution.

Oxalate ion has probably been used more than any other complexing agent to inhibit the precipitation of stannic sulfide. Its use is sharply dependent on acid concentration, however, and markedly different results may be obtained at various pH's. Karsten and Kies[78] have studied the precipitation of SnS_2 from sulfuric acid - oxalic acid solutions as a function of pH, and their data are reproduced in Fig. 5. A constant amount of Sn^{+4} and oxalic acid in a constant volume of solution was used at each pH. SnS_2 was precipitated with H_2S gas and the steam-bath digestion periods were usually 19 hours.

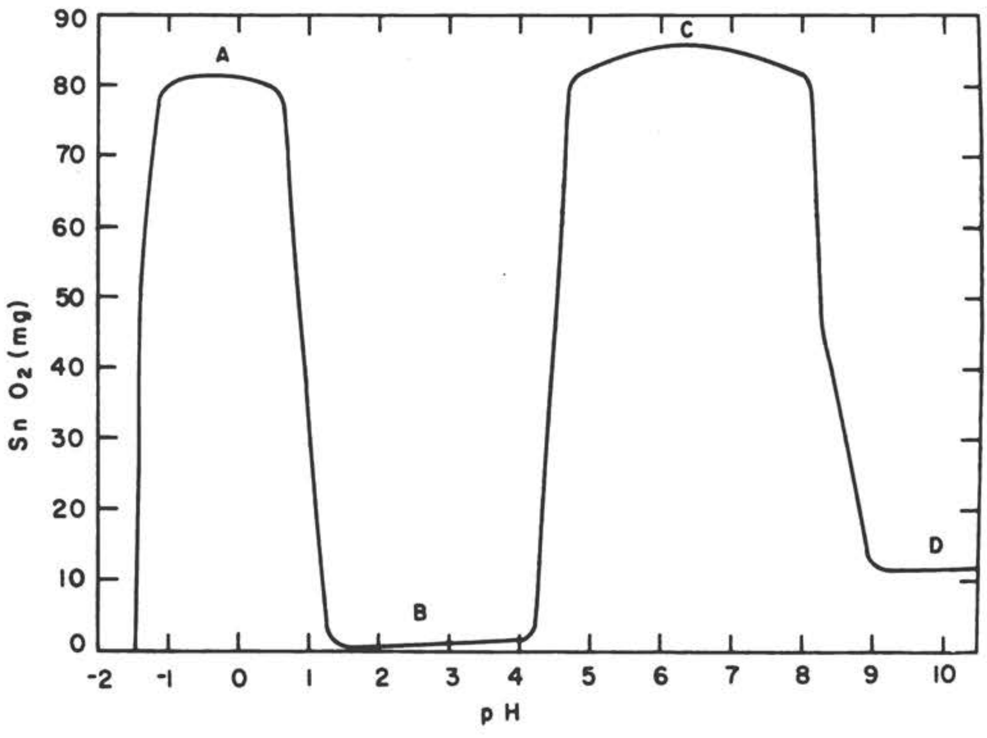


Fig. 5. Precipitation of stannic sulfide in sulfuric acid - oxalic acid solutions as a function of pH.

The SnS_2 precipitates were washed, dried, and ignited to SnO_2 for the values plotted in Fig. 5. Unfortunately the authors give no values for "100% yield" of SnO_2, so that no conclusions can be drawn as to the completeness of precipitation at those pH's where tin is not complexed, but several interesting conclusions as to the relative complexing power of oxalate at various pH's can be drawn. On the curve of Fig. 5. the minimum at B is of primary importance since it is the region where the tin-oxalate complex is strongest. The minimum is not very narrow – it extends from pH 1.5 to 4 -- but the curve rises sharply outside these limits, and apparently one may not deviate from these limits very much without precipitating SnS_2.

The left-hand maximum A is due to the fact that the solution is so acid that oxalate ions exist primarily as undissociated oxalic acid and the weak tin-oxalate complex decomposes, while the right-hand maximum C arises from the fact that the S^{-2} and OH^- ion concentrations are increasing enough to precipitate tin sulfide and hydroxide despite the existence of the tin-oxalate complex in solution. And finally, at high pH's, formation of thiostannate ions once again inhibits precipitation of SnS_2.

Dey and Bhattacharya[39] have reported that oxalate salts are more effective than oxalic acid in inhibiting precipitation of stannic sulfide and that the degree of inhibition decreases with time. Their data are reproduced in Tables 3 and 4. The authors made no attempt to control the pH of their solutions, but from the data they give the solutions were approximately 0.1-0.3$\underline{M}$ in H^+, or on the steepest portion of the curve between A and B in Fig. 5. It is doubtful, therefore, that any credence can be given to the relative complexing powers of oxalate vs oxalic acid shown in Tables 3 and 4. At a given

Table 3. Percentage inhibition of SnS_2 precipitation in the presence of different concentrations of oxalic acid in dilute HCl solutions. (39)

$Sn^{+4}:C_2O_4^{-2}$	Time after filtration (hours) 0	1/2	4	8	96
1:0	2.35%	2.35%	1.90%	--	--
1:0.778	3.08	2.35	2.35	0.29%	0.29%
1:1.542	3.66	3.08	2.78	0.81	0.66
1:3.085	6.30	4.98	4.18	1.50	1.32
1:3.526	73.40	7.18	6.23	2.93	1.54
1:4.113	73.50	7.33	6.30	3.00	1.54
1:6.170	73.50	7.33	6.45	3.15	1.54

Table 4. Percentage inhibition of SnS_2 precipitation in the presence of different concentrations of potassium oxalate in dilute HCl solutions. (39)

$Sn^{+4}:C_2O_4^{-2}$	Time after filtration (hours) 0	1/2	4	8	96
1:0	2.35%	2.35%	1.90%	--	--
1:0.389	9.74	9.29	9.22	8.78%	8.72%
1:0.778	23.22	19.93	19.05	18.54	18.31
1:1.542	34.11	29.28	26.08	19.49	19.32
1:2.075	50.15	32.06	28.18	21.61	20.58
1:2.468	63.37	39.38	32.21	22.91	21.96
1:3.085	87.63	40.56	35.21	23.35	22.04

$Sn^{+4}:C_2O_4^{-2}$ ratio, however, the decrease in inhibition as a function of time ought to be correct since each of the solutions in a given series should be at the same pH. This would indicate that prolonged digestion of Sn^{+4}-$C_2O_4^{=}$-$S^{=}$ solutions is not desirable if tin is to be kept in solution.

Fluoride ion may also be used as an effective complexing agent to inhibit precipitation of stannic sulfide. This technique has been mentioned in the literature,[85] and McCay[121] has shown that Sn^{+4} is quantitatively complexed by strongly acetate-buffered fluoride solutions – no SnS_2 being obtained when H_2S is passed through the solution, and no tin being occluded on a sulfide scavenge. Sn^{+2}, Sb^{+3}, and As^{+3} are quantitatively precipitated as the sulfides in this solution, but Sb^{+5} and As^{+5} are also complexed by the fluoride and no sulfide precipitate is obtained. An important practical reason for preferring fluoride to oxalate is the fact that the tin-fluoride complex may easily be destroyed with borate ion, and SnS_2 may be precipitated without the pH having to be changed significantly. This improves both the separation factor of the SnS_2 precipitation and the speed of the operation, and is the method used by the author to scavenge and precipitate tin sulfide.

The technique of complexing tin in dilute acid, precipitating a scavenging sulfide, and then precipitating tin sulfide may be used to separate tin from a large number of elements, but it is used most often to separate tin from antimony. Examples of Sn-Sb separations of this sort, in which oxalate is used as the complexing agent, may be obtained in articles by Musil, Gagliardi, and Reischl[128] and Villadsen and Poulsen.[185]

The dark brown stannous sulfide, SnS, is precipitated by H_2S in acid solution, with acid concentration limitations very similar to those for stannic sulfide.[113] Precipitation of stannous sulfide is not inhibited by the same complexing agents which work for Sn^{+4}; i.e., stannous oxalate is relatively insoluble and precipitates under conditions where the stannic oxalate complex if formed.[128] Stannous sulfide does not form thiostannite complexes and is insoluble in colorless ammonium polysulfide. In yellow alkali polysulfides, however, it is oxidized to Sn^{+4} and dissolves with the formation of thiostannate complexes:[145]

$$SnS + S + S^{=} = SnS_3^{-2}.$$

IV.4.A.3. Cesium Hexachlorostannate

Browne, Craig, and Davidson[16,33] report that insoluble Cs_2SnCl_6 may be precipitated from 10F HCl solution. They use this precipitate to separate Sn^{+4} quantitatively from Sn^{+2} and give 3.6×10^{-8} as the solubility product for the reaction:

$$2Cs^{+} + (SnCl_6)^{-2} = Cs_2SnCl_6.$$

IV.4.A.4. Selenite

DeCarvalho[22] has used selenous acid (H_2SeO_3) as a quantitative precipitant in the gravimetric determination of tin. The stannic selenite precipitation must be done out of very dilute acid solution ($\leqq$ 2 volume % HCl or H_2SO_4), and easily hydrolyzable elements like Sb, Nb, Te, etc. may be expected to coprecipitate. Quadrivalent ions such as Th^{+4}, Zr^{+4}, Ti^{+4}, and Ce^{+4} also interfere.

IV.4.A.5. Oxalate

Meyer and Kahn[123] have separated Sn^{+2} -Sn^{+4} mixtures in ethyl alcohol by precipitating stannous tin with oxalic acid. Completeness of precipitation is apparently dependent on the Sn^{+4} concentration, but the authors were able to recover at least 86% of the total stannous tin as the oxalate.

IV.4.A.6. Ferrocyanide

Pelagatti[138] has published a procedure for separating tin from lead and trivalent antimony in white metal alloys which involves precipitation of tin with potassium ferrocyanide from a dilute sulfuric acid solution containing tartrate. The solutions must be kept below 60° C to prevent precipitation of antimony, but under the conditions described by the author the Sb^{+3} -Sn^{+4} separation appears to be essentially quantitative.

IV.4.A.7. Phenylarsonic Acid and Related Compounds

Knapper, Craig, and Chandler[86] first described the use of phenylarsonic acid as a reagent for the determination of tin. The precipitation is apparently complete for tin provided that, in HCl solution, the acid concentration is not greater than 5 volume % or, in H_2SO_4 solution, 7.5 volume %. The authors report that phenylarsonic acid may be used to separate tin from Cu, Zn, Pb, Sb, Ni, Fe, Cd, Al, and Bi, and that only Zr and Th interfere; but there is relatively sharp disagreement by authors of other articles dealing with this reagent. The degree and character of the precipitation are almost certainly pH dependent, and Kuznetsov[95] states that phenylarsonic acid precipitates tin quantitatively only with a high concentration of reagent, a solution of low acidity, and in the absence of organic complexing agents. He states further that the phenylarsonic tin can be contaminated by many other ions. In addition, Mack and Hecht[115] have rejected phenylarsonic acid as a precipitant for milligram amounts of tin because of its nonselectivity, particularly for antimony.

From these articles it is apparent that phenylarsonic acid should not be used as an especially selective precipitant for tin, but it is not established that phenylarsonic acid has no applications at all in radiochemical separations. There might conceivably be cases in which this precipitation is of value in spite of the fact that other elements coprecipitate. As an indication of the elements which may or may not interfere with the phenylarsonic tin precipitation, the data of Portnov[142] may be presented, in which the behavior of Cu^{+2}, Be, Mg, Zn, Al, Tl^{+}, Mn, Fe^{+2}, Fe^{+3}, Ag, Ca, Ba, Sr, Cd, Hg^{+1}, Hg^{+2}, Bi, Pb, Sn^{+4}, Sb^{+3}, Co, Ni, Ta, and Nb in aqueous solution with phenylarsonic acid and various substituted phenylarsonic acids was studied qualitatively. Of these elements, Portnov states that only Nb, Ta, Ag, Sn, Sb, and Hg^{+} give insoluble or slightly soluble precipitates with phenylarsonic acid. The substituted phenylarsonic acids (p-NO_2, p-CH_3, p-OH, p-AcNH, and p-NH_2) are much less selective for this group of elements.

Karsten, Kies, and Walraven[79] have used 3-nitro-4-hydroxy-benzenearsonic acid to determine small amounts (0.1-0.2 mg) of tin turbidimetrically in the presence of a thousand times as much antimony. Measurements were carried out in 1.65<u>M</u> H_2SO_4 solutions in which antimony was complexed with tartaric acid.

IV.4.A.8. Tetraphenylarsonium Chloride and Related Compounds

Tetraphenylarsonium chloride may be used to precipitate tin quantitatively from acid solution. Willard and Smith[189] state that precipitation should be made from a solution which is 0.4-2.0<u>M</u> in HCl and 1.5-3.0<u>M</u> in NaCl. Anions which complex tin (oxalate, fluoride, phosphate, citrate) and species which also precipitate with tetraphenylarsonium ion (ReO_4^-, MnO_4^-, IO_4^-, ClO_4^-, I^-, Br^-, F^-, WO_4^{-2}, CrO_4^{-2}, SCN^-, Pt, Fe^{+3}, Bi, Tl^{+3}, Hg^{+2}, Cd^{+2}, Zn^{+2}, Au^{+3}) interfere.

Tetraphenyl phosphonium chloride[191] may also be used to precipitate tin. The solution should be 0.1-1.0<u>M</u> in HCl and 3.0-3.5<u>M</u> in NaCl, but the interfering species are essentially the same as with tetraphenylarsonium chloride.

Tetraphenylstibonium chloride will precipitate tin in HCl solution but its solubility is so low that its use as a reagent is extremely limited.[191]

IV.4.A.9. Tannin

Holness and Schoeller[69] have shown that tannin may be used to precipitate tin in dilute HCl (0.05<u>M</u>) or in ammonium oxalate solution. The method is effective in separating tin from Al, Fe, V, Cu, Pb, Be, Ta, Nb, Zr, and Th, but Sb interferes.

IV.4.A.10. Ammonium Benzoate

Jewsbury and Osborn[74] report that tin may be precipitated quantitatively by ammonium benzoate in hydrochloric acid-ammonium acetate solutions having a pH between 2.5 and 3.0. Sb, Al, Fe^{+3}, Zr, Th, Ce^{+4}, Bi, and Cr^{+3} interfere, but many elements, including Ce^{+3}, Be, Pb, Cu, Co, Ni, Mn, Zn, and Mg do not give a precipitate. Suzuki and Yoshimura[174] report essentially the same results.

IV.4.A.11. 8-Hydroxyquinoline

Hamaguchi, Ikeda, and Osawa[193] have described a gravimetric procedure for tin which involves precipitation of stannic 8-hydroxyquinolate from dilute HCl solution, drying at 110°-120° C, and weighing as $SnCl_2(C_9H_6NO)_2$. The precipitation is very sharply dependent on HCl concentrations, however, and any deviation from 0.2<u>M</u> HCl results in low yields. Species which complex tin, cations which hydrolyze at this acid concentration, or elements which also precipitate with 8-hydroxyquinolate, interfere.

IV.4.A.12. N-Benzoylphenylhydroxylamine

Tin may be precipitated quantitatively by N-benzoylphenylhydroxylamine from 1-8% HCl solution,[146] with the optimum concentration range of 0.5-0.6<u>N</u> HCl.[4] The tin salt, $(C_{13}H_{11}O_2N)_2\ SnCl_2$, has a relatively high melting point (171°C), and may be dried and weighed directly for the gravimetric determination of tin.[146] In acid solutions (> 1% HCl) only vanadium, zirconium, and titanium are precipitated by this reagent.[114] Antimony will hydrolyze in this concentration of HCl, but may be kept in solution with tartaric acid.[4]

IV.4.A.13. Cupferron

Cupferron may be used in fairly strong HCl or H_2SO_4 solutions (10% by volume) to precipitate a number of elements, notably tin, antimony, bismuth, palladium, gallium, iron, and elements of subgroups IVa, Va, and VIa (Ti, V, Zr, Nb, Mo, Hf, Ta, W).[113, 55] Antimony is precipitated completely only if it is in the trivalent state (Sb^{+5} gives no precipitate at all with cupferron).[55] The tin cupferrate cannot be weighed as such, since it decomposes at the temperatures that would be required to dry it, but must be ignited to SnO_2.

Stannic cupferrate is not a selective precipitant for tin by any stretch of the imagination, but Mack and Hecht[115] have used it to separate Sn^{+4}-Sb^{+5} mixtures (with tartaric acid present in solution to keep the antimony from hydrolyzing), and Kling and Lassieur[85] have used cupferron in preference to sulfide to precipitate tin after antimony was removed from a dilute fluoride solution as the sulfide.

IV.4.B. COPRECIPITATION

Little has been published, either on the coprecipitation of other elements with tin, or on the coprecipitation of tin with other elements. It is reasonable to assume, however, that the rules of coprecipitation which apply to most other elements are effective for tin; i.e., elements which form common insoluble salts may be expected to coprecipitate, although the degree of coprecipitation may be controlled to a limited extent by the manner in which the precipitation is carried out.[59]

A coprecipitation reaction for tin which is a little bit out of the ordinary, but which seems to be effective in separating tin (and antimony and bismuth) from large amounts of copper, lead, or silver, has been described by Kallman and Pristera.[76] Sn, Sb, and Bi are carried down quantitatively by precipitating MnO_2 in dilute ($< 0.5\underline{M}$) HNO_3 or H_2SO_4 solution.

Kuznetsov[96] discusses an interesting reaction in which carrier-free colloidal tin is quantitatively removed from $0.6\underline{N}$ H_2SO_4 solution by coprecipitation with methyl violet and tannin. The method is not specific, since elements which hydrolyze under these conditions will also be coprecipitated, but it is a rather unusual way for obtaining carrier-free tin.

IV.4.C. PYROLYSIS

Relatively few data are available on the high temperature behavior of tin salts. Dupuis and Duval,[44] however, have studied the pyrolysis of compounds which are most often used for the quantitative determination of tin, and their curves are reproduced in Fig. 6. The authors recommend cupferron as the best behaved of the six compounds tested, since it decomposes to SnO_2 at 747°, and at higher temperatures the pyrolysis curve is flat.

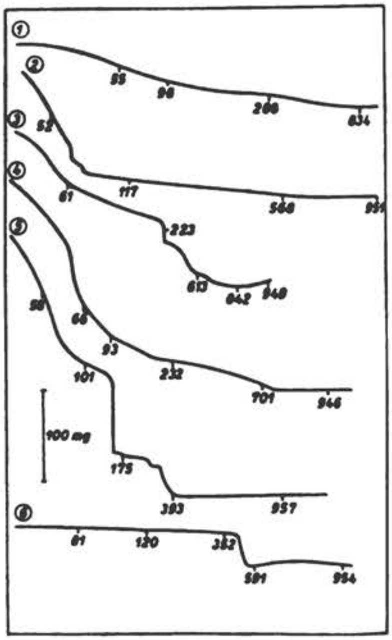


Fig. 6. Pyrolysis of tin compounds: 1. hydroxide, 2. pyridine, 3. tannin, 4. cupferron, 5. sulfide, 6. phenylarsonic acid. (44)

IV.5. SPECTROPHOTOMETRY AND TITRATION

IV.5.A. SPECTROPHOTOMETRY

In general, spectrophotometric and colorimetric methods are seldom used in radiochemistry. This is especially true for tin since the colorimetric methods available at present for the determination of tin cannot be considered entirely satisfactory. A number of papers have appeared on the colorimetric determination of tin, however, and these references will be included here for the information of those for whom this technique might have some value.

In aqueous solution, Sn^{+4} and Sn^{+2} salts are usually colorless, and their absorption spectra possess no distinctive features which are of value in quantitative determinations.[37] Many reagents may be used to give colored compounds or complexes with tin, perhaps the most generally useful of which is dithiol.[147, 158, 50, 25, 134] Diethyldithiocarbamate,[147, 35] phenylfluorene,[111, 112, 9, 58] quercetin,[108, 129] cupferron,[46, 10] morin,[58, 137] 8-hydroxyquinoline,[58, 57] thiourea,[131] silicomolybdic acid,[6] phosphomolybdic acid,[170] stilbazo,[129] hematoxylin,[124] flavonol,[32] 6 nitro-2-naphthylamine-8 sulfonic acid,[2] and various naphthalene derivatives[56] have also been used for the colorimetric determination of tin with varying degrees of success.

IV. 5. B. TITRATION

Titration is by far the most popular method used for the quantitative determination of tin in analytical procedures. As is the case with colorimetry, however, titration is seldom used in radiochemistry because it does not physically separate an element from its contaminants. Here again, references which discuss various titration procedures which have proven useful for the determination of tin are included for the information of those to whom they might prove of value, but no attempt will be made to discuss them in any detail.

Reduction of Sn^{+4} to Sn^{+2}, followed by titration of the Sn^{+2} with a standard I_2 solution, is a standard volumetric procedure for tin which may be found in any quantitative inorganic textbook as well as in a number of literature references.[47, 156, 155, 24, 125, 34, 176, 136] Other volumetric procedures for tin involve the use of ceric ion,[173, 167, 175] chromous ion,[106] hydrogen peroxide,[186] amalgams,[181] chloramine-B,[165] m-nitrophenylarsonic acid,[88] tetraphenylarsonium chloride,[89] and ethylenediaminetetraacetic acid.[54]

IV. 6. COMPLEX IONS AND CHELATE COMPOUNDS

IV. 6. A. HYDROLYSIS

Compared to most other elements, tin forms relatively few complex ions or chelate compounds which are of value in radiochemistry. The chemical properties of Sn^{+4} salts in aqueous solution are dominated by their tendency to undergo hydrolysis, and any complexing agent must compete with the strong affinity of tin for water. The interaction products of tin and water (in the absence of other complexing agents) have been discussed more fully in section IV. 4. A. 1. In most cases these products are insoluble, so that the only soluble species is apparently $Sn(OH)_6^{-2}$, formed in strongly alkaline solution.

A secondary effect of the hydrolytic tendency of tin is manifested in its ability to form "double complexes" in which the coordination sphere is occupied by more than one complexing anion. Examples of this type of complex have been observed by Courtney, Gustafson, Chabarek, and Martell,[31] who obtained the complex of tin with 5-sulfosalicylic acid, $[Sn(OH)_3X]^{-2}$, and with pyrocatechol-3, 5-disodium sulfonate, $[Sn(OH)_2X_2]^{-6}$, where X is the organic anion.

IV. 6. B. HALIDES

In aqueous solution Sn^{+4} reacts with halide ions to form hexacoordinated complex anions; i.e., fluorostannate (SnF_6^{-2}), chlorostannate ($SnCl_6^{-2}$), and bromostannate ($SnBr_6^{-2}$). Iodostannates have not been isolated from aqueous solutions, but such salts have been obtained from alcoholic media.[145]

In acid solution the chlorostannate complex is stable enough to prevent hydrolysis of tin, and HCl solutions of tin have been kept for many months without precipitation of metastannic acid.[75]

In addition to preventing hydrolysis, the fluorostannate complex is stable enough (with a dissociation constant[153] of about 10^{-25}) to prevent precipitation of stannic sulfide in dilute HCl solution.

Stannous tin also reacts with halide ions to form complexes. The weak chlorostannite complexes $SnCl^+$, $SnCl_3^-$, and $SnCl_4^=$ have been reported,[145, 43, 182] having, respectively, stability constants of 14, 50, and 48 at 25°C.[182]

In fluoride solution Schaap, Davis, and Nebergall[153] found the principal stannous fluoride complex to be SnF_3^-, for which at ionic strength 0.8 and 25°C they quote an equilibrium constant of 1.2×10^{-10} for the reaction $SnF_3^- = Sn^{+2} + 3F^-$.

Vanderzee[183] reports that stannous ions in bromide solutions form the complex species $SnBr^+$ and $SnBr_3^-$, but not $SnBr_4^=$, in bromide concentrations up to 0.5 molar. The stability constant for each of these species is smaller than that for the corresponding chlorostannite complex.

IV. 6. C. OXALATE

Stannic tin forms moderately strong complexes with oxalate ion. The degree of complexing is definitely pH dependent (see section IV. 4. A. 2) but little information is available on the size of the stability constant. Evidence has been presented, however, which indicates that the stannic oxalate complex has the formula $Sn(C_2O_4)_4^{-4}$.[41, 42]

IV. 6. D. SULFATE

In dilute sulfuric acid, Brubaker[17, 18] reports the predominant stannic sulfate species to be $Sn(SO_4)^{+2}$ and quotes an equilibrium constant of 5×10^{-2} at 30° C for the reaction $SnO_2(aq) + 2H_2SO_4 = SnSO_4^{+2} + SO_4^{-2} + H_2O$.

IV. 6. E. DIBASIC CARBOXYLIC ACIDS

Mattock[120] has studied the reactions of stannic tin in solutions of dibasic carboxylic acids and concludes that metal-organic anion complexes in the ratios 1:1 and 1:2 are the predominant species formed with tartaric, malic, or succinic acids. The experiments were very seriously complicated by hydrolysis reactions, however, so that no equilibrium constants were measured. The complexes are apparently very weak.

IV. 6. F. ORGANOMETALLIC TIN COMPOUNDS

Tin, being in the fourth group of the periodic table with C, Si, Ge, and Pb, can be made to form a very large number of organometallic compounds. These compounds form an entirely separate branch of tin chemistry, however, and since they are seldom, if ever, used in radiochemistry they will not be discussed here. Those who are interested in detailed information on this interesting group of compounds may consult review articles by Luijten and Van der Kerk[110] or Beduneau.[8]

IV. 7. EXTRACTION

IV. 7. A. METHYL ISOBUTYL KETONE (HEXONE)

In radiochemistry, extraction operations are looked on with favor because they can often be adapted with a minimum of difficulty to carrier-free samples as well as to samples containing macroscopic amounts of carrier. Extraction in a single set of conditions is seldom specific for a given element, but by performing multiple extractions under varied conditions very effective separations may usually be carried out.

The extraction media which have been reported for tin are not numerous, but considering the scarcity of other good tin purification steps they are of great value. Perhaps the most complete set of data on the extraction of tin into an organic solvent is that reported by Goto, Kakita, and Furukawa,[60] who studied the extraction of a large number of elements into methyl isobutyl ketone (hexone). Most of their extractions were made from HCl solutions, but $HClO_4$, HNO_3, and H_2SO_4 solutions were also used for certain elements. In preliminary experiments with the hexone-6M HCl system, the authors found that Fe^{+3}, Sb^{+5}, Sb^{+3}, As^{+5}, As^{+3}, Sn^{+4}, Se^{+4}, Te^{+4}, Ge^{+4}, Cr^{+6}, V^{+5}, Mo^{+6}, and Mn^{+7} could be extracted in significant amounts, while Fe^{+2}, Sn^{+2}, Cr^{+3}, Mn^{+2}, V^{+4}, Li, Na, K, Rb, Ca, Sr, Ba, Be, Al, Mg, Ti, Zr, Nb, Ta, Co, Ni, Cu, Ag, Zn, Cd, W, Hg, Pb, Bi, La, Ce, Pr, Th, U, P, and B were not extracted. Subsequent detailed study of most of the elements which could be extracted yielded curves such as those reproduced in Fig. 7, in which the percent extracted is plotted vs HCl molarity. No detailed data were given for the extraction of Cr^{+6}, V^{+5}, Mo^{+6}, or Mn^{+7}. In Fig. 7 the most notable feature relative to tin extraction is that at low HCl concentrations Sn^{+4} is extracted in significant amounts while Te^{+4}, Sb^{+5}, and As^{+3} are not. Separation of tin from these elements (and Mo) is the most difficult part of

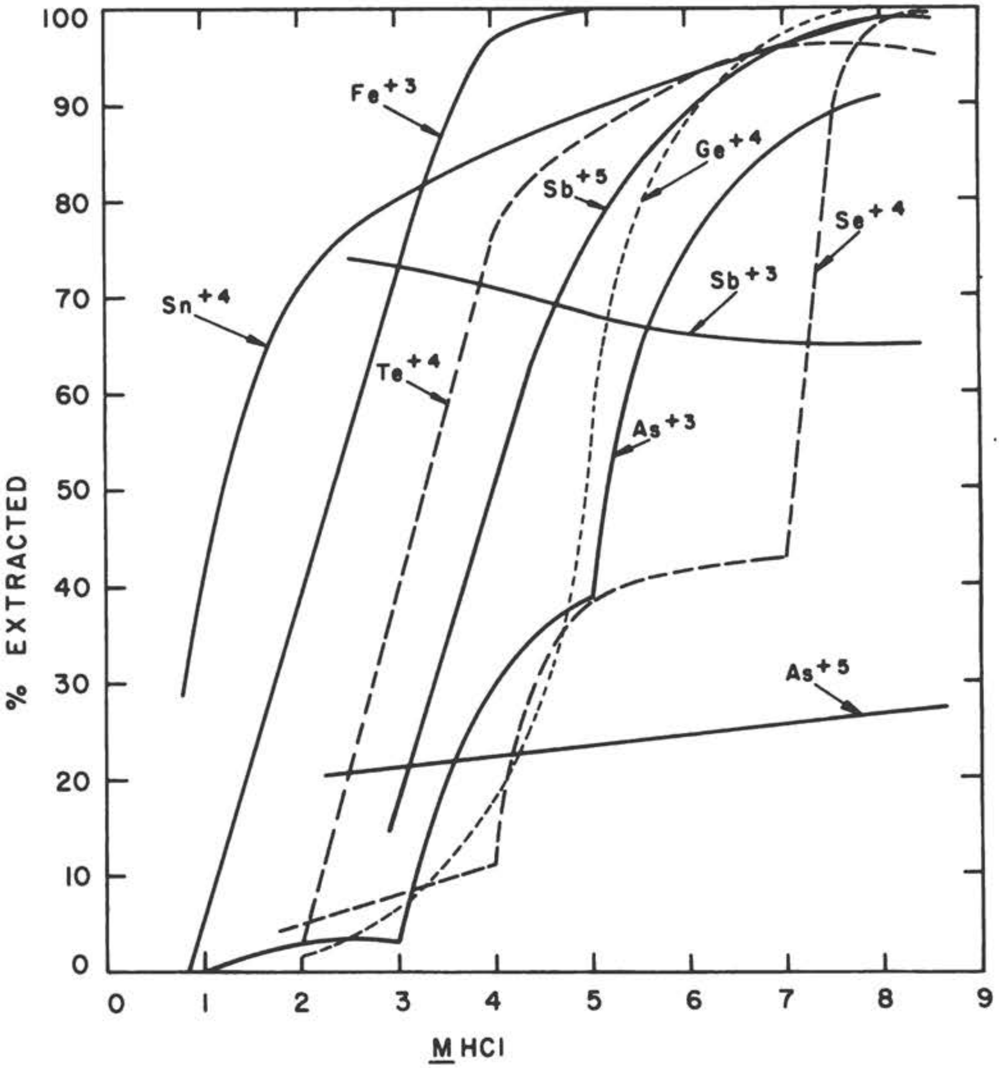


Fig. 7. Extraction by methyl isobutyl ketone (hexone) from HCl solutions. (135)

tin radiochemistry, but from the curves of Fig. 7 it is apparent that very effective separations can be carried out by extracting Sn^{+4} into hexone from 1.5-2M HCl solutions.

Attention should be drawn to the curves for Sb^{+3} and As^{+5} in Fig. 7. Both curves are essentially flat – Sb^{+3} at approximately 70% extracted, and As^{+5} at 25% – for all HCl concentrations between 3 and 8 molar. No data were given for lower acid concentrations, but it would seem prudent to assume that they extract to about the same degree in low HCl concentrations, at least until such time as experimental evidence proves otherwise. Thus it seems improbable that Sn^{+4} can be separated to any useful degree from either Sb^{+3} or As^{+5} by hexone extraction from HCl solutions.

As a note in passing, it might be mentioned that the author has used tin extraction into hexone as part of a routine tin radiochemistry procedure (see section VII) for a number of years. The procedure was developed before the curves of Fig. 7 were available and involved extraction of Sn^{+4}, Sb^{+5}, Mo^{+6}, and Te^{+4} into hexone from a 6$\underline{M}$ HCl solution, with subsequent back-extraction of tin into a 1$\underline{M}$ HCl-0.5$\underline{M}$ $NH_4F \cdot HF$ solution. Most of the antimony remains in the hexone layer, but Te and Mo back-extract with tin.

IV.7.B. IODIDE

Kitahara[81] reports that Sn^{+2} may be quantitatively extracted by diethyl ether from a 6.9$\underline{M}$ HI solution. Sb^{+3}, Hg^{+2}, Cd^{+2}, and Au^{+2} are also completely extracted, while Bi^{+3} (34% extracted), Zn^{+2} (11%), Mo^{+6} (7%), Te^{+4} (6%), and In^{+3} (8%) are extracted to a lesser extent. K, Cs, Ba, Ca, Fe^{+2}, Ni, Cr, Co, Mn, Ti, Zr, Pb, Th, Al, Ga, Be, U, V, Pd, Pt, Ir, Os, and Ru are not extracted.

In another iodide system, Irving and Rossotti[194] state that stannous tin is completely extracted by diethyl ether from a solution which is 1.5$\underline{M}$ in KI and 1.5$\underline{N}$ in H_2SO_4. Be and Fe^{+2} are not extracted at all, while Al is extracted to < 0.1%; Mo^{+6} and W^{+6}, < 1.0%; Bi and Cu, < 10%; Zn and Hg, about 33%; Sb, < 50%; and Cd, 100%.

IV.7.C. FLUORIDE

Stannous or stannic tin may be extracted quantitatively by diethyl ether from a 4.6$\underline{M}$ HF solution.[82, 126] Arsenic is extracted 62.2%, Mo 9.7%, Se 3.1%, and Sb 0.4%, while Ni, Cr, Co, Mn, K, Ti, Zr, Ga, Ag, U, Bi, Te, Cd, Os, Pt, Pd, Ir, Ru, and V are not extracted.

IV.7.D. DITHIOCARBAMATES

In ammoniacal solution carbon disulfide reacts with primary or secondary amines to form dithiocarbamates:[187]

$$R_2NH + CS_2 + NaOH = R_2N{-}CS{-}S\ Na + H_2O.$$

A number of dithiocarbamates have been prepared, several of which have proven of value in extracting tin. Bode[14] states that Sn^{+4} is quantitatively extracted by CCl_4 from diethyldithiocarbamate solutions in the pH range of 4-5.8, while Davies and Easton[35] have used this extraction for the colorimetric determination of tin. The reagent is far from specific for tin, and many elements, including As and Sb, interfere.[187, 192] In addition, alkali diethyldithiocarbamates decompose at a rapid rate in acid solutions. Wyatt[192] has circumvented this problem by using diethylammonium diethyldithiocarbamate, which is more soluble in the organic phase, to extract small amounts of As, Sb, and Sn. Wyatt states that As^{+3}, Sb^{+3}, and Sn^{+2} are quantitatively extracted by this reagent in chloroform from sulfuric acid solutions over the acidity range from 1N to 10N, but that As^{+5}, Sb^{+5}, and Sn^{+4} are not extracted. Apparently a very effective "scavenging extraction" can be performed on a sulfuric acid solution which contains Sn^{+4}, Sb^{+3}, and As^{+3} species, and subsequent destruction of the crganic layer to reclaim the tin can be avoided.

IV.7.E. DITHIZONE

Diphenylthiocarbazone (dithizone),

$$C_6H_5{-}N = N{-}CS{-}NH{-}NH{-}C_6H_5,$$

is widely used for the extraction and colorimetric determination of traces of a large number of elements.[187] The extractions are not specific for any element, but they are fairly strongly pH dependent and it is possible to effect separations of various metals by carefully controlling the pH. In chloroform, Sn^{+2} is extracted quantitatively in the pH range 4-8.5, while in CCl_4 the optimum range is 6-9.[187] Sn^{+4} is not extracted, nor are As, Sb, and Mo. Pappas and Wiles[135] have used this behavior as an essential part of a rapid tin separation from uranium fission products. Sn^{+2} was extracted by dithizone-CCl_4 from an acetate-tartrate solution at pH 8.5, while Sb and Te remained in the aqueous phase.

IV.7.F. 8-HYDROXYQUINOLINE

8-Hydroxyquinoline is a common reagent, used for the precipitation of many elements.[187] The 8-hydroxyquinolate salts are often soluble in organic solvents and may be used satisfactorily in extraction separations. Stannic tin behaves in this manner and is extracted from an 8-hydroxyquinolate solution by chloroform in the pH range of 2.5-5.5.[57] The extraction is not selective for tin at any pH, but arsenic does not interfere and antimony does not interfere in an oxalate solution whose pH is greater than 5.0.[57] Tartrate inhibits the extraction of tin and should not be present. Procedures in which the 8-hydroxyquinoline-chloroform extraction has been used for the colorimetric determination of tin have been published by Wyatt,[192] and Ginzberg and Shkrobot.[58]

IV.7.G.. CUPFERRON

Cupferron is similar to 8-hydroxyquinoline in that it is used for the precipitation of many elements but may also be used in extraction separations.[187] Stannic tin may be extracted even from fairly strongly acidified cupferron solutions by CCl_4. This technique has been used by Bhatki and Radhakrishna[11] to separate carrier-free Sn^{113} from massive amounts of indium, and by Eberius[46] for the photometric determination of traces of tin in zinc and lead. Furman, Mason, and Pekola[55] and the radiochemistry group at MIT,[143] on the other hand, have extracted stannic cupferrate into ethyl acetate from 1M HCl solutions. The extraction is quantitative at 1M HCl but decreases somewhat if the HCl concentration is increased to 6M. Sb^{+5} does not precipitate with cupferron under any conditions and is not extracted, while Sb^{+3} is quantitatively precipitated and extracted. Neither As^{+3} nor As^{+5} is precipitated by cupferron, and presumably neither is extracted. Mo^{+6} and Zr^{+4} are both quantitatively extracted but do not back-extract into oxalic acid solution, while Sn^{+4} can be back-extracted with a saturated oxalic acid solution that is 0.3M in HCl.[143]

IV.7.H. THIOCYANATE

Bock[13] has published a very detailed study of the extraction behavior of a large number of elements in the thiocyanate-HCl-diethyl ether system. Stannic tin is extracted quantitatively from 0.5M HCl solutions at all NH_4SCN concentrations above 1M. The extraction of tin and a number of other elements from 0.5M HCl as a function of NH_4SCN concentration is shown in Fig. 8; extraction curves for Be, Co, Al, Ga, Fe^{+3}, Ti^{+3}, Ti^{+4}, and V^{+4} are also given by Bock.[13] Elements that do not extract, or extract to only a very small degree, include Li^{+}, NH_4^{+}, Cu^{+}, Cd^{+2}, Hg^{+2}, Ge^{+4}, As^{+3}, As^{+5}, Bi^{+3}, Cr^{+3}, Ni^{+2}, and Pd^{+2}. Sb^{+3} hydrolyzes in 0.5M HCl at low thiocyanate concentrations, but in 7M NH_4SCN—0.5M HCl only 2.2% of the Sb^{+3} is extracted. No data are given for Sb^{+5}.

IV.7.I. DIBUTYLPHOSPHORIC ACID

Over 95% Sn^{+4} can be removed from an aqueous solution which contains 3 μg/ml Sn^{+4}, and which has been made 1M in HNO_3 and 3% in H_2O_2, by extracting for 5 minutes with an equal volume of 0.6M dibutylphosphoric acid (containing some monobutylphosphoric acid) in n-butyl ether.[152] Zirconium, Y, and In will also be quantitatively extracted, and substantial amounts of Ta (85%, no H_2O_2), Nb (60%), and Mo (23%), will accompany the Sn^{+4}. Extraction is less than 5% for Cs, Sr, La, Ag, Cd, Ge, Se^{+4}, Te^{+4}, Sb^{+3}, Sb^{+5}, As^{+5}, Pd, Ru and Rh.

IV.7.J. TETRAPHENYLPHOSPHONIUM CHLORIDE

Willard and Perkins[191] state that the tetraphenylphosphonium salts of a number of elements, including Sn^{+4}, are extractable from aqueous solution by chloroform. Reference 191 deals with the precipitation reactions of this reagent, however, and no data are given on the conditions for extraction or on the interfering elements.

IV.7.K. METHYLDIOCTYLAMINE

Coombe[28] states that Sn^{113} tracer is quantitatively extracted from solutions as low as 1N in HCl by 2-3 volume % solutions of methyldioctylamine in xylene. Antimony does not extract in 1M HCl, but at HCl concentrations greater than 6M the extraction is quantitative. No data are given on the oxidation state of either Sn or Sb.

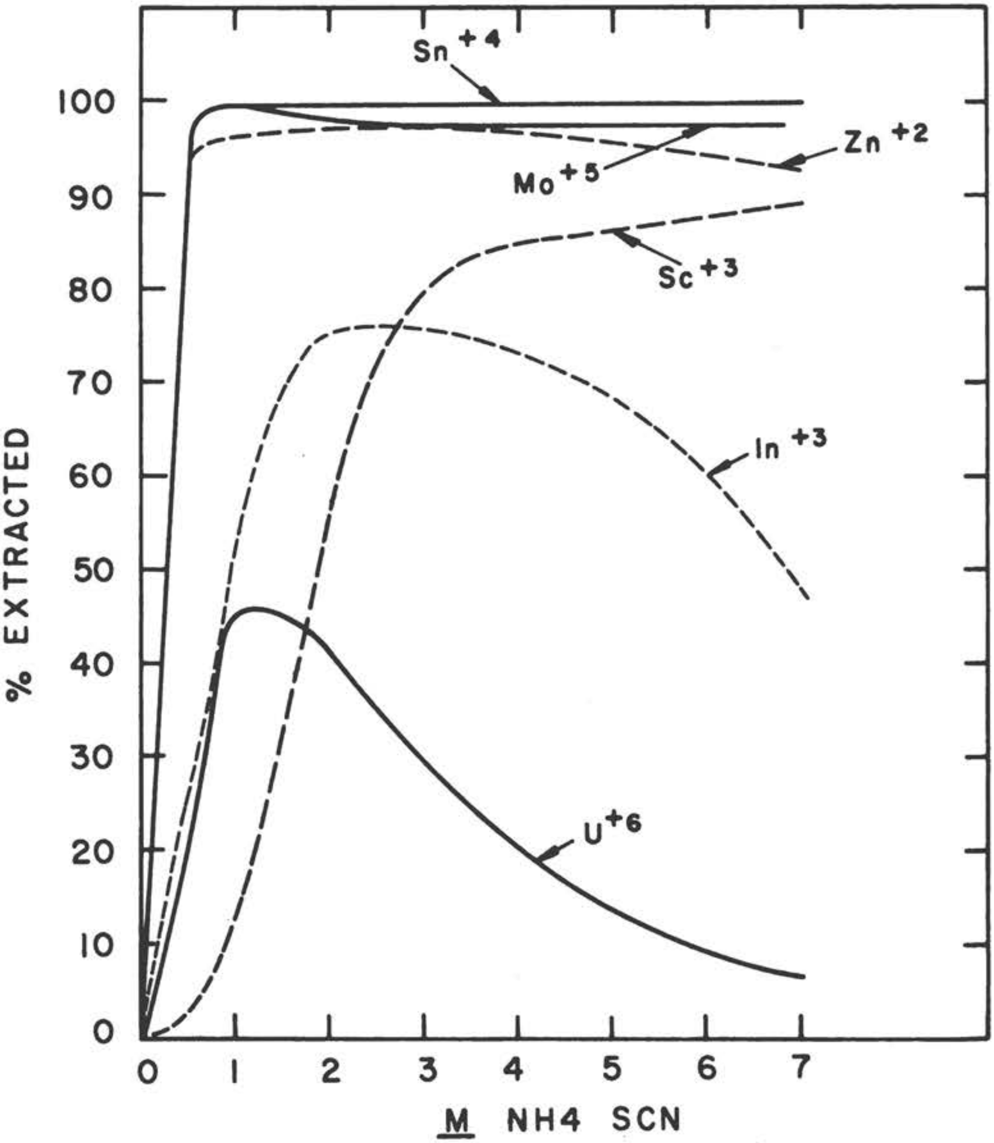


Fig. 8. Extraction by diethyl ether from NH_4SCN-0.5M HCl solutions. (13)

IV.7.L. EXTRACTION OF ANTIMONY FROM TIN

In radiochemistry, antimony is often a very serious contaminant of the tin fraction, and the complete separation of tin from antimony is not always a simple matter. Several extraction procedures have been published, however, in which antimony is extracted while tin remains in the aqueous phase, and these references will be included here for the information of those to whom they might be of value. Khorasani and Khundkar,[80] for example, report that Sb^{+5} may be extracted by ethyl acetate from 6M HCl solution while Sn^{+4} remains in the aqueous layer. The extraction behavior of antimony in the 6<u>M</u> HCl-ethyl ether is well known,[113] but in addition Coombe[29] reports that Sb^{+5} may be quantitatively separated from Sn^{+4} by extracting a 6<u>M</u> HCl solution with isopropyl ether.

IV.8. ION EXCHANGE

IV.8.A. CATION EXCHANGE RESINS

In general, cation exchange resins are not at all satisfactory for separating tin. Stannic tin hydrolyzes so readily that it can be kept in solution only by complexing agents. These agents usually form anionic complexes with tin which, of course, are not adsorbed by cation exchange resins.

An interesting use of cation exchange resins for tin chemistry has been reported by Kraus, Michelson, and Nelson.[92] When a 12<u>M</u> HCl solution containing Sn^{+4} and Sb^{+5} tracers is passed through a Dowex-50 cation exchange resin column, the $SnCl_6^{-2}$ complex is not adsorbed and tin appears in the first column volume of eluant. The antimony, however, is strongly held by the resin and is not eluted even by seven column volumes of 12<u>M</u> HCl. Using this technique, the authors obtained a rapid and very complete separation of tin and antimony activities.

IV.8.B. ANION EXCHANGE RESINS

IV.8.B.1. Chloride

Synthetic anion exchange resins have proven to be more satisfactory for tin separations than any other ion exchange medium, and papers reporting the use of a number of different anionic tin complexes on this type of exchanger have been published. In HCl solutions the very extensive data compiled by Kraus and Nelson with Dowex-1 anion exchange resins is well known.[91] Their curves are reproduced in Fig. 9 and indicate that both Sn^{+4} and Sn^{+2} are fairly strongly adsorbed by Dowex-1 at all HCl concentrations. Indeed, once tin is placed on the resin it is difficult to remove, and chloride columns are disadvantageous for that reason.

Everest and Harrison[48] have found a similar strong adsorption of the stannic chloride complex on Amberlite IRA-400 anion exchange resin. Jentzsch and Pawlik[73] have used Wofatit L 150, and Liska and Klir[109] have used Czech OAL resin with essentially the same results.

The types of separations which may be carried out on anion exchange resins are evident from the curves of Fig. 9. As an example of what has been done, Sasaki[151] has separated tin, antimony, and tellurium on a Dowex-1 column. Antimony (+5) is eluted with 3<u>M</u> HCl, Te (+4) is removed with 1<u>M</u> HCl, and finally Sn^{+4} is stripped off the column with 1.8<u>M</u> $HClO_4$.

IV.8.B.2. Fluoride

Faris[49] has studied the adsorption of a fairly large number of elements

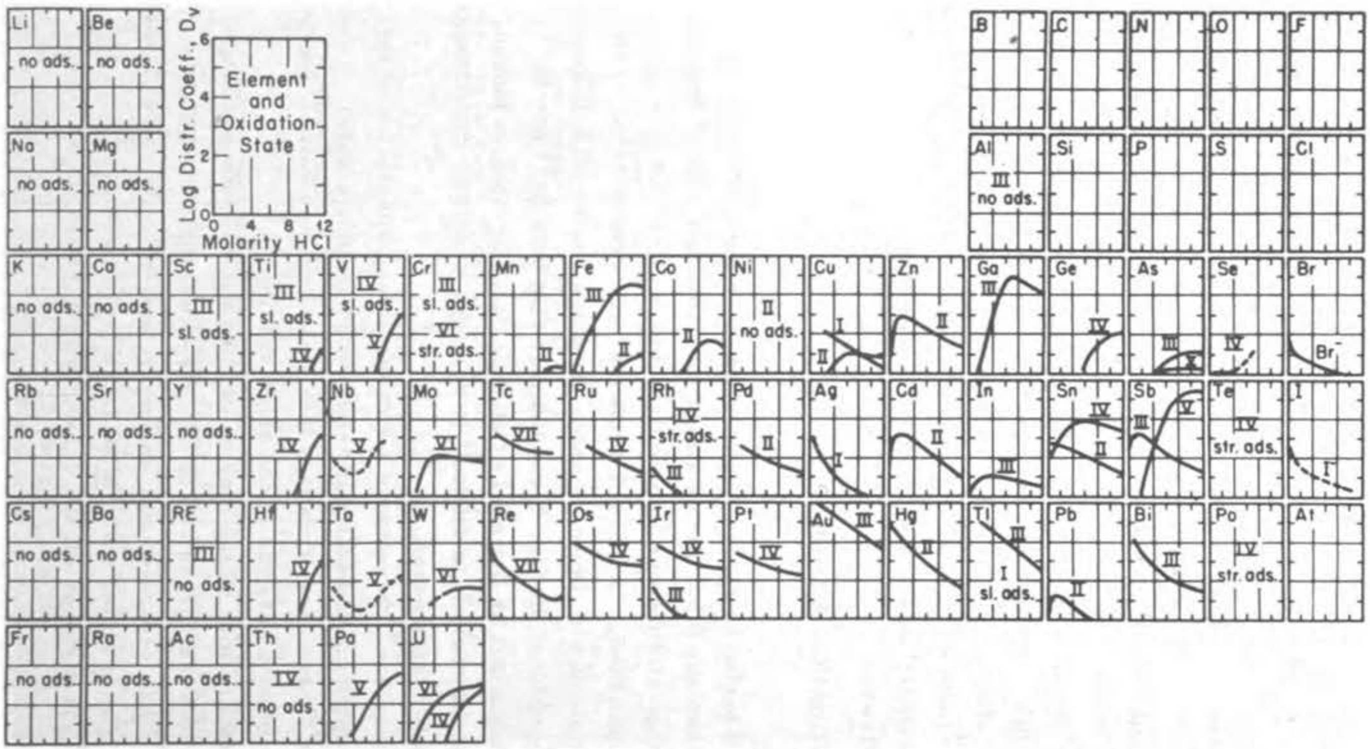


Fig. 9. Adsorption of the elements by Dowex-1 anion exchange resin from hydrochloric acid solution. No ads. = no adsorption for $0.1 < \underline{M}$ HCl < 12; sl. ads. = slight adsorption in $12\underline{M}$ HCl ($0.3 \leqq D_v \leqq 1$); str. ads. = strong adsorption ($D_v >> 1$). (91)

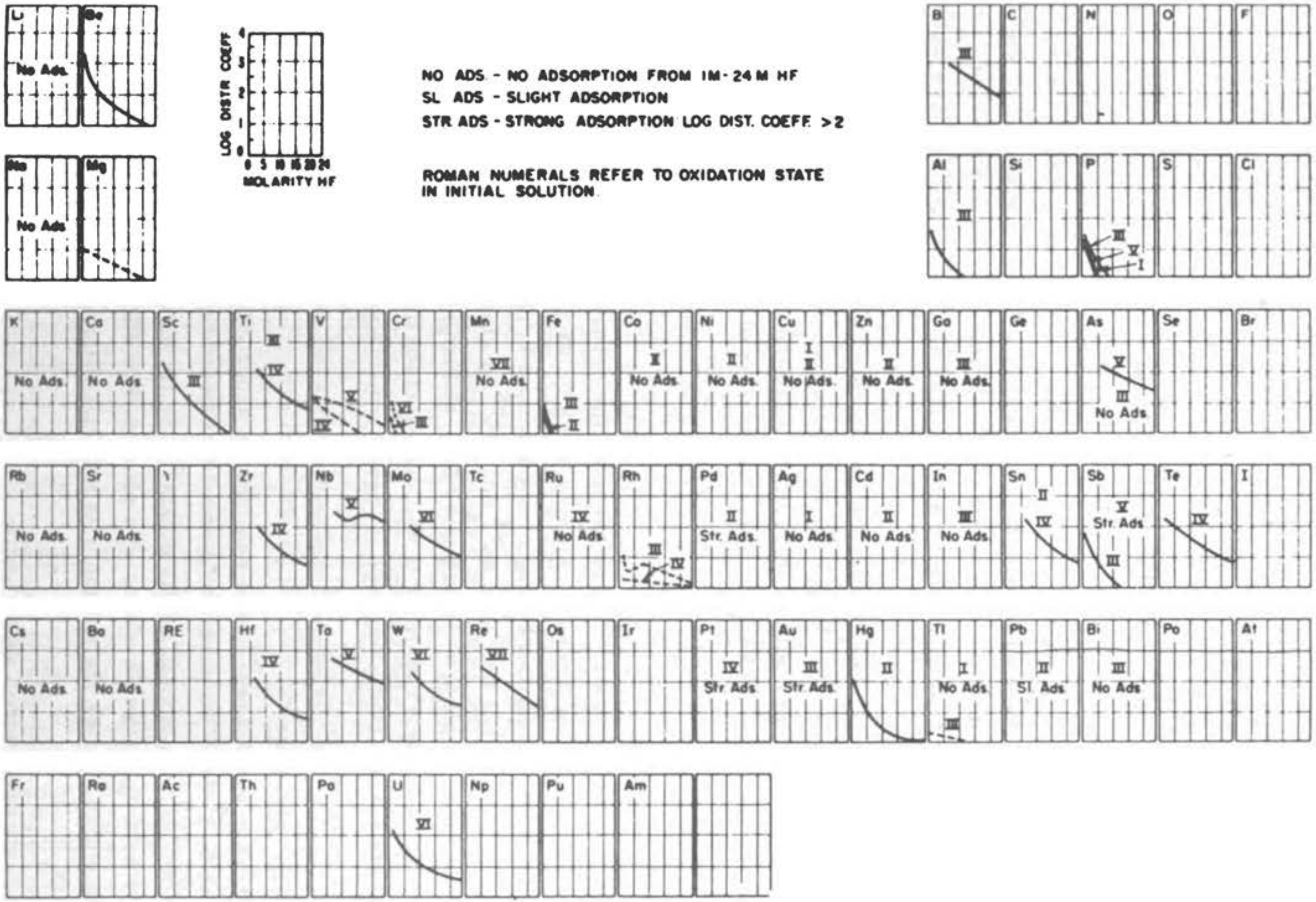


Fig. 10. Removal of elements from solution in 1M to 24M hydrofluoric acid with 200 mesh Dowex-1 anion exchange resin. (49)

by Dowex-1 anion exchange resin in HF solutions (Fig. 10). Sn^{+4} and Sn^{+2} are fairly strongly adsorbed at all HF concentrations, but Sb, Te, and Mo are also adsorbed from these solutions and it does not seem likely that the elements which are most difficult to separate from tin can be removed with an HF-Dowex-1 system.

Results can be varied, however, if a mixed eluant is used. Kraus and Nelson[91] have separated Sn-Sb mixtures by using an HCl-HF solution as eluant, while Nelson, Rush, and Kraus[130] have separated Sn^{+4} from In, Pb, Ge^{+4}, and Bi with the same type of eluant.

IV.8.B.3. Sulfide

In basic solution, stannic tin forms sulfide complexes which are very useful in anion exchange separations. Klement and Kuhn[84] have studied the behavior of the thiostannate ions on Dowex-2 columns and have separated Sn-As-Sb mixtures quantitatively by this technique. The mixed sulfides were dissolved in 3% sodium polysulfide solution and adsorbed on a Dowex-2 anion exchange column in the OH^- form (pre-equilibrated with 3$\underline{M}$ KOH and washed with H_2O). Tin was eluted with 0.5$\underline{N}$ KOH solution, followed by arsenic with 1.2$\underline{N}$ KOH and antimony with 3.5$\underline{N}$ KOH. No elution curves are given in ref. 84, nor are the optimum conditions for separation of these three elements worked out.

IV.8.B.4. Oxalate

Smith and Reynolds[166] have reported the separation of mixtures of Te, Sb, and Sn tracers on Dowex-1 columns using 0.1$\underline{M}$ oxalic acid as the eluant. The tracers were first run through the column in 0.1$\underline{M}$ oxalic acid. Tellurium does not stick, but Sb^{+5} and Sn^{+4} do. Sb^{+5} is eluted with 0.1$\underline{M}$ oxalic acid neutralized to pH 4.8, followed by Sn^{+4} elution with 1$\underline{M}$ H_2SO_4. Antimony must be in the +5 state or it will contaminate the tin fraction. Attempts to separate macroscopic amounts of these elements were not successful because of hydrolysis.

IV.8.B.5. Malonate

Dawson and Magee[45] have published a paper describing the separation of tracer Sn^{+4}-Sb^{+5} mixtures on Amberlite IRA-400 anion exchange resin using ammonium malonate as the eluant. The tin malonate complex is fairly strongly held by the resin while, at a pH of 4.8 in 3% malonate solution, antimony is eluted. After the antimony is off the column, tin is stripped with 9$\underline{N}$ H_2SO_4.

IV.8.C. EXTRACTION—EXCHANGE

Hale[61] has patented a very interesting technique for extracting solutes from a solution. An "ion exchange column" is made up of a synthetic organic high polymer (such as the styrene-divinylbenzene beads used as a starting material for Dowex-1 and Dowex-50 ion exchange resins) which has previously been saturated with an organic solvent in which the species to be extracted is soluble. If it is so desired, a complexing agent may also be incorporated with the organic solvent in the polymer lattice. The column of treated resin is then washed with an aqueous solution to remove excess solvent, after which the sample solution is poured through. Subsequent treatment with selected aqueous eluants can give separations analogous to a normal ion exchange column. In effect, the inventor claims that this technique permits multistage solvent-extraction type operations to be carried out automatically with very simple apparatus and good results.

As illustrations of the sort of applications to which the method can be put, Hale describes the extraction of iodine by a polymer saturated with carbon tetrachloride; the extraction of copper by a polymer saturated with CCl_4-0.005% dithizone, with subsequent recovery of the copper by elution with 2<u>M</u> HCl; and the separation of a Cd-Pb-Sn mixture by a polymer saturated with CCl_4-0.1% dithiol. In 0.1<u>N</u> HCl, Pb and Sn are adsorbed by the column, but Cd is not. Pb is eluted with 2<u>N</u> HCl, while Sn remains on the column. No detailed information is given on any separations but the method seems promising enough to warrant further study.

IV.8.D. INORGANIC EXCHANGERS

A number of articles on the use of inorganic exchangers for separating tin have appeared in the literature. An excellent paper by Pinterovic[141] describes the behavior of tin and a number of other elements on activated alumina columns. In 10% tartaric acid the decreasing order of adsorption is Bi^{+3}, Sb^{+3}, Sn^{+4}, Sn^{+2}, As^{+3}; in HCl or HNO_3 the order is As^{+3}, Sb^{+3}, Bi^{+3}, Sn^{+4}, Sn^{+2}, Cr^{+3}, Fe^{+3}, Pb^{+2}, Cu^{+2}. No detailed data are given on specific separations, but presumably these can be carried out by a proper choice of experimental conditions. Karschulin and Svarc[77] and Ol'shanova and Chmutov[133] also discuss the use of tin on Al_2O_3 columns, but they too give little detailed information.

Inorganic exchangers have also been used by Sen, who has described the qualitative separation of As-Sb-Sn mixtures on calcium sulfate rods[163] and strips of asbestos millboard.[162]

IV.8.E. PAPER CHROMATOGRAPHY

During recent years paper chromatography has become a very popular method for separating mixtures of cations. The technique is usually limited to essentially carrier-free samples, but if that is not a severe handicap paper chromatography can be used for the separation of a fairly large variety of elements.[102]

As applied to tin separations, most of the published papers on the subject deal with the Sn^{+2} ion. Chromatograms are most often developed by an organic solvent containing HCl, and a number of solvents have been reported, including ethyl acetate,[19, 20] methyl acetate,[20] ether,[1] acetone,[116] acetylacetone-acetone,[20] and ethyl,[101] isopropyl,[101] butyl,[101, 20, 62] and amyl[101] alcohols. All of these solvents can be used for separating Sn^{+2}-Sb^{+3}-As^{+3} mixtures, but the Sb-Sn separations tend to be incomplete because of the Sn^{+2} tailing back into the Sb^{+3} band. Burstall, Davies, Linstead, and Wells[20] recommend acetylacetone-0.5% (V/V) HCl (d. 1.18)-25% (V/V) acetone as the best solvent for effecting clean-cut Sn^{+2}-Sb^{+3} separations.

Good separations of Sb^{+5}-Sn^{+4} mixtures can be made with a butyl alcohol-HCl solvent.[62, 139, 140] In a developer whose composition is 100 parts butanol: 7 parts HCl(d. 1.19): 20 parts H_2O, for example, Sb^{+5} hardly moves down the paper (R_f = 0.1), while Sn^{+4} moves a great deal (R_f = 0.70). As^{+5} (R_f 0.69) accompanies the Sn^{+4} and is not separated.[62]

IV.8.F. ELECTROCHROMATOGRAPHY

A variation of the paper chromatography separation technique involves the use of an electric field to induce mobility of ionic species. The method is a very flexible one because uncomplexed cations as well as complexed anionic species can be separated in a single operation; but here again separations are usually restricted to essentially carrier-free samples.

Maki[118] has published a very fine series of articles on the electrochromatographic separation of a large number of elements. The equipment consists of three trays placed in series, the first and third containing the electrodes and the aqueous solution while the center tray contains an inert organic cooling bath (in this case C_6H_5Cl) to prevent scorching of the paper strip. In making a separation, the sample is placed on a small spot on a strip of filter paper (2 × 50 cm) which has previously been wetted by the aqueous solution from the end trays. The ends of the paper strip are then placed in trays one and three, its length is immersed in the organic bath, and the current is turned on. The potential and the running time vary according to the separation being made, but 200 volts for 1.5-3 hours is a typical run. Many elements were studied in this work, which included investigation of the behavior of Sn^{+2} ions in $4\underline{M}$ NH_4OH-$0.1\underline{M}$ ammonium tartrate, in $0.11\underline{M}$ ethylenediamine-$0.1\underline{M}$ ammonium tartrate, and in $0.1\underline{M}$ triethanolamine-$0.1\underline{M}$ ammonium tartrate. Separation of mixtures of Sn^{+2}, Sb^{+3}, and As^{+3} is roughly comparable to that obtained by paper chromatographic methods; i.e., the three elements are separated, but the distance between Sn^{+2} and

Sb^{+3} is less than the distance between Sb^{+3} and As^{+3}. Sn^{+2} is the fastest migrating species of these three complexes, and if it tails severely the Sb^{+3} spot could easily be contaminated.

The direction as well as the speed of migration of a given element can be controlled by the proper choice of electrolyte. This applies to tin as well as other elements, and Majumdar and Singh[117] have reported the migration behavior of the copper and tin group metals (Hg^{+2}, Pb^{+2}, Bi^{+3}, Cu^{+2}, Cd^{+2}, As^{+3}, Sb^{+3}, Sn^{+2}) in 26 different aqueous media. Stannous tin behaves as a cation and migrates toward the cathode in most of the solutions used, but in several solutions (0.1$\underline{N}$ oxalate, citrate, iodide, tartrate, and EDTA – 0.1$\underline{N}$ NH_4OH) it behaves as an anion and moves in the opposite direction. The most useful behavior, however, seems to be in 0.1$\underline{M}$ KI or 0.1$\underline{M}$ oxalic acid, where Sn^{+2} migrates toward the anode, As^{+3} toward the cathode, and Sb^{+3} stands still.

V. DISSOLUTION AND EXCHANGE

V.1. DISSOLUTION

The chief occurrence of tin in ores is as cassiterite, SnO_2, and less often in combination with sulfur and sulfides of other metals. Dissolution of these ores, or any other tin sample, for that matter, is complicated by the fact that tin hydrolyzes to metastannic acid in neutral and most acid solutions, and that tin halide compounds are appreciably volatile.

For these reasons, most tin dissolution procedures involve either a fusion or reduction to the metal. The more common methods include:

1. Fusion with sodium peroxide or a mixture of 75% Na_2O_2-25% Na_2CO_3. Heating the melt to a cherry-red color in a nickel crucible for 3-5 minutes is usually enough to permit subsequent dissolution of the sample in HCl.[65]
2. Dissolution in a strong caustic solution in an autoclave at 200-300° C for 3-4 hours.[180]
3. Fusion with borax in Pt at 900° C for 1.5-2 hours.[15]
4. Fusion with equal parts of sodium or potassium carbonate and sulfur.[149,65]
5. Fusion with sodium thiosulfate in an oxygen-free atmosphere.[65]
6. Fusion with potassium bifluoride.[190]
7. Reduction in a stream of pure, dry, hydrogen or ammonia gas at 750° C for several hours.[65]
8. Reduction to the metal by fusion with KCN.[159]
9. Sintering with quicklime or zinc oxide, or heating with zinc dust.[184]

After the fusion or reduction step the sample may be dissolved in HCl without loss of tin. Stannic chloride solutions should not be permitted to evaporate to dryness, however, or appreciable volatilization of $SnCl_4$ might occur.

V.2. EXCHANGE

Few data are available on the rate of exchange between Sn^{+2} and Sn^{+4} ions in aqueous solution. Measurable exchange rates have been observed in 10F HCl,[33] methyl alcohol,[124] and ethyl alcohol.[123] The hydrolysis products of tin are known to be quite intractable and to change their form very slowly, and since so little information is available on the exchange of tin in aqueous solution, it seems prudent to assume that all tin exchange rates are slow. Therefore, whenever tin activity and tin carrier are mixed, and complete exchange is desired, tin should be reduced to the metal and reoxidized to Sn^{+4} as a preliminary step.

V.3. SZILARD-CHALMERS REACTIONS

Tin forms many organometallic compounds, some of which have been used for preparing tin samples of high specific activity by the Szilard-Chalmers reaction.

Spano and Kahn[169] have used tetraphenyltin for production of tin isotopes by neutron irradiation. After bombardment, the tetraphenyltin was dissolved in benzene and extracted with 3M HCl, 6M HCl, or 1M NaOH, with enrichment factors of 2-3000 in each case. Sharp,[164] however, has irradiated tetraphenyltin, dissolved it in chloroform, and extracted the activity with dilute HCl with enrichment factors of only about 150.

Murin and Nefedov[127] have used triphenyltin chloride or triphenyltin iodide, dissolving in ether and extracting into dilute HCl for enrichment factors on the order of 150 with a radioactive tin yield of 80%.

VI. COUNTING TECHNIQUES

Few data are available on counting techniques peculiar to tin activities. In the great majority of cases, samples of tin activities may be counted by using standard β^- and γ counting techniques.

VII. COLLECTED RADIOCHEMICAL PROCEDURES FOR TIN

No.	Tin separation:	Procedure by:	Page:
1	From fission products	W. Nervik	40
2	" " "	R. G. Monk, et al.	41
3	" " "	G. B. Cook	43
4	" " "	J. A. Seiler	44
5	" " "	G. A. Cowan	45
6	From Fe, Sb, Cu, and chemical wastes	W. R. McDonell	48
7	From Sn target	A. S. Newton and W. R. McDonell	49
8	From Sb target	M. Lindner	50
9	Carrier-free from Cd target	R. D. Maxwell, et a..	51
10	Distillation from fission products	J. W. Winchester	53
11	Distillation from fission products	G. Wilkinson and W. E. Grummitt	55

Sn Procedure No. 1

W. E. Nervik

This procedure was designed specifically to separate Sn^{121} and Sn^{125} activities from fission product mixtures. Although rather involved, it gives tin samples in about 50% yield which are free of Sb, Mo, and Te contamination.

NOTE: Allow all of Sn^{127} to decay out before starting chemistry.

1\. a) Add Sn carrier, 3 mg each of Sb, Mo, Te (as tellurate), 3 mg Te metal. Adjust to 25 ml 6M HCl, add $NaClO_3$, digest hot 10 min.

2\. a) Extract 1× w/25 ml hexone, wash hexone 2× w/20 ml 6M HCl.

b) Back-extract 1× w/25 ml F^- soln. (25 ml 1M HCl + 2 ml 6M $NH_4F \cdot HF$).

c) Transfer F^- layer to a new sep. funnel, wash 1× w/20 ml hexone.

3\. a) Saturate cold w/H_2S, digest hot 10-15 min, cent., scavenge with preformed As_2S_3, cent., filter (No. 44 paper).

b) Add 5 ml sat'd. H_3BO_3, pass in H_2S, digest, cent., wash SnS_2 1× w/H_2O.

4\. a) Dissolve SnS_2 in Br_2 + 6M HCl, add 1 mg Mo carrier, dilute to ≈30 ml 0.5M HCl (have slight excess Br_2 present).

b) Add alpha benzoin oxime, digest, cent.; add 1 drop Mo carrier, digest, cent., filter.

c) Pass in H_2S, digest, cent., wash SnS_2 1× w/H_2O.

5\. a) Dissolve SnS_2 in 2 ml sat'd. Na_2S, add 15 ml H_2O, put on anion column (6mm × 10 cm Dowex-1 × 8 resin, 50-100 mesh, preconditioned w/1M NaOH), wash w/15 ml H_2O.

b) Elute Sn w/15 ml sat'd. Na_2S (collect in 125-ml Erlenmeyer flask).

c) Acidify carefully w/6M HCl, cent., wash SnS_2 1× w/H_2O.

6\. a) Dissolve SnS_2 in BrO_3^- + 6M HCl, reduce Br_2 w/$NH_2OH \cdot HCl$. Dilute to 25 ml, filter.

b) Adjust to ≈pH 6 w/HAc-Ac^-, digest, cent., wash 1× w/dil. pH 6 soln., 1× w/acetone, dry, ignite, weigh as SnO_2.

Sn Procedure No. 2

R. G. Monk et al.[195]

Species Considered

Sn-117m	14.0d
Sn-119m	245d
Sn-121	27.5h
Sn-123	130d
Sn-125	9.4d
Sb-125	2.7y

Outline of Purification Scheme

1. Fusion with caustic potash to ensure exchange.
2. Two molybdenum scavenges from 0.5M hydrochloric acid.
3. One tellurium sulfide scavenge from 6M hydrochloric acid.
4. Two neodymium hydroxide scavenges from sodium hydroxide and sulfide solution.
5. Three antimony sulfide scavenges from ammonium-hydrogen fluoride solution.

Procedure

1. Transfer the sample of paper to a nickel crucible and moisten it with the minimum of 0.1M potassium hydroxide. Dry under the lamp and ignite at 550° C until all the carbon has burnt off.

2. Add 1 mg each of carriers for tin (as sodium stannate), antimony (as potassium antimonyl tartrate), tellurium (as sodium tellurate), and molybdenum (as ammonium molybdate), and dry under the lamp. Add 0.1 g of potassium hydroxide and heat carefully over a burner until a tranquil melt is obtained. Raise the temperature to a dull red heat and maintain at this temperature for 5 minutes, keeping the melt swirled the whole time.

3. Centrifuge and dissolve any insoluble matter by warming with 0.5 ml of concentrated hydrochloric acid. Carefully add the acid to the alkaline supernate and, if necessary, add more hydrochloric acid until the solution is just acid to methyl red. Add 0.2 ml concentrated hydrochloric acid in excess and dilute to 4-5 ml.

4. Precipitate the molybdenum by the addition of 0.25 ml of 1% alcoholic α-benzoin oxime and allow to stand for 5 minutes. Centrifuge and, if required, reserve precipitate for molybdenum purification.

5. To the supernate add 0.2 mg of molybdenum carrier and a further 0.1 ml of α-benzoin oxime. Stand 15 minutes, centrifuge, and reject precipitate.

6. Saturate with hydrogen sulfide and, if necessary, reserve supernate for tellurium recovery (N. B. tellurium as tellurate will not precipitate with hy-

drogen sulfide). Wash the precipitate (sulfides of tin, antimony, and tellurium) once with water, after transferring it to a 3-ml tube. Add 0.5 ml of 6M hydrochloric acid and heat in boiling water for a few minutes, removing hydrogen sulfide by passage of a current of air. Centrifuge and, if required, reserve the insoluble tellurium disulfide for tellurium purification.

7. Add 0.1 mg of neodymium carrier to the supernate followed by 6M sodium hydroxide until a faint permanent precipitate appears. Just clear the solution by the dropwise addition of 2M hydrochloric acid. Add the solution slowly with stirring to a solution containing 1 ml of 1M sodium hydroxide and 0.25 ml of fresh 10% sodium sulfide. Centrifuge and reject precipitate.

8. Add the solution carefully to 0.2 ml of glacial acetic acid, centrifuge, and reject the supernate. Dissolve the precipitate of tin and antimony sulfides in 0.2 ml of concentrated hydrochloric acid, heating in boiling water and passing a current of air for a few minutes to remove hydrogen sulfide. Add a drop of methyl red followed by 6M ammonia until the solution is just alkaline. Make just acid with 6M hydrochloric acid followed by 0.25 ml in excess. Add 1 ml of 10% ammonium fluoride and saturate with hydrogen sulfide. Centrifuge and, if required, reserve the antimony sulfide precipitate for purification.

9. Add about 0.1 g of boric acid to the supernate followed by 0.3 ml of 6M hydrochloric acid. (N. B. the reaction between ammonium bifluoride and boric acid results in the pH rising sufficiently to prevent precipitation of stannic sulfide. Hydrochloric acid is therefore added to neutralize this alkalinity.) Warm to dissolve the boric acid and pass more hydrogen sulfide to ensure complete precipitation of stannic sulfide. Centrifuge and wash the precipitate twice with 0.2M hydrochloric acid.

10. Add 0.1 mg of neodymium carrier to the precipitate followed by a solution containing 1 ml of 1M sodium hydroxide and 0.25 ml of fresh 10% sodium sulfide. Stir well, centrifuge, and reject the precipitate.

11. Add the solution carefully to 0.2 ml of glacial acetic acid, centrifuge, and reject the supernate.

12. Dissolve the precipitate in 0.2 ml of 11M hydrochloric acid, heating in boiling water and passing a current of air for a few minutes to remove hydrogen sulfide. Add 0.2 g of antimony carrier (trivalent) and make just alkaline to methyl red with 6M ammonia. Make just acid with 6M hydrochloric acid and add 0.25 ml in excess. Add 1 ml of 10% ammonium fluoride and saturate with hydrogen sulfide. Reject the precipitate.

13. Repeat step (9).

14. Repeat step (12).

15. Repeat step (9).

16. Dissolve the stannic sulfide in 0.2 ml of concentrated hydrochloric acid, heat in boiling water and pass a current of air for a few minutes to remove hydrogen sulfide. Dilute to about 1.5 ml and make ammoniacal. Centrifuge off the stannic hydroxide and dissolve it in 0.1 ml of 6M hydrochloric acid. Dilute to 0.3-1 ml as appropriate, and prepare sources on distrene, adding 2 drops of 3M hydrofluoric acid before evaporating to prevent volatilization of tin.

Sn Procedure No. 3

G. B. Cook[27]

1. Dissolve uranyl sulfate target material in 0.5N HCl. Add stannic tin (20 mg) and copper (20 mg) carriers and precipitate the mixed sulfides.
2. Dissolve Sn out of the sulfide precipitate with a minimum amount of ammonium polysulfide. Acidify the ammonium polysulfide with acetic acid, centrifuge the SnS_2.
3. Redissolve SnS_2 in sodium polysulfide, add a few mg Pb carrier, centrifuge the PbS scavenge.
4. Acidify with acetic acid, centrifuge SnS_2, dissolve in conc. HCl, add Fe^{+3} carrier, precipitate $Fe(OH)_3$ in NaOH solution.
5. Neutralize and ppt. $Sn(OH)_4$.
6. Dissolve $Sn(OH)_4$ in a few ml 6M HCl, add 1 g citric acid, 2 mg Sb^{+3}, and ppt. Sn with 5 ml hot saturated phenylarsonic acid solution.
7. Dissolve ppt. in strong KOH soln., add 1 g citric acid, 2 mg Sb^{+3}, 5 ml saturated phenylarsonic acid solution, and acidify with HCl to ppt. phenylarsonic tin.
8. Repeat step (7) once more.
9. Wash, dry, and mount the phenylarsonic tin for counting.

Sn Procedure No. 4

J. A. Seiler[161]

1. To 5 ml or less of uranyl nitrate solution, add 1.5 ml of conc. HCl and 30 mg of standardized tin carrier. Boil for several minutes. Dilute to 20 to 25 ml with H_2O, warm, and pass in H_2S for several minutes. Centrifuge, and wash twice with 20 ml of hot 2% HCl.

2. Dissolve the precipitate from step (1) in 1.5 ml of conc. HCl and boil off the H_2S. Add 20 ml of saturated oxalic acid and 10 mg of Sb(III) carrier. Warm to about 80° C. Pass in H_2S for several minutes. Centrifuge. Filter the supernatant solution if it is not clear.

3. Repeat the Sb_2S_3 precipitation by adding 10 mg more of Sb(III) carrier to the supernatant solution and continue as in step (2). Repeat the Sb_2S_3 precipitation a third time.

4. Add 5 mg each of zirconium and niobium carriers to the solution from step (3), neutralize, and add 3 ml excess of conc. NH_4OH. Warm, and pass H_2S into the mixture for several minutes. Centrifuge. Add about 5 mg more of zirconium and niobium carriers and 1 ml of conc. NH_4OH, and pass in H_2S for several minutes. Centrifuge. Repeat the separation a third time.

5. Carefully add 6$\underline{N}$ HNO_3 to the solution from step (4) until it is acid. Pass in H_2S to precipitate SnS, centrifuge, and wash the precipitate with water. The solution may require further H_2S gassing to precipitate the SnS completely.

6. Dissolve the SnS precipitate as in step (2) and repeat the Sb_2S_3 precipitation. Centrifuge.

7. Neutralize the solution from step (6) with conc. NH_4OH and pass in H_2S. Make just acid with 6$\underline{N}$ HNO_3 and centrifuge off the SnS.

8. Add 5 to 6 ml of conc. HNO_3 to the SnS precipitate from step (7), and boil down to about 3 ml in a centrifuge tube with stirring to prevent bumping. If SnO_2 does not precipitate out, repeat by adding more HNO_3 and boiling. Dilute with 15 ml of hot H_2O, warm for several minutes just below 100° C with stirring, and filter on a Whatman No. 42 filter paper. Ignite over a Meeker burner to SnO_2, weigh on a watch glass, mount, and count.

Sn Procedure No. 5

G. A. Cowan[83]

1. Introduction

The procedure consists of four sulfide precipitations, two ferric hydroxide scavenging steps in sodium hydroxide solution, and a final precipitation of tetrapositive tin by means of cupferron reagent.*

To promote complete exchange between fission-product tin and Sn(IV) carrier, the former is oxidized to the tetrapositive state by means of bromine water. Tetrapositive tin is separated from other substances giving acid-insoluble sulfides by precipitation of the sulfides from hydrofluoric acid, which strongly complexes Sn(IV), probably as $SnF_6^{=}$. The fluo complex is destroyed by the addition of boric acid (BF_4^- ion being formed) and SnS_2 is precipitated. The latter is dissolved in concentrated hydrochloric acid, and iron scavenging steps are carried out in a medium which contains an excess of sodium hydroxide to keep tin in solution as stannate. Sn(IV) is finally precipitated with cupferron reagent in hydrochloric acid medium. The precipitate is ignited to SnO_2, in which form the tin is counted. The chemical yield approximates 70%. Duplicate analyses require about 4 hours.

2. Reagents

Sn carrier: 10 mg Sn/ml, added as $SnCl_4$-H_2O in 4M HCl, standardized
Te carrier: 10 mg Te/ml, added as Na_2TeO_3 in 6M HCl
Mo carrier: 10 mg Mo/ml, added as aqueous $(NH_4)_6Mo_7O_{24}$-$4H_2O$
Sb carrier: 10 mg Sb/ml, added as $SbCl_3$ in 6M HCl
La carrier: 10 mg La/ml, added as aqueous $La(NO_3)_3 \cdot 6H_2O$
HCl: 1M
H_2SO_4: conc.
HF: conc.
HI: conc.
H_3BO_3: saturated solution
H_2S: gas

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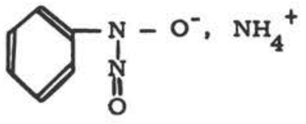
*Cupferron, the ammonium salt of nitrosophenylhydroxylamine,



reacts with Sn(IV) in hydrochloric or sulfuric acid to give an insoluble tin salt, the ammonium ion being replaced by an equivalent of tin. The test is not specific for tin and can only be used after the large number of interfering ions have been removed.

Br_2-H_2O

NaOH: conc.

Cupferron reagent: 10% in H_2O (kept in refrigerator).

3. Equipment

Drying oven

Centrifuge

Fisher burner

Block for holding centrifuge tubes

Forceps

Mounting plates

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

Filter flask (one per sample)

Filter chimneys (one per sample)

Pt crucibles (one per sample)

Pipets: 2-ml

Wash bottle

40-ml conical centrifuge tubes: Pyrex 8320 (seven per sample; one per standardization)

No. 41 H Whatman filter paper: 7/8-in. diameter

Stirring rods.

4. Preparation and Standardization of Carrier

Dissolve 28.0 g of $SnCl_4 \cdot 4H_2O$ in H_2O and dilute to 1 liter.

Pipet 2.0 ml of the carrier solution into a 40-ml centrifuge tube, dilute to 15 ml, add conc. NaOH until the solution is alkaline, and then add 2 drops in excess. Add 2 ml of the cupferron reagent and conc. HCl dropwise until the precipitate formed no longer redissolves. Then add 1 additional drop of conc. HCl. Filter onto No. 41 H Whatman paper and wash thoroughly with H_2O. Dry the precipitate at 110° for 15 min. Ignite and weigh as SnO_2.

These standardizations are ordinarily sufficient. The spread in results is about 3%.

5. Procedure

1. To the sample in a 40-ml centrifuge tube, add 2 ml of 1<u>M</u> HCl and 2 ml of Sn carrier. Add Br_2-H_2O in slight excess (total volume should be about 15 ml) and saturate with H_2S. Centrifuge. Wash with 1<u>M</u> HCl and centrifuge, discarding the supernate.

2. Dissolve the precipitate in 1 ml of conc. HCl and add Br_2-H_2O dropwise to slight excess. Add 4 drops each of Te, Mo, and Sb carriers. (Br_2 should still be present in excess.) Add 0.5 ml of conc. H_2SO_4 and 0.5 ml of conc.

HF. Dilute to 15 ml and saturate with H_2S for 2 to 3 min. Add 1 ml of conc. HI, heat to boiling for 1 min, and again saturate with H_2S (Note 1). Add 1 ml La carrier, stir, and centrifuge (Note 2). Transfer the supernate to a clean centrifuge tube, discarding the precipitate. Add 10 ml of saturated H_3BO_3 and resaturate with H_2S. Centrifuge, discarding the supernate.

3. Repeat all of step (2) three times.

4. Dissolve the SnS_2 precipitate in 1 ml of conc. HCl and oxidize with Br_2-H_2O. Dilute to 15 ml and add 6 drops of Fe carrier and an excess of conc. NaOH. Centrifuge. Transfer the supernate to a clean centrifuge tube, discarding the precipitate. Add 6 drops of Fe carrier, stir, and repeat centrifugation.

5. Transfer the supernate to clean centrifuge tube, discarding the precipitate. Add 1.5 ml of cupferron reagent solution. Add conc. HCl dropwise until the precipitate formed does not redissolve. Then add 1 additional drop of conc. HCl. Filter through No, 41 H Whatman paper and wash thoroughly with H_2O.

6. Dry the precipitate at 110° for 15 min. Ignite, weigh, and mount (Note 3).

Notes

1. The reduction of fluoride [Sb(V) complexed with HI to Sb(III) which is then precipitated with H_2S] is a little tricky. If difficulty is encountered, boil longer with HI and afterwards saturate longer with H_2S.

2. In addition to carrying down rare-earth and neptunium activities, the LaF_3 scavenger also removes suspended sulfides which were not carried down by centrifugation.

3. If Sn is separated and counted immediately after bombardment, 8.6h Sb^{126} and 94h Sb^{127} are likely to grow into the purified Sn (50m Sn^{126}, 27h Sn^{121}, 9.75d Sn^{125}, and 130d Sn^{123}) and complicate the decay curve. If the tin is separated and counted several hours after bombardment, only 2.7y Sb^{125} will grow in, and in quantity negligible compared to the total counting rate. In the latter case, the observed activities will be 27h Sn^{121}, 9.75d Sn^{125}, and 130d Sn^{123}. The last-named will be present in very low yield and will be barely resolvable from the 2.7y Sb^{125} tail.

Sn Procedure No. 6

W. R. McDonell[122]

Element separated: Tin (≈ 10 mg)

Target material: Recovery from chemical wastes after bbdt. including 50 mg Fe, 30 mg Sb, 20 mg Cu

Time for sep'n: 3-4 hr

Equipment required: Centrifuge

Yield: 90-95%

Degree of purification: At least factor of 100 from metals present in macro amount

Advantages: High recovery yield

Procedure

1. Combine wastes, crush and dissolve residues in HCl (Note 1), HNO_3 or aqua regia (Note 1), using alkali fusions (Na_2CO_3 or NaOH) where necessary.

2. Neutralize with NH_4OH or NaOH, make 0.25-1.0N acid with HCl, pass in H_2S to saturation, ppt. acid sulfide group (usually black) + sulfur. Centrifuge, decant.

3. Add 15 cc Na_2S_x soln. (Note 2) to ppt. Heat 60-80° C with stirring. Add ≈ 15 ml hot 0.6N NaOH, centrifuge, decant. Wash with second portion of Na_2S_x. Combine filtrates. Acidify slowly with HCl to neutral litmus, then make 0.25-1N acid. Saturate with H_2S. Centrifuge, decant.

4. Add conc. HCl, warm with stirring to dissolve sulfides and coagulate sulfur (Note 3). Centrifuge, decant. Wash sulfur with hot 6N HCl. Combine solutions, which now contain Sn, Sb (and As if any was originally present) and only small amounts of Cu group metals.

5. Do the tin-antimony separation as outlined in 50-2 procedure (selective sulfide ppt. or ≈ Fe reduction, etc.). (Note 4.)

Notes

1. Avoid boiling conc. chloride solutions of Sn, since $SnCl_4$ is somewhat volatile.

2. Na_2S_x is used instead of $(NH_4)_2S_x$ because it affords a better separation from Cu, a major contaminant. (Ref., "A System of Chemical Analysis," E. H. Swift, Prentice-Hall, Inc., New York, 1940, p. 215.) Specifications for Na_2S_x soln.: dissolve 480 g $Na_2S \cdot 9H_2O$ + 40 g NaOH in minimum amt. of water, dissolve 16 g powdered sulfur in this soln., dilute to 1 liter.

3. A large quantity of sulfur is present in the ppt. However, it coagulates very well on heating in acid solution, while adsorbing very little of the sulfide, thus allowing satisfactory extraction.

4. Traces of Cu are dissolved by Na_2S_x solution. This, however, follows the Sb in the subsequent Sb-Sn separations (selective sulfide pptn. or Fe reduction).

Sn Procedure No. 7

A. S. Newton and W. L. McDonell[122]

Element separated: Tin

Target material: Tin (plus Cu of target holder)

Time for sep'n: 1 1/2 hr

Type of bbdt: Low energy d, p, n

Equipment required: Centrifuge, hot plate, glassware

Yield: 50-70%

Degree of purification: $\approx 10^6$

Advantages: Simpler than oxalate or distillation procedures

Procedure

1. Dissolve target in HCl, heating (Note 1) and adding drop Br_2 or few drops of HNO_3 where necessary to effect rapid solution (Note 2). Add 10 mg Sb, In carriers.

2. Make 3-4N HCl. Add iron powder to excess (hydrogen evolution), heat with stirring, ppt. Sb and Cu metal (black), filter by vacuum through sintered glass filtering crucible.

3. To filtrate add drop of Br_2 ($Fe^{++} \rightarrow Fe^{+++}$, $Sn^{++} \rightarrow Sn^{++++}$). Neutralize with NH_4OH to appearance of red $Fe(OH)_3$, add just enough HCl to redissolve $Fe(OH)_3$ (acidity 1N), pass in H_2S to saturation, ppt. yellow SnS_2 (Note 3).

4. Dissolve SnS_2 in HCl (3 cc of 12N) by heating (Note 1), stirring. Add 10 mg Sb carrier, stirring. Dilute to 2.5N acid ($\approx$ 14 cc), heat in boiling water bath, pass in H_2S to saturation, ppt. orange Sb_2S_3. Centrifuge hot (SnS_2 may ppt. in cold), decant. Dilute to 1.5N ($\approx$ 25 cc), pass in H_2S, ppt. SnS_2 (yellow). Repeat step (3) once or twice.

5. Dissolve SnS_2 in 1 cc 12N HCl. Add Fe^{+++} carrier (10 mg). Dilute slightly, add excess NaOH with stirring, heat well (Note 4). Centrifuge. Add further In and Fe(5 mg each) carrier to basic soln., ppting hydroxides. Centrifuge on top of previous ppt., decant. Repeat step (4) if necessary.

6. Acidify to $\approx$ 1N HCl. Pass in H_2S, ppt. SnS_2. Centrifuge, decant. Dissolve ppt. in minimum conc. HNO_3, add 3-5 cc fuming HNO_3, a knife point of NH_4NO_3. Boil several minutes to ppt. white metastannic acid. Evaporate aliquots of the slurried soln. on watchglass and mount for counting. To determine chemical yield dilute after ppting H_2SnO_3, add filter paper pulp, filter through ashless paper, recycling filtrate till clear, dry, and ignite to SnO_2 (Note 5). Weigh as SnO_2 (Note 6).

Notes

1. Avoid boiling concentrated Cl^- solns. of Sn; $SnCl_4$ appreciably volatile (also $SbCl_3$, $SnCl_3$, etc.).

2. A black residue replates out on the dissolving Sn, sometimes necessitating a mechanical agitation of the Sn surface.

3. InS_3 ppts. properly only at 0.05N HCl; however, it is partially coprecipitated at higher acidities with other sulfides of the Sn and Cu groups.

4. $In(OH)_3$ is peptized by fixed alkali hydroxides but reppts. on boiling. It is very slightly amphoteric.

5. Do not use Pt crucible for ignition as Sn metal is produced which alloys badly with Pt. Procelain crucible should be used.

6. SnO_2 difficult to dissolve after igniting, has been found to go into HCl soln. after fusion with Na_2CO_3 (anhyd.) in Pt crucible.

Sn Procedure No. 8

M. Lindner[122]

Element separated: Tin

Target material: Sb (≈ 0.5 g metal)

Time for sep'n: ≈ 1 hr

Type of bbdt: 184-in. α and D_2

Equipment required: Lusteroid tubes, centrifuge, cones, tank SO_2, H_2O

Yield: 50% or greater

Degree of purification: At least factor of 100

Procedure

1. To the target add 15 drops 27N HF in Lusteroid tube in hot water bath. Add conc. HNO_3 dropwise until dissolved (10 min). Dilute to ≈ 20 ml.

2. Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge.

3. Divide supn. into two equal parts.

4. Evaporate one part to near dryness. Cool, add 20 ml 3N HCl.

5. Boil the supn. to expel SO_2, add 5 ml H_2O.

6. Saturate hot with H_2S until Sb_2S_3 pptn. complete.

7. Evaporate the supn. to near dryness. Take up in 15 ml 1N NaOH.

8. Add 2 mg In^{+++} and 2 mg Cd^{++} to the supn. containing $SnO_3^=$. Centrifuge.

9. Neutralize the supn. dropwise with conc. H_2SO_4, make 0.3$\underline{N}$ in HCl, saturate with H_2S.

10. Dissolve the SnS_2 in 2 ml conc. HCl, boil to expel H_2S, and dilute to 12 ml. Reject any undissolved material (Sb).

11. Add 2 mg Sb^{+++} carrier to the Sn^{+4} solution and saturate with H_2S.

12. Boil to expel H_2S, make 0.3$\underline{N}$ in HCl. Resaturate with H_2S.

13. Dissolve SnS_2 in minimum HCl.

14. Evaporate an aliquot to dryness. Take up in 10 ml 16$\underline{N}$ HNO_3, boil to near dryness, repeat several times. Filter.

15. Transfer the $SnO_2 \cdot xH_2O$ ppt. to a crucible. Ignite 1 hr to SnO_2 and weigh.

Sn Procedure No. 9

R. D. Maxwell[119]

The cyclotron is the only practical source of many carrier-free[a] radioisotopes. The preparation and radiochemical isolation of a number of these activities, produced in the 60-inch cyclotron of Crocker Laboratory, will be presented in this paper and in subsequent papers of this series. Most of the carrier-free radioisotopes discussed here were prepared for use in biological systems and the final preparations were in the form of isotonic saline solutions at a range of pH from 5 to 8.

The present paper reports the radiochemical isolation of carrier-free Sn^{113} and In^{114} produced by bombarding cadmium with 38-Mev alpha particles. At this energy, Sn^{113} and In^{114} are produced in a thick target by the nuclear reactions[b] $Cd^{110}(\alpha, n)Sn^{113}$, $Cd^{111}(\alpha, 2n)Sn^{113}$, $Cd^{112}(\alpha, 3n)Sn^{113}$, $Cd^{111}(\alpha, p)In^{114}$, and $Cd^{112}(\alpha, pn)In^{114}$. The shorter-lived tin and indium activities, together with the possible radioisotopes of silver produced by (n, p) reactions, were allowed to decay out prior to the chemical separations.

The target, a block of cadmium metal soft-soldered to a water-cooled copper plate, was bombarded with 58-Mev alpha particles for a total of 450

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[a] This term is used to indicate that no stable isotopic carriers have been intentionally added. In a "carrier-free" separation the specific activity is determined by the chemical purity of the reagents.

[b] G. T. Seaborg and I. Perlman, Revs. Modern Phys. 20, 585 (1948).

μa-hr at an average beam intensity of 3.4 μa. After aging for one week, the bombarded surface was milled off and dissolved in a minimum volume of 16N HNO_3.

0.2 g of target cadmium nitrate was dissolved in 25 ml of water, and the tin and indium activities were carried quantitatively on 10 mg of $Fe(OH)_3$ precipitated with NH_4OH. The $Fe(OH)_3$ was dissolved in 15 ml of 36N H_2SO_4 and transferred to an all-glass distilling flask.[c, d] 9N HBr was added dropwise while a stream of CO_2 was bubbled through the solution at 220° C. The distillate, containing the carrier-free Sn^{113}, HBr, Br_2, and traces of H_2SO_4, was caught in a series of traps filled with 12N HCl; the indium activity remained in the residue. (Carrier-free radiotin, collected in HNO_3 or H_2SO_4, forms a radiocolloid[e, f] and is adsorbed onto the walls of the containing vessel. 12N HCl keeps the radiotin in solution presumably as the chlorostannate complex.) The trap contents were treated with 5 ml of 16N HNO_3 to destroy HBr, 15 mg of citric acid was added and the solution was evaporated on a steam bath to the 1- to 2-ml volume of H_2SO_4 carried over in the distillation. (Citric acid prevents the formation of radiocolloid after removal of HCl.)

The H_2SO_4 solution was diluted with 25 ml of water and the radiotin was carried down on $Fe(OH)_3$ precipitated with NH_4OH. The $Fe(OH)_3$ was dissolved in 8N HCL and iron was extracted with isopropyl ether. The aqueous phase, containing HCl, Sn^{113}, and equilibrium amounts of the In^{113} daughter, was evaporated to dryness on 10 mg of sodium citrate. The activity dissolved quantitatively in distilled water.

The carrier-free Sn^{113} was identified by its 105-day half-life and by the 0.39-Mev conversion electron of the In^{113} daughter.[g] The indium fraction from a chemical separation of an equilibrium mixture using tin and indium carriers showed the 105-min period of In^{113}.

The residue from the tin distillation, containing Fe^{+++} and In^{114}, was neutralized with NH_4OH. The $Fe(OH)_3$ plus indium activity was dissolved in 8N HCl, and extracted with isopropyl ether. The HCl solution of In^{114} was

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[c] J. A. Scherrer, J. Research Nat. Bur. Standards 21, 95 (1938).

[d] J. Schwaibold, W. Borchers, and G. Nagel, Biochem. Z. 306, 113 (1940).

[e] O. Hahn, Applied Radiochemistry (Cornell University Press, Ithaca, N. Y., 1936).

[f] The colloidal properties of carrier-free radiotin are being investigated. The results will be published elsewhere.

evaporated to dryness on 10 mg of NaCl. The activity dissolved quantitatively with the addition of distilled water. The In^{114} was identified by the assigned 48-day half-life and by the 0.19-Mev conversion electron.[g,h]

July 1949

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[g] S. W. Barnes, Phys. Rev. 56, 414 (1939).

[h] J. L. Lawson and J. M. Cork, Phys. Rev. 57, 982 (1940).

Sn Procedure No. 10

J. W. Winchester

Element: Sn-1

Separated from: Neutron-irradiated UO_2Cl_2 solution

Chemicals: 5% cupferron solution, saturated phenylarsonic acid solution

Equipment

An all-glass distilling apparatus is used, consisting of a 50-ml round-bottom flask with a single 19/38 neck to which is attached a second neck for supporting a 10/30 250° C thermometer about 8 mm from the bottom of the flask. The distillation head, which fits into the 19/38 neck, consists of a short 15-mm column with a horizontal 6-mm air condenser beginning about 12 cm above the bottom of the flask. The condenser, 22 cm long, rises slightly to permit any spray to return to the flask, and is connected to a vertical delivery tube 12 cm long which dips beneath the surface of the solution in the receiver. A current of air and HBr solution from a dropping funnel are admitted through a 6-mm tube which extends down through the center of the column to about 6 mm from the bottom of the flask.

Procedure

1. An aliquot of the sample is pipetted into a beaker, 10 mg Sn(II), 10 ml conc. H_2SO_4, and 1 ml H_3PO_4 are added, and the solution is evaporated to fumes of SO_3 over a burner.
2. The solution is then introduced into the distilling apparatus, the temperature raised to 220° C, and $SnBr_4$ distilled into 10 ml conc. HCl in a 50-ml centrifuge tube with a current of air (1-2 drops/sec) upon the dropwise addition of 10 ml 48% HBr. (Note 1.)

3. The distillate is evaporated to 5 ml insuring complete removal of Br_2 (Note 2), and 2 ml 5% cupferron solution (Note 3) is added which forms a precipitate with the Sn.

4. The mixture is transferred to a separatory funnel containing 15 ml of ethyl acetate, and the Sn extracted with gentle swirling (Note 4). The aqueous phase is discarded.

5. The organic phase is washed three times by swirling with 10-ml portions of 1<u>M</u> HCl. (Note 4.)

6. The Sn is extracted out of the organic phase by shaking with 10 ml saturated oxalic acid. Note time as time of Sb separation (Note 5).

7. The oxalic acid solution is diluted to 25 ml, heated to boiling, and Sn is precipitated upon the addition of 5 ml saturated phenylarsonic acid.

8. The precipitate is filtered, washed with hot 4% NH_4NO_3 until free from Cl^- (Note 6), and dried by washing with alcohol and ether.

9. The chemical yield is determined after counting, by igniting at 1000° C and weighing as SnO_2.

Notes

1. The temperature should be maintained > 200° C during the distillation.

2. The presence of Br_2 interferes with the extraction.

3. The cupferron solution should be stored in a dark bottle, kept in the refrigerator, and used only as long as it remains clear and colorless.

4. An emulsion, which separates very slowly, is formed upon vigorous shaking.

5. This step should be accomplished as soon as possible after step (5) since Sb is also back-extracted by the oxalic acid solution.

6. The presence of Cl^- will result in an erroneous high yield.

Remarks

A yield of 60% can be expected and the time required is 20 minutes.

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Sn Procedure No. 11

G. Wilkinson and W. E. Grummitt[188]

Tin carrier is added to the U solution and exchange achieved by oxidation-reduction cycles between Sn^{II} and Sn^{IV}. Germanium, As, and Se are then distilled from the 40% HBr solution, Sn remaining in the Sn^{II} state. About 0.2 ml strong H_2SO_4 is added to the residue followed by strong HNO_3 or other oxidizing agent to oxidize Sn^{II} to Sn^{IV} (in which state it is volatile as $SnCl_4$ which boils at 114° C), and Sb^{III} to Sb^{V} ($SbCl_5$ is less volatile in HCl solutions than $SbCl_3$ which boils at 223.5° C). The Sn is then distilled from 12<u>N</u> HCl solution. The distillate is collected, holdback carriers for Sb and other elements are added, and the procedure repeated. The second distillate is neutralized with NH_4OH, Sb carrier added, and the solution saturated with oxalic acid. Hydrogen sulfide is then passed into the hot oxalic acid solution to precipitate Sb_2S_3; Sn remains in the solution as the complex oxalate.

The oxalate filtrate is boiled to remove H_2S; Sb carrier is added, and the Sb_2S_3 again precipitated. Finally, the oxalate is destroyed by the addition of a slight excess of $KMnO_4$ to the hot solution acidified with H_2SO_4. The solution is treated with Fe to reduce the tin to the Sn^{II} state, and to remove any traces of Sb. The solution is then centrifuged and, after adjusting the acidity to 0.4<u>N</u>, SnS is precipitated. Chemical yields of Sn are about 70% with separation factors of about 10^6 when separation cycles are repeated three times. The procedure is very tedious.

REFERENCES

1. J. R. A. Anderson and Alice Whitley; "The Determination of R_f Values of Metallic Ions Using Diethyl Ether as Solvent"; Anal. Chim. Acta 6, 517-20 (1952).

2. J. R. A. Anderson and S. L. Lowy; "A Fluorimetric Determination of Tin"; Anal. Chim. Acta 15, (3), 246-53 (1956).

3. R. H. Atkinson, J. Steigman, and C. F. Hiskey; "Analytical Chemistry of Niobium and Tantalum"; Anal. Chem. 24, 477-88 (1952).

4. D. Bailey, W. M. Dowson, R. Harrison, and T. S. West; "Studies in Qualitative Inorganic Analysis. IV. A Test for the Detection of Tin (IV)"; Mikrochim. Acta 1958, (1) 137-39.

5. E. H. Baker; "Autooxidation of Tin Solutions: The Action of Inhibitors"; J. Appl. Chem. (London) 3, 323-28 (1953).

6. I. Baker, M. Miller, and R. S. Gibbs; "Colorimetric Determination of Tin by Silicomolybdate"; Ind. Eng. Chem., Anal. Ed. 16, 269-71 (1944).

7. F. Basolo; "Theories of Acids, Bases, Amphoteric Hydroxides, and Basic Salts, as Applied to the Chemistry of Complex Compounds"; Chap. 12 of "The Chemistry of Coordination Compounds"; J. C. Bailar, Jr. (Ed.); Reinhold Publishing Corp., New York, 1956.

8 H. Beduneau; "Organic Derivatives of Tin. Properties and Uses"; Rev. prod. chim. 56, 1-6, 46-50 (1953).

9. R. L. Bennett and H. A. Smith; "Spectrophotometric Determination of Tin with Phenylfluorone"; Anal. Chem. 31, 1441-42 (1959).

10. L. Bertiaux; "Colorimetric or Nephelometric Determination of Very Small Quantities of Elements"; Ann. chim. anal. 27, 209-15 (1945).

11. K. S. Bhatki and P. Radhakrishna; "Carrier-Free Separation of Sn^{113} from Indium"; Proc. Indian Acad. Sci. 45A, No. 1, 30-34 (1957).

12. I. A. Blyum and N. G. Zyryanova; "Determination of Small Quantities of Tin in Ores"; Zavodskaya Lab. 22, No. 1, 46-47 (1956); Brutcher Trans. No. 4003 (1960).

13. R. Bock; "Separation of Inorganic Mixtures by Partition Between Two Solvents. IV. Partition of Metal Thiocyanates Between Aqueous Solution and Diethyl Ether"; Z. Anal. Chem. 133, 110-35 (1951).

14. H. Bode; "Systematic Investigation of the Application of Diethyldithiocarbamate in Analysis. IV. Formation of Metal Dithiocarbamates and Their Extractability in Relation to the pH of the Solution"; Z. Anal. Chem. 144, (3), 165-86 (1955).

15. I. D. Borneman-Starinkevitch; "Decomposition of Cassiterite by Fusion with Borax and Some Details of Its Complete Chemical Analysis"; Compt. rend. acad. sci. U.R.S.S. 24, 253-56 (1939). (In English.)

16. C. I. Browne, R. P. Craig, and N. Davidson; "Spectrophotometric and Radiochemical Investigations of the Interaction Between Tin (II) and (IV) in Hydrochloric Acid Solutions"; JACS 73, 1946-51 (1951).

17. C. H. Brubaker, Jr.; "The Hydrolysis of Tin (IV) in Sulfuric Acid"; JACS 77, 5265-68 (1955).

18. C. H. Brubaker, Jr.; "Sulfate Complexes of Tin (IV)"; J. Phys. Chem. 61, 696-97 (1957).

19. F. H. Burstall, G. R. Davies, R. P. Linstead, and R. A. Wells; "Inorganic Chromatography on Cellulose"; Nature 163, 64 (1949).

20. F. H. Burstall, G. R. Davies, R. P. Linstead, and R. A. Wells; "Inorganic Chromatography on Cellulose. Part II. The Separation and Detection of Metals and Acid Radicals on Strips of Absorbent Paper"; J. Chem. Soc. 1950, 516-28.

21. E. R. Caley and M. G. Burford; "Separation of Stannic Oxide from Various Oxides by Ignition with Ammonium Iodide"; Ind. Eng. Chem., Anal. Ed. 8, 114-18 (1936).

22. R. G. de Carvalho; "A New Gravimetric Method for the Estimation of Tin: Precipitation as Stannic Selenite"; Rev. quim. pura e apl. (4), 1, No. 1, 24-41 (1950); UCRL Trans. 558(L) (1960).

23. F. W. Chapman, Jr., G. G. Marvin, and S. Y. Tyree, Jr.; "Volatilization of Elements from Perchloric and Hydrofluoric Acid Solutions"; Anal. Chem. 21, 700-01 (1949).

24. B. L. Clarke, L. A. Wooten, and J. D. Struthers; "Separation and Determination of Impurities in Lead. I. Tin"; Ind. Eng. Chem., Anal. Ed. 9, 349-51 (1937).

25. R. E. D. Clark; "The Colorimetric Determination of Tin by Means of Toluene-3:4-Dithiol ("Dithiol")"; Analyst 62, 661-63 (1937).

26. G. E. Collins and J. K. Wood; "The Amphoteric Character of Stannic Hydroxide and Its Bearing on the Isomerism of the Stannic Acids"; J. Chem. Soc. (London) 121, 441-49 (1922).

27. G. B. Cook; "Analytical Methods for Fission Product: Tin and Antimony"; AERE C/R 424 (1949) (Publ. 1955).

28. D. J. Coombe; "Anal. Chem. Quart. Progress Report for Period Ending March 26, 1952"; Oak Ridge National Lab., Tenn.; ORNL-1276 (Del.).

29. D. J. Coombe; "Analytical Chemistry Division Semiannual Progress Report for Period Ending October 20, 1953"; Oak Ridge National Lab., Tenn.; ORNL-1639 (Del.).

30. W. C. Cooper; "The Polarographic Behavior of Dropping Tin Amalgam Electrodes"; JACS 77, 2074-76 (1955).

31. C. R. Courtney, R. L. Gustafson, S. Chabarek, Jr., and A. E. Martell; "Hydrolytic Tendencies of Metal Chelate Compounds. II. Effect of Metal Ion"; JACS 80, 2121-28 (1958).

32. C. F. Coyle and C. F. White; "Fluorometric Determinations of Tin with Flavonol"; Anal. Chem. 29, 1486-88 (1957).

33. R. P. Craig and N. Davidson; "The Photochemical Exchange Reaction Between Tin (II) and Tin (IV) in Hydrochloric Acid Solution"; JACS 73, 1951-54 (1951).

34. M. Dannenmuller; "The Determination of Tin. New Rapid Method"; Rev. mét. 38, 137-52 (1941).

35. J. Davies and A. J. Easton; "Colorimetric Determination of Tin"; Metal Ind. (London) 82, 418 (1953).

36. J. A. Dean and J. A. Reynolds; "Rapid Method for the Separation and Determination of Bismuth, Antimony, and Tin by Controlled Cathode Electroanalysis"; Anal. Chim. Acta 11, 390-95 (1954).

37. M. M. de Maine and P. A. D. de Maine; "Spectrophotometric Studies of Tin (+2) and Tin (+4) Dissolved Separately in Water, Methanol, and Hydrochloric Acid"; J. Inorg. Nuclear Chem. 11, 13-19 (1959).

38. J. R. DeVoe, C. K. Kim, and W. W. Meinke; "Radiochemical Separations by Amalgam Exchange"; Talanta 3, 298-99 (1960).

39. A. K. Dey and A. K. Bhattacharya; "Quantitative Study of the Extent of Inhibition of the Precipitation of Stannic Sulfide by Oxalic Acid and Oxalates"; Proc. Nat. Acad. Sci. India 15A, 86-90 (1946).

40. A. K. Dey; "Quantitative Study of the Extent of Inhibition of the Precipitation of Stannic Sulfide in the Presence of Soluble Tartrates"; Proc. Nat. Acad. Sci. India 16A, 27-30 (1947).

41. A. K. Dey and A. K. Bhattacharya; "Physico-Chemical Studies in the Formation of Complex Stannioxalates. Part I. Conductometric Study of the $Sn(OH)_4$-$H_2C_2O_4$ System"; J. Indian Chem. Soc. 25, 571-74 (1948).

42. A. K. Dey; "Physico-Chemical Studies in the Formation of Complex Stannioxalates. Part V. Spectroscopic Study of the System: $SnCl_4$:$K_2C_2O_4$";

Proc. Nat. Acad. Sci. India A26, Pt. 2, 126-28 (1957).

43. F. R. Duke and W. G. Courtney; "The Stannous Chloride Equilibrium"; Iowa State Coll. J. Sci. 24, 397-403 (1950).

44. T. Dupuis and C. Duval; "Sur la thermogravimétrie des précipités analytiques. XXXVI. Dosage de l'étain"; Anal. Chim. Acta 4, 201-03 (1950).

45. J. Dawson and R. J. Magee; "The Anion Exchange Separation of Tin and Antimony"; Mikrochim. Acta 1958, (3), 325-29, 330-36.

46. E. Eberius; "Photometric Determination of Tin in Zinc and Lead"; Metall 12, 721-24 (1958).

47. B. S. Evans and D. G. Higgs; "The Hypophosphorous Acid Reduction of Tin. An Improved Procedure and Notes on Its Mechanism"; Analyst 69, 201-06 (1944).

48. D. A. Everest and J. H. Harrison; "Anion Exchange Studies of Solutions of Stannic Chloride in Hydrochloric Acid"; J. Chem. Soc. 1957, 1439-40.

49. J. P. Faris; "Adsorption of the Elements from Hydrofluoric Acid by Anion Exchange"; Anal. Chem. 32, 520-21 (1960).

50. M. Farnsworth and J. Pekola; "Determination of Small Amounts of Tin with Dithiol"; Anal. Chem. 26, 735-37 (1954).

51. A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger; "The Preparation and Some Properties of Hydrides of Elements of the Fourth Group of the Periodic System and of Their Organic Derivatives"; JACS 69, 2692-96 (1947).

52. H. Flaschka and J. H. Jakobljevich; "Die Verwendung von Thioacetamid in der quantitativen analyse. VIII. Die Bestimmung von Zinn"; Anal. Chim. Acta 5, 60-62 (1951).

53. H. Flaschka; "Uber Sulfidfallungen mittels Thioacetamid und deren Beeinflussung durch Athylenediaminetetraessigsaure(Komplexon)"; Z. Anal. Chem. 137, 107-15 (1952).

54. H. Flaschka, A. J. Barnard, Jr., and W. C. Broad; "The EDTA Titration: Applications IV"; Chemist Analyst 47, 78-84 (1958).

55. N. H. Furman, W. B. Mason, and J. S. Pekola; "Extraction of Cupferrates"; Anal. Chem. 21, 1325-30 (1949).

56. J. L. Garnett and L. C. Lock; "The Use of Naphthalene Derivatives in Inorganic Analysis. Part IV. The Nitronaphthylamines as Fluorimetric Reagents for Stannous Tin"; Anal. Chim. Acta 17, 574-78 (1957).

57. C. H. R. Gentry and L. G. Sherrington; "Extraction and Photometric Estimation of Some Metals with 8-Hydroxyquinoline"; Analyst 75, 17-21 (1950).

58. L. B. Ginzberg and E. P. Shkrobot; "The Determination of Small

Amounts of Tin in Ores by Fluorescent or Colorimetry Methods"; Zavodskaya Lab. 23, 527-33 (1957); Chem. Abstr. 52, 970 f.

59. L. Gordon; "Precipitation from Homogeneous Solution"; Anal. Chem. 24, 459-62 (1952).

60. H. Goto, Y. Kakita, and T. Furukawa; "Studies on Methyl Isobutyl Ketone Extraction and Determination of Metallic Salts. I. Extraction of Iron, Antimony, Tin, Arsenic, Selenium, Tellurium, and Germanium from Hydrochloric Acid Solutions"; Nippon Kagaku Zasshi 79, 1513-20 (1958); UCRL Trans. 541(L) (1960).

61. D. K. Hale; "Methods or Processes of Extracting a Solute from a Solution"; British Patent 738, 500; Oct. 12, 1955.

62. S. Harasawa; "Studies in Inorganic Paper Chromatography. VII. Separation of Salts of Tin and Antimony, and Analysis of Metals of the Tin Group in the State of Higher Valence"; J. Chem. Soc. Japan, Pure Chem. Sect. 72, 423-26 (1951); UCRL Trans. 544(L) (1960).

63. M. M. Haring and J. C. White; "Amalgam Activities and Standard Electrode Potentials. I. Tin"; J. Electrochem. Soc. 3, 211-21 (1938).

64. W. Heuss; "A Simplified Method for the Quantitative Determination of Arsenic, Antimony, and Tin"; Rev. Tech. Sulzer 1945, No. 1., 110-14; Chim. & ind. (Paris) 55, 363 (1946).

65. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman; "Applied Inorganic Analysis," 2nd Edition; John Wiley & Sons, Inc., New York, 1953; pp. 70-75, 285-96.

66. C. D. Hodgman (Editor in Chief); "Handbook of Chemistry and Physics," 39th Edition; Chemical Rubber Publishing Co., Cleveland, 1958.

67. J. I. Hoffman and G. E. F. Lundell; "Volatilization of Metallic Compounds in Perchloric or Sulfuric Acid"; J. Research Nat. Bur. Standards 22, 465-70 (1939).

68. W. A. Hoffman, Jr. and W. W. Brandt; "The Volatilization of Tin"; Ph.D. Thesis (for W.A.H.), Purdue Univ. (1955).

69. H. Holness and W. R. Schoeller; "The Precipitation of Tin by Tannin"; Analyst 71, 70-74 (1946).

70. F. Hudswell and J. S. Nairn; "The Purification of Semimicro Quantities of Tin"; AERE-C/R-650 (Jan. 1951).

71. D. T. Hurd; "An Introduction to the Chemistry of the Hydrides"; John Wiley & Sons, Inc., New York, 1952; pp. 116-18.

72. G. Jantsch, A. Hummer-Kroupa, and I. Gansinger; "Uber die Bestimmung von kleinsten Zinnmengen"; Z. Anal. Chem. 128, 451-58 (1948).

73. D. Jentzsch and I. Pawlik; "Use of Ion Exchangers in Analytical Chemistry. III. The Elution Constants of Different Elements in Hydrochloric Acid Solutions"; Z. Anal. Chem. 146, 88-102 (1955).

74. A. Jewsbury and G. H. Osborn; "Some Further Analytical Applications of Ammonium Benzoate. An Investigation into the Uses and Limitations of Ammonium Benzoate for the Quantitative Estimation of Tin, Titanium, Zirconium, Thorium, Bismuth, and Cerium, and for Their Separation from Other Elements"; Anal. Chim. Acta 3, 642-55 (1949).

75. J. S. Johnson and K. A. Kraus; "Hydrolytic Behavior of Metal Ions. IX. Ultracentrifugation of Sn (IV) in Acidic Chloride and Perchlorate Solutions"; J. Phys. Chem. 63, 440-41 (1959).

76. S. Kallman and F. Pristera; "Rapid Determination of Antimony, Tin, and Bismuth"; Ind. Eng. Chem., Anal. Ed. 13, 8-11 (1941).

77. M. Karschulin and Z. Svarc; "Chromatographic Studies. I. Chromatographic Analysis of Elements of Group (IIb) with the Aid of Active Alumina from Lozovac (Croatia)"; Kem. vjestnik (Arhiv kem. i tehnol.) 17, 99-105 (1943).

78. P. Karsten and H. L. Kies; "The Separation of Tin (IV) and Antimony According to F. W. Clarke"; Rec. trav. chim. 67, 753-60 (1948).

79. P. Karsten, H. L. Kies, and J. J. Walraven; "Turbidimetric Determination of Tin (IV) with 3-Nitro-4-Hydroxy-Benzene-Arsonic Acid"; Anal. Chim. Acta 7, 355-59 (1952).

80. S. S. M. A. Khorasani and M. H. Khundkar; "Solvent Extractions of Antimony (V) with Ethyl Acetate"; Anal. Chim. Acta 21, 24-28 (1958).

81. S. Kitahara; "Ether Extraction of Iodides and Iodates of Various Elements"; Repts. Sci. Research Inst. (Tokyo) 24, 454-57 (1948); Chem. Abstr. 45, 2290 i; UCRL Trans. 559(L) (1960).

82. S. Kitahara; "Ether Extraction of Fluorides or Hydrofluoric Acid Solutions of Various Elements"; Repts. Sci. Research Inst. (Tokyo) 25, 165-67 (1948); Chem. Abstr. 45, 3743 f.

83. J. Kleinberg; "Collected Radiochemical Procedures"; LA-1721, 2nd Edition (1958).

84. R. Klement and A. Kuhn; "Separation of Arsenic, Antimony, and Tin by Anion Exchange"; Z. Anal. Chem. 152, 146-53 (1956).

85. A. Kling and A. Lassieur; "Séparation de l'étain et de l'antimoine. Dosage de l'étain par le cupferron"; Compt. rend. 170, 1112-14 (1920).

86. J. J. Knapper, K. A. Craig, and G. C. Chandler; "Phenylarsonic Acid as a Reagent for the Determination of Tin"; JACS 55, 3945-47 (1933).

87. F. G. Kny-Jones, A. J. Lindsey, and A. C. Penney; "The Quantitative Electrodeposition of Tin from Chloride Solutions"; Analyst 65, 498-501 (1940).

88. I. M. Kolthoff and R. A. Johnson; "Amperometric Titrations with m-Nitrophenylarsonic Acid"; J. Electrochem. Soc. 98, 138-45 (1951).

89. I. M. Kolthoff and R. A. Johnson; "Amperometric Titrations of Sn(IV)

and Hg(II) with Tetraphenylarsonium Chloride"; J. Electrochem. Soc. 98, 231-33 (1951).

90. P. N. Kovalenko; "Polarographic Determination of the Beginning of Precipitation of Stannous Hydroxide from Hydrochloric Acid Solution and Calculation of Its Solubility Product"; Zhur. Neorg. Khim. 3, 1065-70 (1958); Chem. Abstr. 52, 19609c.

91. K. A. Kraus and F. Nelson; "Metal Separations by Anion Exchange"; ASTM Spec. Tech. Publ. No. 195 (1958).

92. K. A. Kraus, D. C. Michelson, and F. Nelson; "Adsorption of Negatively Charged Complexes by Cation Exchangers"; JACS 81, 3204-07 (1959).

93. T. Krokowski; "Uber die Fallung des Zinns aus alkalischer Losung mit Bromwasser"; Z. Anal. Chem. 117, 105-09 (1939).

94. N. K. Kulrestha, A. K. Dey, S. Ghoch; "Untersuchungen uber hydratisiertes Zinnoxyd. Tell II: Konduktometrische Untersuchung der Fallung und Hydrolyse"; Kolloid-Z. 141, 106-09 (1955).

95. V. I. Kuznetsov; "Precipitation of Tin with Benzenearsonic Acid"; J. Appl. Chem. (U.S.S.R.) 13, 1512-16 (1940).

96. V. I. Kuznetsov; "Organic Coprecipitants in Analytical Chemistry"; Sessiya Akad. Nauk S.S.S.R. Mirnomu Ispol 'zovaniyu Atomnoi Energii. Moscow, 1955. Zasedan. Otdel. Khim. Nauk, 301-18; English translation: Conf. Acad. Sci. U.S.S.R. Peaceful Uses of Atomic Energy. Moscow, 1955. Sess. Div. Chem. Sci., 177-86; Chem. Abstr. 50, 111h, 7002a.

97. N. A. Lange; "Handbook of Chemistry"; Handbook Publishers, Inc., Sandusky, Ohio, 1956.

98. W. M. Latimer; "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Edition; Prentice-Hall, Inc., New York, 1952.

99. S. J. Leachman and F. C. Tompkins; "The Autooxidation of Inorganic Reducing Agents. Part II. Stannous Chloride (Experimental)"; Trans. Faraday Soc. 40, 130-36 (1944).

100. S. J. Leachman and F. C. Tompkins; "The Autooxidation of Inorganic Reducing Agents. Part III. Stannous Chloride (Theoretical)"; Trans. Faraday Soc. 40, 136 (1944).

101. M. Lederer; "Paper Chromatography of Inorganic Cations. Part II"; Anal. Chim. Acta 5, 185-90 (1951); Part III, Ibid. 5, 191-94 (1951).

102. M. Lederer; "Recent Advances in Chromatography. III. Paper Chromatography of Radioelements"; Actualités sci. et ind., No. 1240 (1956).

103. D. Lee and G. B. Cook; "The Separation and Mounting of Some Fission Elements by Electrodeposition"; AERE-C/R-430 (1955).

104. H. A. Liebhafsky and A. F. Winslow; "The Reactivity of Amalgams"; JACS 63, 3137-42 (1941).

105. J. J. Lingane; "Polarographic Behavior of Chloro and Bromo Complexes of Stannic Tin"; JACS 67, 919-22 (1945).

106. J. L. Lingane and C. Auerbach; "Reductometric Titration of Antimony, Copper, and Tin with Chromous Ion"; Anal. Chem. 23, 986-89 (1951).

107. J. A. Lingane and S. L. Jones; "Controlled Potential Electrolytic Separation and Determination of Copper, Bismuth, Lead, and Tin"; Anal. Chem. 23, 1798-1806 (1951).

108. K. Liska; "Colorimetric Determination of Tin with Quercetin"; Chem. listy 49, 1656-60 (1956); Chem. Abstr. 50, 726 d.

109. K. Liska and L. Klir; "Use of Anion Exchangers in Analytical Chemistry. I. Sorption of Chloride Complexes of Certain Metals in OAL Anion Exchangers"; Chem. listy 51, 1467-70 (1957); UCRL Trans. 536(L) (1960).

110. J. G. A. Luijten and G. J. M. Van der Kerk; "A Survey of the Chemistry and Applications of Organotin Compounds"; Publ. by the Tin Research Institute, Fraser Rd., Perivale, Greenford, Middlesex, England (1952).

111. C. L. Luke; "Photometric Determination of Tin with Phenylfluorone. Determination of Tin in Lead and 1% Antimony-Lead Alloys"; Anal. Chem. 28, 1276-79 (1956).

112. C. L. Luke; "Photometric Determination of Tin in Copper-Base and Lead-Base Alloys"; Anal. Chem. 31, 1803-04 (1959).

113. G. E. F. Lundell and J. I. Hoffman; "Outlines of Methods of Chemical Analysis"; John Wiley & Sons, Inc., New York, 1938.

114. G. D. Lutwick and D. E. Ryan; "Aromatic Hydroxylamines as Organo-Analytical Reagents"; Can. J. Chem. 32, 949-55 (1954).

115. M. V. Mack and F. Hecht; "Mikrogravimetrische Trennung von Zinn und Antimon"; Mikrochim. Acta 2, 227-41 (1937).

116. A. K. Majumdar and M. M. Chakrabartty; "Paper Chromatography in the Separation of Ions"; Anal. Chim. Acta 17, 415-16 (1957).

117. A. K. Majumdar and B. R. Singh; "Electrochromatography in the Separation of Ions, Part IV. Separation of Copper and Tin Group Metals"; Anal. Chim. Acta 18, (3) 220-23 (1958); Part I, Ibid. 15, 547 (1956); Part II, Ibid. 17, 228 (1957); Part III, Ibid. 17, 541 (1957).

118. M. Maki; "Electrochromatography. V. Separation of Inorganic Cations by Complex Ion Formation"; Japan Analyst 4, 21-25 (1955); Part I, Ibid. 3, 39-40 (1954); "Part II. Effect of Time, Potential Gradient, Temperature, Concentration, and Volume of Sample", Ibid. 3, 311-14 (1954); "Part III. Separation of Some Cations by Changing the pH of the Buffer Solution", Ibid. 3, 314-16 (1954); "Part IV. Separation of Inorganic Cations by the Formation of Complex Ions", Ibid. 3, 393-97 (1954).

119. R. D. Maxwell, H. R. Haymond, D. R. Bomberger, W. M. Garrison, and J. G. Hamilton; "Carrier-Free Radioisotopes from Cyclotron Targets. I. Preparation and Isolation of Sn^{113} and In^{114} from Cadmium"; UCRL-403 (1949).

120. G. Mattock; "The Complex-Forming Behavior of Tin, Germanium, and Titanium with Some Dibasic Carboxylic Acids"; J. Chem. Soc. 1954, 989-97.

121. L. W. McCay; "The Separation of Tin and Antimony"; JACS 31, 373-81 (1909).

122. W. W. Meinke; "Chemical Procedures Used in Bombardment Work at Berkeley"; UCRL-432 (1949).

123. E. G. Meyer and M. Kahn; "The Exchange Reaction Between Tin (IV) and Tin (II) in Absolute Ethyl Alcohol"; JACS 73, 4950-53 (1951).

124. E. G. Meyer and M. A. Melnick; "The Exchange Reaction Between Tin (+4) Chloride and Tin (+2) Chloride in Absolute Methanol"; J. Phys. Chem. 61, 367-69 (1957).

125. C. C. Miller and L. R. Currie; "The Volumetric Determination of Tin on a Small Scale and Its Application to Nonferrous Alloys"; Analyst 73, 377-80 (1948).

126. G. H. Morrison and H. Freiser; "Solvent Extraction in Analytical Chemistry"; John Wiley & Sons, Inc., New York, 1957.

127. A. N. Murin and V. D. Nefedov; "Concentration of Artificial Radioactive Isotopes of Groups IV and V by Method of Recoil Atoms"; Primenenie Mechenykh Atomov v Anal. Khim., Akad. Nauk S.S.S.R., Inst. Geokhim. Anal. Khim. im. V. I. Vernadskogo, 1955, 75-78; UCRL Trans. 552(L).

128. A. Musil, E. Gagliardi, and K. Reischl; "Trennung Arsen-Antimon-Zinn mit Thioformamid"; Z. Anal. Chem. 140, 342-49 (1953).

129. T. N. Nazarchuk; "On the Photometric Determination of Tin"; Zhur. Anal. Khim. 14, 696-99 (1959); Nuclear Sci. Abstr. 14, 6274.

130. F. Nelson, R. M. Rush, and K. A. Kraus; "Anion-Exchange Studies. XXVII. Adsorbability of a Number of Elements in HCl-HF Solutions"; JACS 82, 339-48 (1960).

131. W. Nielsch and G. Boltz; "Photometric Determination of Tin with Thiourea"; Z. Anal. Chem. 143, 161-67 (1954).

132. G. Norwitz; "Electrolytic Determination of Tin"; Z. Anal. Chem. 131, 266-68 (1950).

133. K. M. Ol'shanova and K. V. Chmutov; "Chromatographic Method in Qualitative Analysis. III. Analysis of As^{+3}, Sb^{+3}, and Sn^{+2}"; Zhur. Anal. Khim. 11, 94-98 (1956); J. Anal. Chem. U.S.S.R. 5, 605-10 (1956).

134. T. C. J. Ovenston and C. Kenyon; "The Adsorptiometric Determination of Tin by Means of Dithiol"; Analyst 80, 566-67 (1955).

135. A. C. Pappas and D. R. Wiles; "New Short-Lived Isotopes of Tin Found in Fission"; J. Inorg. & Nuclear Chem. 2, 69-78 (1956).

136. T. D. Parks and L. Lykhen; "Reduced-Scale Methods for Micro and Semimicro Analysis. Part II"; Petrol. Refiner 29, No. 9, 112-14 (1950).

137. V. Patrovsky; "Use of Morin in Chemical Analysis. III. Photometric Determination of Sn^{+4}"; Chem. listy 48, 1694-95 (1954); Chem. Abstr. 49, 4449 h.

138. U. Pelagatti; "A New Method of Separating Tin and Antimony and Its Applications in the Analysis of White Alloys"; Chim. e ind. (Milan) 20, 724-26 (1938); Chem. Abstr. 33, 2066^{2}.

139. E. Pfeil, G. Ploss, and H. Saran; "Separation of the Hydrogen Sulfide Group by Paper Chromatography"; Z. Anal. Chem. 146, (4), 241-43 (1955).

140. E. Pfeil, A. Friedrich, and T. Wachsmann; "Qualitative Inorganic Analysis by Paper Chromatography; Separation of Common Cations"; Z. Anal. Chem. 158, (6),429-34 (1957).

141. Z. Pinterovic; "Inorganic Chromatography. II. Adsorption of Tin on a Column of Alumina"; Bull. soc. chim. Belges 58, 522-27 (1949).

142. A. I. Portnov; "Application of Aromatic Arsenic Compounds in Chemical Analysis. I."; Zhur. Obshchei Khim. 18, 594-600 (1948); Chem. Abstr. 43, 57 c.

143. "Progress Report" (No. 32 for Dec. 1, 1953 to Feb. 28, 1954); Lab. for Nuclear Sci., Mass. Inst. Technol. (1954).

144. "The Properties of Tin"; Tin Research Institute, Fraser Rd., Perivale, Greenford, Middlesex, England (1954).

145. H. Remy; "Treatise on Inorganic Chemistry"; Elsevier Publishing Co., Houston, 1956, Chap. 12.

146. D. E. Ryan and G. D. Lutwick; "N-Benzoylphenylhydroxylamine as a Reagent for Tin"; Can. J. Chem. 31, 9-12 (1953).

147. E. B. Sandell; "Colorimetric Determination of Traces of Metals," 3rd Edition; Interscience Publishers, Inc., New York, 1959, Chap. XLIV.

148. J. Sara; "Polarographic Determination of Tin in a Dichromic Acid Medium"; Chem. prumysl 8, 636-37 (1958); Chem. Abstr. 53, 12095a.

149. I. Sarudi; "The Freiberger Fusion"; Z. Anal. Chem. 131, 424-26 (1950).

150. I. Sarudi; "Das Verfahren der Antimon-Zinntrennung nach Vortmann und Metzl"; Z. Anal. Chem. 148, 21-25 (1955).

151. Y. Sasaki; "Separation of the Three Elements, Tin, Antimony, and Tellurium, by an Anion Exchange Resin"; Bull. Chem. Soc. Japan 28, 615-16 (1955).

152. E. M. Scadden and N. E. Ballou; "Solvent Extraction Separation of Zirconium and Niobium"; Anal. Chem. 25, 1602-04 (1953).

153. W. B. Schaap, J. A. Davis, and W. H. Nebergall; "Polarographic Study of the Complex Ions of Tin in Fluoride Solution"; JACS 76, 5226-29 (1954).

154. G. W. Schaeffer and Sister M. Emelius; "The Preparation of Stannane"; JACS 76, 1203 (1954).

155. J. A. Scherrer; "Determination of Tin in Irons and Steels"; J. Research Nat. Bur. Standards 8, 309-20 (1932).

156. J. A. Scherrer; "Determination of Arsenic, Antimony, and Tin in Lead-, Tin-, and Copper-Base Alloys"; J. Research Nat. Bur. Standards 21, 95-104 (1938).

157. R. Scholder and R. Patsch; "Das Amphotere Verhalten von Metallhydroxiden. V. Uber Stannite"; Z. anorg. u. allgem. Chem. 216, 176 (1933).

158. J. Schwaibald, W. Borchers, and G. Nagel; "A Method for Determining Minute Amounts of Tin and Its Applicability to Biochemical Materials"; Biochem. Z. 306, 113-22 (1940).

159. W. W. Scott (N. H. Furman, Ed.); "Standard Methods of Chemical Analysis," 5th Edition; D. Van Nostrand Co., Inc., New York, 1939.

160. A. Seidell; "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition; D. Van Nostrand Co., Inc., New York, 1940.

161. J. A. Seiler; "Determination of Tin Activity in Fission"; Paper 269 of Book 3, "Radiochemical Studies: The Fission Products"; C. D. Coryell and N. Sugarman, Eds.; McGraw-Hill Book Co., Inc., New York, 1951 (National Nuclear Energy Series).

162. B. N. Sen; "Asbestos Partition Chromatography"; Australian J. Sci. 13, 49-50 (1950).

163. B. N. Sen; "Chromatography with Calcium Sulfate Rods in the Qualitative Cu-Cd and As-Sb-Sn Separations"; Z. anorg. u. allgem Chem. 268, 99-100 (1952); Ibid. 273, 183-85 (1953); Anal. Chim. Acta 12, 154-57 (1955).

164. R. A. Sharp; "Szilard-Chalmers Processes"; GA 617 (Dec. 16, 1958); R. A. Sharp and A. Schmitt; "Studies of the Szilard-Chalmers Processes"; GA 910 (Aug. 15, 1959).

165. A. Singh; "Chloramine-B as a Volumetric Reagent. Part I"; Research Bull. Panjab Univ. 43, 17-20 (1954).

166. G. W. Smith and S. A. Reynolds; "Anion Exchange Separation of Tin, Antimony, and Tellurium"; Anal. Chim. Acta 12, 151-53 (1955).

167. K. P. Smolyarov; "Use of Ultraviolet Rays in Analytical Chemistry. Cerimetry in Ultraviolet Rays"; Zhur. Anal. Khim. 9, 141-49 (1954); Chem. Abstr. 48, 9257 g.

168. C. H. Sorum and H. A. Wolf; "The Solubilities of the Sulfides of Arsenic, Antimony and Tin in Hydrochloric Acid"; J. Chem. Educ. 27, 614-16 (1950).

169. H. Spano and M. Kahn; "Enrichment of Tin Activity Through the Szilard-Chalmers Separation"; JACS 74, 568-69 (1952).

170. N. Strafford; "A Colorimetric Method for the Determination of Minute Amounts of Tin in Organic Matter"; Mikrochim. Acta 2, 306-13 (1937).

171. D. P. Stricos and J. T. Porter; "Determination of Silver, Cadmium, Indium, and Tin in Silver Base Alloys"; KAPL-M-DPS-1, 13 pp. (1958).

172. N. Subramanian and P. B. Janardhanan; "Controlled Potential Electro-Gravimetric Analysis"; J. Madras Univ. 25B, No. 3, 341-52 (1955).

173. N. Subramanian; "Potentiometric Titration of Tin (II) with Ceric Sulphate"; J. Sci. Ind. Research (India) 16B, 375-76 (1957).

174. S. Suzuki and C. Yoshimura; "Determination of the Precipitation Range of Metal Benzoates and the Masking Action of Some Organic Acids"; J. Chem. Soc. Japan, Pure Chem. Sect. 72, 428-31 (1951).

175. S. Suzuki; "Determination of Antimony and Tin in Their Mixtures"; J. Chem. Soc. Japan, Pure Chem. Sect. 73, 89-91, 115-17 (1952).

176. D. F. Swinehart; "Stannous Chloride-Iodine and Zinc-Ferrocyanide Titrations. Application of the Dead-Stop End Point"; Anal. Chem. 23, 380-81 (1951).

177. I. K. Taimni and R. P. Agarwal; "The Application of Thiosalts in Analysis. II. Estimations Based on Decomposition of Thiosalts. Part B. Estimation of Molybdenum and Tin"; Anal. Chim. Acta 9, 203-07 (1953); Ibid. 9, 116-20 (1953); Ibid. 9, 121-28 (1953).

178. Fritz Ephraim (P. C. L. Thorne and E. R. Roberts, Eds.); "Inorganic Chemistry," 5th Edition; Interscience Publishers, Inc., New York, 1949.

179. R. S. Tobias; "Studies on the Hydrolysis of Metal Ions. 21. The Hydrolysis of Tin (II) Ion, Sn^{+2}"; Acta Chem. Scand. 12, 198-223 (1958).

180. V. G. Tronev and A. L. Khrenova; "Decomposition of Cassiterite in Alkaline Solutions"; Compt. rend. acad. sci. U.R.S.S. 54, 611-13 (1946).

181. V. A. Tsimmergakl and R. S. Khaimovich; "Stepwise Titration of an Amalgam as a Method of Analyzing Metals with Low Melting Points"; Zavodskaya Lab. 14, 1289-1300 (1948).

182. C. E. Vanderzee and D. E. Rhodes; "Thermodynamic Data on the Stannous Chloride Complexes from Electromotive Force Measurements"; JACS 74, 3552-55 (1952).

183. C. E. Vanderzee; "The Stability Constants of the Stannous Bromide Complexes from 0° to 45° from Electromotive Force Measurements"; JACS 74, 4806-08 (1952).

184. W. Van Tongeren; "Determination of Tin"; Chem. Weekblad 37, 654-61 (1940).

185. J. V. Villadsen and K. C. Poulsen; "A New Volumetric Method for Determination of Tin Beside Antimony"; Acta Chem. Scand. 11, 1671-76 (1957).

186. J. Vulterin and J. Zyka; "Titration of Tin (II) Salts with Hydrogen Peroxide"; Chem. listy 50, 311-12 (1956); Chem. Abstr. 50, 9221 c.

187. F. J. Welcher; "Organic Analytical Reagents"; D. Van Nostrand Co., Inc., New York, 1948.

188. G. Wilkinson and W. E. Grummitt; "Chemical Separations of Fission Products"; Nucleonics 9, No. 3, 52-62 (1951).

189. H. H. Willard and G. M. Smith; "Tetraphenylarsonium Chloride as an Analytical Reagent"; Ind. Eng. Chem., Anal. Ed. 11, 269-74 (1939).

190. H. H. Willard and H. Diehl; "Advanced Quantitative Analysis"; D. Van Nostrand Co., Inc., New York, 1943.

191. H. H. Willard and L. R. Perkins; "Tetraphenylphosphonium and Tetraphenylstibonium Chlorides as Analytical Reagents"; Anal. Chem. 25, 1634-37 (1953).

192. P. F. Wyatt; "Diethylammonium Diethyldithiocarbamate for the Separation and Determination of Small Amounts of Metals. II. The Isolation and Determination of Arsenic, Antimony, and Tin in Organic Compounds"; Analyst 80, 368-79 (1955).

193. H. H. Amaguchi, N. Ikeda, and K. Osawa; "A New Compound of Tin (IV) with 8-Quinolinol and Its Use in Gravimetric Analysis"; Bull. Chem. Soc. Japan 32, 656-57 (1959).

194. H. M. Irving and F. J. C. Rossotti; "The Solvent Extraction of Group IIIB Metal Halides"; Analyst 77, 801-12 (1952).

195. R. G. Monk, et al.; "Radiochemical Methods"; AERE Report NR/C-17/59 (August 1959).

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