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The Radiochemistry of Indium

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The Radiochemistry of Indium

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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

CONTENTS

INTRODUCTION

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

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 The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of indium which might be included in a revised version of the monograph.

The Radiochemistry of Indium

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May 1960

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

Pp. 576-577 in Vol. I of "Analytical Chemistry", F. P. Treadwell, tr. and rev. by William T. Hall, John Wiley and Sons, Inc., New York, ninth edition, 1937.

Chapter 17, pp. 734-768 in "Inorganic Chemistry", T. Moeller, John Wiley and Sons, Inc., New York, 1952.

Page 211 in "Solvent Extraction in Analytical Chemistry", G. H. Morrison and H. Freiser, John Wiley and Sons, Inc., New York, 1957.

Pp. 387-405 in Vol. 5 of "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", J. W. Mellor, Longmans, Green, and Co., London, 1924.

"Indium", M. T. Ludwick, Indium Corporation of America, New York, 1950.

Pp. 481-485 in "Applied Inorganic Analysis", W. F. Hillebrand and G. E. F. Lundell, John Wiley and Sons, Inc., New York, second edition, 1953.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF INDIUM

"Radiochemical Separations of Indium", D. N. Sunderman, I. B. Ackermann, and W. W. Meinke, Analytical Chemistry 31, 40, January 1959.

"The Development and Evaluation of Radiochemical Separation Procedures for Barium, Calcium, Strontium, Silver, and Indium", Duane N. Sunderman, AECU-3159, February 1956.

III. TABLE OF ISOTOPES OF INDIUM

Isotope	Half Life	Primary Radiations		Method of Preparation
		Type of Decay	Gamma Rays	
In^{107}	30 min	β^+ ~ 2 Mev	0.22 Mev	Cd^{106} (d, n)
In^{108m}	55 min	IT β^+	0.246 0.330 0.637 0.88 1.05	Ag^{107} (α, 3n)
In^{108}	40 min	β^+ 3.5	0.637	Ag^{107} (α, 3n), daughter of In^{108m}
In^{109m}	1.3 min	IT (100%)	0.658	Daughter of Sn^{109}
In^{109}	4.2 hrs.	EC (94%) β^+ 0.80 (6%)	0.058 0.205 0.227 0.285 0.325 0.347 0.427 0.632	Ag^{107} (α, 2n), daughter of In^{109m}
In^{110m}	4.9 hrs.	EC (99+ %) IT 0.119 (0.6%)	0.119 0.661 0.885 0.935	Ag^{107} (α, n)
In^{110}	66 min.	EC β^+ 2.25	0.656	Ag^{107} (α, n), Cd^{110} (p, n)
In^{111}	2.81 days	EC	0.172 0.247	Cd^{111} (p, n)
In^{112m}	20.7 min.	IT 0.155 (100%)	0.155	Ag^{109} (α, n), In^{113} (n, 2n)
In^{112}	15 min.	β^- 0.656 (44%) β^+ 1.52 (24%) EC (32%)	none	Daughter of In^{112m}
In^{113m}	1.74 hrs.	IT 0.392 (100%)	0.392	Daughter of Sn^{113}
In^{113}	Stable (4.33%)			

III. TABLE (CONTINUED)

		Primary Radiations		
Isotope	Half Life	Type of Decay	Gamma Rays	Method of Preparation
In^{114m}	50.0 days	IT 0.192 (96.5%) EC (3.5%)	0.192 Mev 0.556 0.723	In^{113} + neutrons
In^{114}	72 sec.	β^- 1.984 (98%) 0.68 (0.1%) β^+ 0.4 (4×10^{-3}%) EC (1.9%)	1.30 (0.09%)	In^{113} + neutrons
In^{115m}	4.5 hrs.	IT 0.335 (95%) β^- 0.83 (5%)	0.335	Fission product, daughter of Cd^{115}
In^{115}	6×10^{14} yrs. (95.67%)	β^- 0.63	none	Exists in nature
In^{116m}	54 min.	β^- 1.00 (51%) 0.87 (28%) 0.60 (21%)	0.137 (3%) 0.406 (25%) 1.085 (54%) 1.274 (75%) 1.487 (21%) 2.090 (25%)	In^{115} + neutrons
In^{116}	13 sec.	β^- 3.29	none	In^{115} + neutrons
In^{117m}	1.9 hrs.	β^- 1.77 (55%) 1.62 (23%) IT 0.311 (22%)	0.161 0.311	Fission product, daughter of Cd^{117}
In^{117}	1.1 hrs.	β^- 0.74	0.161 0.565	Fission products, daughter of In^{117m}
In^{118}	4.5 min.	β^- 1.5		Sn^{118} (n,p)
In^{118}	5.5 sec.	β^- 4.4		Daughter of Cd^{118}
In^{119}	17.5 min.	β^- 2.6	0.4	Daughter of Cd^{119}
In^{120}	~ 55 sec.	(β^-)	~1	Sn^{120} (n,p)

For more complete information on the radiations of the isotopes of indium and for references to the original literature, see "Table of Isotopes", D. Strominger, J. M. Hollander, and G. T. Seaborg, Reviews of Modern Physics 30, No. 2, Part II, April 1958.

IV. REVIEW OF THOSE FEATURES OF INDIUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. Metallic Indium

Indium is a relatively rare metal (1 x 10^{-5}% of the earth's crust) and is never found in concentrated deposits. It was discovered in zinc ores and has also been found associated with tungsten. One of the reasons for interest in indium chemistry is its high capture cross-section for thermal neutrons which makes its presence in reactor materials undesirable.

The physical properties of indium are intermediate between those of gallium and thallium. Indium has a low melting point of 156 C, a boiling point of 1450 C, and a density of 7.30 g/cc. It is a very soft and ductile metal. In appearance it is white and lustrous, resembling platinum.

Indium is closely related in its chemistry to aluminum, gallium, and thallium. Metallic indium may be prepared by electrodeposition or by thermal reduction of the oxide with hydrogen or carbon. The metal is slowly oxidized in contact with air, and it is not attacked by water. Metallic indium dissolves in acids with liberation of hydrogen and formation of trivalent indium ions. The oxidation potential in acidic solution for the In(o) - In(III) couple is 0.34 volts.

2. Soluble Salts of Indium

The trivalent ion of indium is the only ion stable in aqueous solutions. The +1 and +2 states exist as the solid halides. The soluble salts of indium include the chloride, nitrate, sulfate, bromide, iodide, and perchlorate.

3. Insoluble Salts of Indium and Precipitation and Coprecipitation Characteristics of Indium

The common insoluble salts of indium are listed in Table 1. The general references listed in Parts I and II describe the insoluble compounds of indium and their use in analyses. Quantitative methods for the separation and determination of indium generally involve precipitation of either the hydrous oxide or the sulfide. Many radiochemical separations of indium have utilized modifications of both the hydrous oxide and sulfide precipitations[1,2].

TABLE 1. INSOLUBLE COMPOUNDS OF INDIUM

Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
OH^-	$In(OH)_3$	insoluble $K_{sp} \approx 10^{-33}$	soluble in acids soluble in excess KOH or NaOH
H_2S in 6N $HC_2H_3O_2$	In_2S_3	insoluble	soluble in mineral acids slightly soluble in Na_2S
$CO_3^{=}$	$In_2(CO_3)_3$	insoluble	soluble in excess, cold $(NH_4)_2CO_3$ solution
$K_4[Fe(CN)_6]$	$In_4[Fe(CN)_6]_3$	slightly soluble	soluble in acids
8-hydroxyquinoline	$In(oxinate)_3$	insoluble $K_{sp} = 10^{-36.7}$	soluble in chloroform
$C_2O_4^{=}$ in NH_4OH	$In_2(C_2O_4)_3$	slightly soluble	soluble in acids
KCN	$In(CN)_3$	insoluble (decomposes in time)	soluble in excess KCN with dilution
$NaC_2H_3O_2$, boil	$InOH(C_2H_3O_2)_2$	slightly soluble	soluble in acids
PO_4^{-3} in $HC_2H_3O_2$	$InPO_4$	insoluble	soluble in acids
IO_3^{-3}	$InIO_3$	slightly soluble (0.067 g/100 ml)	soluble in dil. H_2SO_4 or HNO_3

Sulfide. A critical evaluation of the radiochemical separation of indium by the sulfide precipitation has been made[3]. In Table 2 are listed the yields for indium and for contamination by 15 typical tracer activities as determined in this study. To obtain these results, 5 ml of solution containing 10 mg of indium and 10 mg of a carrier and tracer for the contaminating ion was adjusted to a pH of 1 and buffered at that pH with a sulfate-bisulfate buffer. The solution was heated to 90 to 95 C, and hydrogen sulfide was passed through for 1 minute. The indium sulfide precipitate was digested for 5 minutes, centrifuged, transferred to a planchet, dried, and radioassayed.

The indium yield and cobalt contamination were also determined at pH 2 and 3. At pH 2 the indium yield was 98.8 ± 1.8 per cent, and the cobalt contamination was 4.1 per cent. At pH 3 the yield and contamination was 98.1 ± 1.1 and 6.2 per cent, respectively. The precipitation at pH 1 was chosen for contamination studies because the precipitate formed at this pH showed better decontamination from cobalt. The precipitate which forms at pH 1 is red-orange and much more dense and crystalline than the yellow-orange variety formed at pH 2 and 3.

The contamination of the indium sulfide precipitate is very high for most of the activities studied, and thus the sulfide precipitation has very limited applicability for radiochemical separations of indium. It is, however, a high yield method (particularly at pH 2 or 3) for reducing the indium to a form suitable for counting and yield determinations.

Salaria has utilized an indium sulfide precipitation by a sodium sulfide reagent to separate indium from alkaline earth metals[4]. He treated a solution of milligram quantities of indium, barium, strontium, calcium, and magnesium with NH_4OH until a turbidity appeared. He then added 40 to 50 ml of 2N Na_2S reagent, enough 6N acetic acid to give an acidity of about 3N, and 10-15 g of ammonium acetate to precipitate the indium as In_2S_3, leaving the alkaline earths in solution.

Hydroxide. The precipitation of indium hydroxide has been employed

TABLE 2. CONTAMINATION OF INDIUM SEPARATED BY SULFIDE PRECIPITATION[3]

Tracer	Per Cent Carried[(a)]
Ag^{110}	100
Ce^{144}, Pr^{144}	20 - 70
Co^{60}	1.7
Cr^{51}	1.0
Cs^{134}	2.0
In^{114}	91.8 ± 2.5[(b)]
I^{131}	4.3
Ir^{192}	4.9
Ru^{106}, Rh^{106}	96
Sb^{124}	96
Se^{76}	80
Sn^{113} - In^{113m}	97
Sr^{90}, Y^{90}	100
Ta^{182}	1.6
Zr^{95}, Nb^{95}	8.7

(a) Average of duplicate runs except for indium.

(b) Average of quadruplicate runs. Errors are "standard deviations".

in many radiochemical separations of indium; however, it has been shown that a precipitate of indium hydroxide carries down traces of metals normally soluble in ammoniacal solution[5]. An hydroxide precipitation with subsequent ignition to the oxide is frequently useful, however, for a final separation of the indium for counting and yield determinations. Hudgens and Nelson[6] employed an hydroxide precipitation for this purpose.

Indium hydroxide is usually precipitated by adding an excess of NH_4OH and heating to coagulate the precipitate[1,5]. The precipitation is quantitative, $In(OH)_3$ having a solubility product of the order of 10^{-33}.[7]

Oxinate. 8-hydroxyquinoline (oxine) quantitatively precipitates indium from neutral or slightly basic solution as In(oxinate)$_3$. LaCroix[8] has discussed the oxinates of aluminum, gallium, and indium. He reports that In(oxinate)$_3$ begins to precipitate at pH 2.65 and precipitation is complete at pH 7.5. He gives a value of $10^{-36.7}$ for the solubility product of indium oxinate.

The precipitation of the 8-hydroxyquinoline derivative of indium has been utilized in radiochemical procedures to obtain the indium in a final form suitable for weighing and counting[9,10]. Smales, Smit, and Irving[9] precipitated the oxinate of indium by adding 2 ml of a 5 per cent solution of 8-hydroxyquinoline in ethanol to a 15 ml HCl solution of indium, heating to 50-60 C, and slowly adding 5 ml of a sodium acetate-acetic acid buffer. Cowan[10] performed the precipitation by adding a 5 per cent solution of hydroxyquinoline in 2M acetic acid to a previously buffered indium solution.

Basic Acetate. Indium basic acetate, $InOH(C_2H_3O_2)_2$, is precipitated by boiling an aqueous solution of indium with excess sodium acetate. Wilkinson and Grummitt applied this precipitation to a separation of indium from cadmium[2].

Magnesium Hydroxide as a Carrier for Indium. Indium, in trace amounts, has been separated from cadmium by precipitation of the indium as the hydroxide with a magnesium carrier[11]. The trace amounts of indium were produced by a cyclotron irradiation of cadmium. The cadmium target was dissolved in nitric acid, and 100 mg of magnesium carrier were added. Excess NH_4OH was added to precipitate $Mg(OH)_2$, and the mixture was heated to digest the precipitate. Over 90 per cent of the indium and only traces of cadmium were carried with the precipitate. The indium was separated from the magnesium by redissolving the precipitate and electroplating the indium, leaving the magnesium in solution.

Ferric Hydroxide as a Carrier for Indium. Ferric hydroxide has been used frequently as a scavenger in radiochemical procedures. A study has been made of the scavenging properties of $Fe(OH)_3$ for indium and 14

TABLE 3. SCAVENGING BY PRECIPITATION OF HYDROUS OXIDES[12]

	Percentage Remaining in Solution*			
	$Fe(OH)_3$ pptn.		$La(OH)_3$ pptn.	
Element	Carrier Present	Carrier **Absent**	Carrier Present	Carrier **Absent**
Antimony	18.	8.1	0.9	0.8
Cerium	0.045	0.16	0.11	2.4
Cesium	96.	92.	97.8	97.7
Chromium	0.30	0.26	0.46	0.23
Cobalt	83.	23.	89.	79.
Indium	0.12	0.21	0.14	0.20
Iodine	95.8	92.7	86.9	75.
Iridium	15.	3.9	4.4	1.0
Ruthenium	30.	6.5	2.7	1.4
Selenium	71.	36.	9.	11.
Silver	91.3	91.4	97.3	96.5
Strontium	96.3	11.	85.	85.
Tantalum	0.03	0.08	0.3	0.1
Tin	1.7	0.3	0.12	0.19
Zirconium-Niobium	0.02	0.14	0.04	4.9

* Results are the average of duplicate determinations.

other elements, and the data obtained in this study are given in Table 3[12]. Ten milligrams of iron (III) and either 10 mg or carrier-free quantities of the species investigated were used in the study. The precipitation was performed by adding 1 ml of concentrated NH_4OH to 9 ml of the solution of iron and the other species. The precipitate was digested at room temperature for 5 minutes.

Ferric hydroxide forms a gelatinous precipitate in slightly acid solution (about pH 3), and the ions removed from solution to the largest degree by the $Fe(OH)_3$ scavenger are those which form hydrous oxides in slightly acid or neutral solution. Ferric hydroxide is a very effective scavenger for indium, removing greater than 99 per cent of the indium from solution, both with and without indium carrier present. Cerium, tantalum, tin, chromium, and zirconium-niobium are also carried to an extent of greater than 99 per cent.

Ferric hydroxide has been employed as a carrier in a separation of trace quantities of indium from a cadmium target[13]. The indium is recovered by dissolution of the ferric hydroxide in 8N hydrochloric acid and extraction of the iron into isopropyl ether, leaving the indium in the aqueous phase.

Lanthanum Hydroxide as a Carrier for Indium. Lanthanum hydroxide is also an effective carrier for indium, and a study of the scavenging properties of $La(OH)_3$ has also been made[12]. The precipitation of the $La(OH)_3$ was performed under the same conditions as for the $Fe(OH)_3$, except that 10 mg of lanthanum carrier were substituted for the iron. The results of this study are also given in Table 3. The $La(OH)_3$ precipitate forms in the neutral range, at a pH of about 7 to 8, and is less voluminous and slower to coagulate than the ferric hydroxide.

Greater than 99 per cent of the indium is removed from solution with the $La(OH)_3$, both with and without indium carrier. The other cations carried to the same extent are antimony, cerium, chromium, tantalum, tin, and zirconium-niobium.

4. Complex Ions of Indium

Indium forms a number of complex ions in solution, particularly with the halogens; however, relatively little information is available in the literature on this subject. The complexes of chief interest to radiochemists are the chloride and bromide complexes which find utility in anion exchange and solvent extraction.

The absorption of indium on anion exchange resins from hydrochloric acid solutions has been explained by the presence of $InCl_6^{-3}$ and $InCl_4^-$ ions[14,15]. The rapid decrease in absorbability of indium from solutions less than two molar in HCl indicates a substantial reduction in stability of these complexes in dilute acid. Schufle, Stubbs, and Witman have studied chloride complexes of indium, and they report that the $InCl_4^-$ ion is unstable in aqueous solutions except with high chloride concentrations[16]. They determine dissociation constants ranging from 6 to 13 for the $InCl_4^-$ ion in 8 to 11.6 N HCl. In more dilute HCl solutions they report a positive complex ion, $InCl_2^+$, with a dissociation constant of 1.5×10^{-2} to 3.3×10^{-2} in 1 to 4 N HCl.

Rossotti has studied the nature of the indium bromide species extracted into organic solvents[17]. He reports an $InBr_4^-$ complex, which at high acidities is extracted into organic solvents as $HInBr_4$. At low acidities he states that the predominant species extracted are $InBr_3$ and $NaInBr_4$. Positive fluoride complexes of indium have also been reported[18]. These are InF^{+2} and InF_2^+.

Hepler and Hugus have studied the hydrolysis of indium halides[19]. In dilute solutions of the halides they report the existence of two complex ions, $InOH^{+2}$ and InX^{+2}, in addition to In^{+3}. (X represents a halogen.) In concentrated solutions the complex ions predominate. LaCroix has studied the neutralization of a solution of indium chloride, and he reports the formation of an $InOH^{+2}$ complex prior to precipitation of $In(OH)_3$[20]. LaCroix also reports an indium oxalate complex, $In(C_2O_4)_2^-$.

5. Chelate Complexes of Indium

Chelate complexes are employed extensively in the radiochemistry of indium. At least one of the chelates is insoluble and thus employed in precipitation reactions. Others are soluble in organic solvents. Very few of the stability constants are available in the literature for these complexes. Martell and Calvin[21] and the more recent text by Chaberek and Martell[22] list stability constants for only two chelates of indium, those with glycolic acid and EDTA. The constants for these chelates are given in Table 4.

From the little information available on the stability of indium chelates, it is difficult to compare their stabilities with chelates of other metals. Irving and Williams report that the order of decreasing

TABLE 4. STABILITY CONSTANTS FOR CHELATES OF INDIUM

Chelating Agent	Indium Chelate Formed	Log K	Ionic Strength	Reference
glycolic acid	InA	2.93	2.0	a
	InA_2	2.59	2.0	a
	InA_3	1.78	2.0	a
	InA_4	0.65	2.0	a
ethylene-diamine-tetraacetic acid (EDTA)	InA	24.95	0.1	b
	InHA	1.0	0.1	c
	InAOH	8.80	0.1	c

a. N. Sunden. Svensk Kem. TidsKr. 65, 12 (1953).

b. G. Schwarzenbach, R. Gut, and G. Arderegg, Helv. Chim. Acta 37, 937 (1954).

c. K. Saito and H. Terrey, J. Chem. Soc. 1956, 4701.

stability, Tl > Fe ≥ Ga > In ≥ Al > Cr > Sc > rare earths, holds roughly for a few chelate complexes. They emphasize, however, that this is merely a basis for discussion.

The strong yellow color of the 8-hydroxyquinoline complex of indium in chloroform solution has long served as a basis for a colorimetric method of analysis for indium[24,25]. The solvent extraction of indium hydroxyquinolate is discussed more completely in a later section. Indium hydroxyquinolate precipitates from aqueous solutions at pH 7.5[8], and this precipitation has been employed in radiochemical procedures to obtain the indium in a form suitable for radioassay[9,10].

The dithizone complex of indium has also been employed in colorimetric methods of analysis[25,26]. This complex also finds utility in solvent extraction procedures[27]. Other chelate complexes of indium employed in solvent extraction procedures are those with TTA[3], acetylacetone[28], and diethyldithiocarbamine[29,30,31]. The acetylacetone extraction procedure is unique in that the chelating agent also serves as the organic solvent.

The chelate complex formed between indium and EDTA forms the basis of a complexometric titration procedure for indium analysis[32]. The indium is titrated with EDTA at pH 2.3 to 2.5 using 1-(2-pyridylazo)-2-naphthol as an indicator. This complex of indium is very stable.

6. Extraction of the Thenoyl Trifluoroacetone (TTA) Complex of Indium Into Organic Solvents

The extraction of the thenoyl trifluoroacetone complex of indium into benzene has been studied[3]. The investigations reported were for both carrier and carrier-free quantities of indium and for concentrations of 0.10, 0.25, and 0.50 M thenoyltrifluoroacetone in benzene. Curves were obtained for the percentage extraction of indium as a function of pH, and there was little difference between the curves for carrier and carrier-free extractions. The extraction of indium is negligible below pH 1.3 with 0.50 M TTA in benzene, below pH 1.5 with 0.25 M TTA in benzene, and below pH 1.7 with 0.10 M TTA in benzene. The percentage extraction increases sharply above these pH values until it reaches approximately 95 per cent at pH 2.2 with 0.50 M TTA, pH 2.5 with 0.25 M TTA, and pH 3.1 with 0.10 M TTA.

Contamination studies were made for indium extraction into 0.5 M TTA in benzene at a pH of 2.1[3]. The extractions were made from 20 ml of acid phthalate buffer of pH 2.1 containing 10 mg of indium carrier and tracer (carrier-free) for the contaminating element. The volume of each phase was 20 ml, and the extraction time was 5 minutes. The results are given in Table 5. The separation is clean for all of the elements tested except for iodine, tin, tantalum, and zirconium.

7. Extraction of Indium Into Organic Solvents

Solvent extraction has been employed to some extent in the radiochemical analysis for indium. The methods reported for solvent extraction of indium involve the extraction of chelate complexes or inorganic salts of indium into organic solvents. The extraction of indium bromide into various ethers has been studied by several investigators and is evaluated below. Two chelate complexes of indium which have found application in solvent extraction procedures are those with acetylacetone and 8-hydroxyquinoline. These and other procedures are discussed below. An excellent review of solvent extraction methods has been published by Morrison and Freiser[33].

TABLE 5. CONTAMINATION OF INDIUM SEPARATED BY TTA EXTRACTION INTO BENZENE[3]

Tracer	Per Cent Extracted[(a)]
Ag^{110}	1.0
Ce^{144}, Pr^{144}	0.3
Co^{60}	0.5
Cr^{51}	0.6
Cs^{134}	0.05
In^{114} (plus 10 mg of carrier)	89.4
I^{131}	7
Ir^{192}	0.35
Ru^{106}, Rh^{106}	0.7
Sb^{124}	0.1
Se^{76}	0.1
Sn^{113} - In^{113m}	8
Sr^{90} - Y^{90}	0.5
Ta^{182}	3.1
Zr^{95}, Nb^{95}	49.5

(a) Average of duplicate runs.

Diethyl Ether - The extraction of indium bromide into diethyl ether has been studied by several investigators[3,12,33,34,35]. These authors report 90 to 95 per cent extraction of indium bromide from a solution 4 to 6 molar in HBr. A critical evaluation of this separation method has been made, and the efficiency of the separation of indium from several other elements has been studied[3]. Table 6 gives the results of this study.

TABLE 6. CONTAMINATION OF INDIUM SEPARATED BY BROMIDE EXTRACTION INTO DIETHYL ETHER[3]

Tracer	Per Cent Extracted(a)
Ag^{110}	0.055
Ce^{144}, Pr^{144}	0.01
Co^{60}	0.009
Cr^{51}	0.012
Cs^{134}	0.015
In^{114} (plus 10 mg of carrier)	93.0 ± 2.0(b)
I^{131}	6.7, 6.8*
Ir^{192}	0.017
Ru^{106}, Rh^{106}	0.015
Sb^{124}	2.2, 0.25*
Se^{76}	23, 7*
Sn^{113} - In^{113m}	48, 40*
Sr^{90} - Y^{90}	0.006
Ta^{182}	0.08
Zr^{95}, Nb^{95}	0.018

(a) Average of duplicate runs except for indium.

(b) Average of quadruplicate runs. Errors are "standard deviations".

* Values for procedures with two 4.5 M hydrobromic acid washes.

The extraction procedure used to obtain the results in Table 6 was as follows: ten ml of 4.5 M hydrobromic acid solution containing 10 mg of indium and a tracer (no carrier) for the contaminating element was starred rapidly for 2 minutes with 30 ml of diethyl ether in an extraction tube. The aqueous phase was drained off, allowing one drop of the organic phase to pass through the stopcock. The ether phase was washed by stirring for 2 minutes with 10 ml of 4.5 M hydrobromic acid. The aqueous phase was again drawn off. Two wash steps were used to obtain the percentages stirred in Table 6. The indium was back-extracted by stirring for 2 minutes with 10 ml of 6 M hydrochloric acid. Yields were determined by radioassaying an aliquot of the aqueous phase in a scintillation well counter.

The high distribution coefficient obtained with diethyl ether under the conditions described above gives an indium yield of over 90 per cent, with phase equilibrium being reached in 1 to 2 minutes of rapid stirring. None of the elements tested were appreciably extracted with indium except for iodine, antimony, selenium, and tin. A second wash step was useful to reduce the contamination by antimony and selenium.

Irving and Rosotti[36] have investigated the extraction of other indium halides into diethyl ether. They found that greater than 99 per cent of the indium iodide is extracted from 0.5 to 2.5 N hydriodic acid solutions containing from 0.6 mg/l to 3 g/l of InI_3. They report that 1 to 7 N sulphuric acid containing 1.5 M potassium iodide can be used in place of the hydriodic acid in the extraction. They also found that indium chloride was not significantly extracted into diethyl ether from hydrochloric acid solutions. As described above, indium has been back-extracted from diethyl ether into 6 M hydrochloric acid solutions. The distribution factor in this extraction was less than 0.005, allowing complete recovery of the indium from the diethyl ether[3,12]. Bock[37] reports that indium chloride can be extracted into diethyl ether from hydrochloric acid solutions containing NH_4SCN. He obtained 75 per cent extraction from a solution 0.5 molar in HCl, 2.0 to 3.0 molar in NH_4SCN, and 0.1 molar in $InCl_3$.

Isopropyl Ether - Isopropyl ether has also been used for the extraction of indium bromide[6,38]. Hudgens and Nelson[6] recommend the use of specially purified isopropyl ether in the radiochemical separation of indium by solvent extraction. They separated indium from zinc, iron, tellurium, and aluminum by extraction of 10 mg of indium from 20 ml of 4.5 M hydrobromic acid solution into 20 ml of isopropyl ether. Two extractions yielded 98 per cent of the indium. The indium was removed from the organic phase with 5 M hydrochloric acid. Kosta and Hoste[38] separated indium from zinc by extracting the indium from 6 M hydrobromic acid into isopropyl ether. With $InBr_3$ concentrations of from 1.4×10^{-4} to 10^{-1} moles per liter, greater than 97 per cent of the indium was extracted. The extraction of the zinc was negligible.

The use of commercially available isopropyl ether has been attempted in the extraction of indium bromide, but it was impossible to obtain distribution coefficients greater than 5 with 4.5 M hydrobromic acid and 10 mg of indium carrier[3]. With one wash of the organic phase the indium yield was reduced to about 60 per cent.

Cyclohexanone - Cyclohexanone has been employed as the organic phase in a solvent extraction separation of 10 to 15 mg of indium from 10 mg of gallium[39]. The indium as indium iodide was quantitatively extracted into the cyclohexanone leaving greater than 99 per cent of the gallium in the aqueous phase. The aqueous phase was 0.25 molar in KI and 0.1 normal in sulfuric acid. The volume of each phase was 50 ml.

8-Hydroxyquinoline in Chloroform - Indium can be quantitatively extracted into a solution of 8-hydroxyquinoline in chloroform[8,40,41]. The solubility in chloroform of the chelate formed between indium and 8-hydroxyquinoline is 0.24 molar at 18 C[8]. Knox and Spinks contacted a 2 ml, acetate buffered solution of 10 mg of indium with 0.5 ml of 1 M 8-hydroxyquinoline in chloroform and obtained practically complete extraction of the indium[40]. Milner extracted indium into 0.5 per cent solution of 8-hydroxyquinoline in chloroform from aqueous solutions in the pH range of 3.5 to 4.5[41]. LaCroix employed a 0.1 M solution of 8-hydroxyquinoline in chloroform and an aqueous solution at a pH of 3.4 to extract indium[8].

Acetylacetone - The chelate complex formed between indium and acetylacetone can be extracted into acetylacetone from an indium solution in the pH range of 3 to 6[28]. Greater than 99 per cent of the indium is extracted, but a number of other metals also extract under these conditions.

Diethyl Dithiocarbamine in Chloroform or Carbon Tetrachloride - The diethyldithiocarbamine (DDTC) complex with indium has been extracted into chloroform and CCl_4[29,30,31]. Claassen, Bastings, and Visser[29] separated indium from aluminum by extracting the indium into chloroform from an aqueous solution containing sodium acetate and sodium diethyldithiocarbamate at a pH of approximately 4. Bode[30,31] reports quantitative extraction of the DDTC complex of indium into CCl_4 from aqueous solutions of pH 4 to 10 and from solutions containing KCN at pH 8 to 11. Morrison and Freiser[33] recommend a CCl_4 extraction of indium from a solution at pH 9 containing NaCN and sodium diethyldithiocarbamate. The extraction is complete in 1 minute. Manganese, antimony, tellurium, and small quantities of iron also extract.

Dithizone in Chloroform - Luke and Campbell[27] report an extraction of indium into a 0.01% solution of dithizone (diphenylthiocarbazone) in chloroform. The aqueous phase was an alkaline solution containing NaCN.

Erio OS in Butanol - Flaschka[42] has studied the extraction into butanol of the Erio OS (nonsulfonated Eriochrome Black T) complex of indium. He investigated the effects of several hold-back ions or masking agents and found that at pH 10 indium could be extracted into butanol and Erio OS from solutions containing potassium cyanide, oxalate ions, or ammonium ions. The indium was not extractable from solutions containing Complexon III or tartrate ions.

Butylphosphoric Acid in Butyl Ether - Greater than 95 per cent of the indium can be extracted from 1 M HNO_3 containing 3 per cent H_2O_2 into a 0.06 M butyl ether solution of dibutylphosphoric acid (containing some monobutylphosphoric acid)[43]. The mole ratio of dibutylphosphoric acid (DBPA) to monobutylphosphoric acid was 4.5:1. The same results were obtained with a 0.6 M solution. Five minutes of mixing were required with equal volumes of the organic and aqueous phases.

With an aqueous phase consisting of 1 M H_2SO_4, 2.5 M $(NH_4)_2SO_4$, 0.004 M oxalic acid, and 6 per cent H_2O_2 and an equal volume of 0.06 M DBPA in butyl ether, 85 per cent of the indium was extracted in 15 minutes. Greater than 95 per cent was extracted in 5 minutes from this same aqueous solution into 0.6 M DBPA.

8. Ion Exchange Behaviour of Indium

The majority of the ion exchange separations of indium found in the literature are anion exchange procedures. Hicks and coworkers[44] have described qualitatively the separation of indium from other elements by anion exchange, and Krause, Nelson and Smith[14] have reported some quantitative work.

Indium (III) shows appreciable adsorption on an anion exchange column with a hydrochloric acid concentration greater than 0.5 molar, but it is never very strongly adsorbed[14]. Krause, et al., report that the adsorbability of indium decreases very rapidly below 2 M HCl, and they state that this is probably due to a decrease in the fraction of the indium in the form of an adsorbable complex ($InCl_6^{-3}$ or $InCl_4^{-}$)[14].

Jentzsch, et al., have employed ion exchange in a quantitative analysis scheme to separate indium from iron, aluminum, manganese, and arsenic[45]. They added the indium to the column in a 5 M HCl solution and eluted the indium with 0.1 M HCl. Jentzsch and Frotscher report elution of indium from a Wofatit L150 anion resin with HCl, 1 molar or weaker[15].

An anion exchange separation of indium, aluminum, gallium, and thallium has been reported by Krause and coworkers[14]. They added a 7 M HCl solution of these elements to a 20 cm x 0.4 cm^2 column of Dowex-1 (200-230 mesh). Using a flow rate of 0.3 to 0.8 cm/min and a 7 M HCl eluant, they eluted aluminum in the first 20 ml and indium in the next 50 to 60 ml. They next eluted gallium with 20 ml of 1 M HCl and thallium with 800 ml of 4 M $HClO_4$.

The contamination of indium separated by anion exchange from 15 other species has been investigated[3,12]. The resin used was Dowex 2 with 8 per cent cross-linking, 200 to 400 mesh, in the chloride form. An 8.5 cm x 0.4 cm column was employed with a flow rate of 1 ml in 3 minutes. The sample in a small volume of 6 M HCl was added to the top of the resin column and allowed to seep into the resin bed. The elution was performed with 6 M HCl, and greater than 95 per cent of the indium was in the 6 through 20 ml portion. The results of the contamination studies are given in Table 7. Carrier-free quantities of indium and the contaminating isotopes were used.

The results given in Table 7 were found to be reproducible when care was taken in adding the sample to the top of the column[3]. The sample volume should be kept to a minimum and added directly to the resin bed in such a manner that the reservoir above the resin is not permitted to become contaminated. The eluant should be allowed to fall dropwise onto the top of the resin, with no more than 1 ml in the reservoir above the resin. This prevents contamination of a large volume of the eluant and subsequent spreading of the elution band.

The contaminants fall into three groups. In the first group are the elements so slightly adsorbed as to be eluted almost completely before the indium begins to appear (Ce, Cs, Cr, Se, Sr, Ir, and Ru). All but iridium and ruthenium contaminate to less than one per cent. The second group includes the elements whose elution curves overlap to a great extent that of indium (Co, Ag, and Zr-Nb). The third group are those which had not yet appeared to any significant degree at the 20 ml point in the elution (Sb, I, Ta, and Sn). The highest contamination in this group is caused by tantalum, which is eluted continuously but at a low rate.

Anion exchange with 6 M HCl is considerably better for separation of indium from tin and selenium and somewhat better for iodine than solvent extraction and sulfide precipitation (See Tables 2, 5, and 6). It cannot, however, compete with solvent extraction for separation of indium from most elements.

TABLE 7. CONTAMINATION OF INDIUM SEPARATED BY ANION EXCHANGE[3]

Tracer	Per Cent Carried[(a)]
Ag^{110}	25
Ce^{144}, Pr^{144}	0.13
Co^{60}	43
Cr^{51}	0.6
Cs^{134}	0.11
In^{114}	95.5 ± 1.2[(b)]
I^{131}	1.1
Ir^{192}	3.7
Ru^{106}, Rh^{106}	22
Sb^{124}	2.0
Se^{76}	0.3
Sn^{113} - In^{113m}	0.4
Sr^{90} - Y^{90}	0.1
Ta^{182}	6.2
Zr^{95}, Nb^{95}	31

(a) Average of duplicate runs except for indium.

(b) Average of quadruplicate runs. Errors are "standard deviations".

Faris has studied the adsorption of about 50 elements including indium on a strongly basic anion exchange resin in a hydrofluoric acid medium[46]. With a Dowex 1-X10 (200 mesh) resin in the fluoride form he found no adsorption of indium from HF solutions ranging in concentration from 1 molar to 24 molar.

Klement and Sandman report a separation of indium from other metals by cation exchange[47]. They employed a 100 cm x 0.8 cm column of Dowex 50 (20-50 mesh) in the H+ form and a flow rate of 10 ml per minute. They found that indium could be eluted with hydrochloric acid, 0.4 normal or stronger. The volume of HCl required to elute 0.2 g of indium was about 2 liters. The concentrations of HCl required to elute some of the other elements tested were: Pb and Zn, 0.5 N; Cu, 0.7 N; Fe(III), 1.0 N; and Ga, 1.3 N.

V. DISSOLUTION OF MATERIALS CONTAINING INDIUM

Many materials in which indium might be found are soluble in mineral acids. This would include most minerals, the common insoluble salts of indium, and some cyclotron targets. Cyclotron-bombarded cadmium targets have been dissolved in a few drops of hot, concentrated HNO_3[1] and also in a larger volume of 1:1 HNO_3[11]. Antimony metal cyclotron targets have been dissolved by heating with 15 drops of 27 N HF in a lustroid tube while adding concentrated HNO_3 dropwise[1]. One example of a mineral containing indium is cylindrite[48]. Cylindrite may be dissolved by heating with 5 ml of concentrated HCl and then adding 1 ml of concentrated HNO_3 and reheating.

Some minerals and rocks do not dissolve so easily and must be brought into solution by means of a fusion. Smales, Smit, and Irving have reported an alkaline peroxide fusion procedure for this purpose[9]. They mixed 3 to 4 grams of powdered sodium peroxide with 0.5 g of the mineral or rock in a silica crucible. A thin layer of sodium peroxide was spread over the top of the mixture, and the crucible was heated at 480 to 500 C for 10 to 15 minutes to fuse the mixture. The melt was then cooled and dissolved in 200 ml of water. A similar fusion procedure has been reported for the dissolution of meteorite samples[49]. A 1 g sample of the meteorite (finely ground) was fused with 8 g of sodium peroxide for 2 minutes in a nickel crucible and dissolved with caution in 50 ml of water. Adequate safety precautions, such as the use of heavy plastic shielding, should be used with these fusions, for an occasional sample may explode violently.

VI. RADIOASSAY TECHNIQUES FOR INDIUM

In the radioassay of solutions or precipitates containing radioactive isotopes of indium particular attention must be paid to the decay schemes and radiations of these isotopes. Such factors as half life, type of radiation, and energy of radiation must be considered. The nuclear characteristics of the isotopes of indium can be found in the literature[50] and are summarized in Section III.

Indium has one radioactive isotope which occurs in nature, In^{115}. The natural abundance of In^{115} is 95.67 per cent[51]. The other naturally occurring isotope of indium is stable In^{113}, and it has an abundance of 4.33 per cent[51]. Indium-115 emits only beta particles with a maximum energy of 0.63 Mev; so it can be radioassayed readily with a beta counter. The specific activity of natural-occurring In^{115} has been determined to be 10.9 disintegrations per minute per gram of indium, and from this specific activity the half life is calculated to be 6×10^{14} years[52].

In a thermal neutron activation of indium In^{114m}, In^{114}, In^{116m}, and In^{116} are produced. The In^{114} and In^{114m} are genetically related and can be treated as one isotope in radioassay procedures. Either beta or gamma assay techniques can be applied. In a gamma scintillation spectrum photopeaks are observed at 0.192, 0.556, and 0.723 Mev, but the two higher energy gamma rays are low in intensity. Indium-114 may be determined by counting the 1.984 Mev beta particles with a Geiger or proportional counter, but corrections must be applied for the electrons from the 0.192 Mev isomeric transition which is approximately 80 per cent internally converted. Hudgens and Nelson[6] report that one In^{114} disintegration yields 0.97 beta particles and 1.08 gamma rays; and since the 0.192 Mev gamma rays are highly converted, the observed beta counting rate is approximately equal to twice the beta disintegration rate.

Indium-116m emits beta particles with maximum energies of 1.00 Mev, 0.87 Mev, and 0.60 Mev; so it may be radioassayed with a Geiger or proportional counter. This isomer of In^{116} also emits several gamma rays (See Section III) which may be determined with a scintillation detector. No genetic relationship has been established between the two isomers of In^{116}, so the 13 second In^{116} isomer should not be encountered in an activated sample unless work is begun immediately after irradiation. Indium-116 emits only beta particles with a maximum energy of 3.29 Mev, so it can be radioassayed only by beta counting techniques. Both $In^{114 \& 114m}$ and In^{116m} are used as radiotracers for indium..

The fission product isotopes of indium are In^{115m} and In^{117}. Indium-115m has a half life of 4.5 hours and emits both beta particles and gamma rays. The 0.83 Mev beta particles can be determined with a Geiger or proportional counter, and the 0.335 Mev gamma rays can be determined with a scintillation counter. Indium-117 has two genetically related isomers with half lives of 1.9 hours and 1.1 hours. Both isomers emit both beta particles and gamma rays and can be determined by counting either. Indium-115m is also encountered in neutron activation of cadmium, as it is the daughter of Cd^{115}.

The other radioactive isotopes of indium are not frequently encountered, and most of them are short-lived. The pure beta emitters are In^{112}, In^{118m}, and In^{118}. The others, with the exception of In^{111} and In^{113m} emit both beta particles and gamma rays; so they may be determined either by means of a Geiger or proportional counter or a scintillation detector. Indium-111 decays by electron capture, so it is best determined by measurement of its 0.172 or 0.247 Mev gamma rays. Indium-113m decays by a 0.392 Mev isomeric transition to In^{113}, so it can be determined by radioassay of the 0.392 Mev gamma rays.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR INDIUM

PROCEDURE 1

RADIOCHEMICAL DETERMINATION OF INDIUM

1. Introduction

A radiochemical procedure for indium has been developed from the yield and contamination data presented in Tables 5 and 6 in Section IV. The procedure consists of two solvent extraction steps, a bromide extraction into diethyl ether and a thenoyl trifluoroacetone (TTA) extraction into benzene. The method is applicable to both carrier and carrier-free quantities of indium and results in yields of from 70 to 80 per cent. Decontamination factors on the order of 10^5 to 10^7 are achieved for most elements. The procedure is neat and rapid, is easily adapted to routine operation, and may be performed with materials readily available in sufficient purity to realize the full capability of the method.

2. Equipment

The extraction vessel is an open-top glass cylinder, 3 cm in diameter and 9 cm high, tapered sharply at the bottom to a 1 mm bore stopcock. The electric stirrer, continuously variable speed, is a glass rod 7 mm in diameter, flattened and twisted on the end for stirring rod.

3. Reagents

Hydrobromic acid, 4.5 M

Diethyl ether, ACS analytical reagent, absolute

Hydrochloric acid, 6 M

Buffer solution - Reagent grade potassium acid phthalate plus hydrochloric acid (0.2 M) in proper proportions to make pH 2.4

Thenoyl trifluoroacetone (TTA), 0.5 M in benzene.

4. Procedure

An outline of the procedure is given in Table 1 along with the yields and decontamination factors. A more complete description of each step is given below.

Step 1. Make the solution 4.5 molar in hydrochloric acid.

TABLE 1. RADIOCHEMICAL DETERMINATION OF INDIUM

In, Ag, Ce, Co, Cr, Cs, I, Ir, Ru, Sb, Se, Sn, Sr, Ta, Zr

1. Make solution 4.5 M HBr
2. Add triple volume diethyl ether, stir 2 minutes
3. Wash twice with 4.5 M HBr, 2 minutes
4. Re-extract with 6 M HCl, stir 2 minutes

Decontamination factors:

1-10	Sn
10-100	I, Se
10^2-10^3	Sb, Ta
10^3-10^4	Ag, Ce, Co, Cr, Cs, Ir, Ru, Sr, Zr

Bromide Extraction of Indium Yield 90-95%

5. Evaporate to ~ 1 ml
6. Add NaOH to about pH 2-3
7. Add potassium acid phthalate buffer (pH 2.4) to 20 ml
8. Add equal volume 0.5 M TTA in benzene, stir 5 minutes
9. Separate layers

Decontamination factors:

1-10	Sn
10^2-10^3	I
10^3-10^4	Zr
10^4-10^5	Se, Ta
10^5-10^6	Ag, Ce, Sb
10^6-10^7	Co, Cr, Cs, Ir, Ru, Sr

TTA Extraction of Indium Yield 70-80%

10. Count aliquot of organic layer

Step 2. Contact this solution with a triple volume of diethyl ether in the cylindrical separatory funnel with rapid stirring for a period of two minutes. Discard the aqueous phase.

Step 3. Add a volume of 4.5 M hydrobromic acid equivalent to the volume of the solution in Step 1. Stir two minutes and discard the aqueous phase. Repeat the wash.

Step 4. Add a volume of 6 M hydrochloric acid equivalent to the previous aqueous volumes. Stir two minutes.

Step 5. Draw off the aqueous volume and evaporate to about one ml.

Step 6. Add sodium hydroxide to bring the pH to between 2 and 3.

Step 7. Add potassium acid phthalate buffer of pH 2.4 to bring the volume to 20 ml.

Step 8. Add 20 ml of 0.5 M TTA in benzene and stir 5 minutes.

Step 9. Draw off the aqueous phase and discard it.

Step 10. Pipet an aliquot of the organic layer for counting.

If tin is a major interference in the sample, the procedure may be varied by substituting an anion exchange step for the thenoyl trifluoroacetone extraction. The solution from Step 5 is added directly to the resin column, and the indium is eluted with 6 M hydrochloric acid. The alternative procedure (from Step 6 on) is as follows:

Step 6a. Add the 1 ml solution to the top of an 8.5 cm x 4 mm column of resin (Dowex-2 in the chloride form) and allow to seep into the resin bed.

Step 7a. Elute with 6 M hydrochloric acid using a flow rate of 1 ml in three minutes and saving the 6 through 20 ml portion which contains the majority of the indium.

Step 8a. Count an aliquot of the eluant.

5. Discussion

The procedure described above is useful for many types of mixtures and is readily adapted to remote control operation. In some cases the decontamination factors obtained in the bromide extraction might be sufficient and the TTA extraction would be unnecessary. The TTA extraction is particularly useful for decontamination from antimony and selenium, but aids very little in separations from tin, iodine, and zirconium. When tin is a major contaminant an anion exchange step substituted for the TTA extraction will raise the decontamination factor for tin to 10^2-10^3 and will result in an indium yield of 80 to 90 per cent.

PROCEDURE 2

INDIUM

Source - R. C. Lilly in report AECD-2738, edited by
W. W. Meinke, August 1949.

Target material: Cd (separated isotopes)

Time for separation: 2-3 hours

Type of bombardment: Deuterons and protons - 60"

Equipment required: Beakers, funnels, Hirsch funnel, separatory funnels, pH meter

Yield: Approximately 90%

Degree of purification: good - at least factor of 100 from other activities present

Advantages: Good separation

Procedure:

(1) Dissolve the Cd target, weighing 10-15 mg, in a few milliliters of conc. HNO_3 in a small beaker. When all of the material has dissolved, evaporate to dryness to drive off excess HNO_3.

(2) Add 3-4 mg In and 3-4 mg Ag as the nitrate solutions and dilute to approximately 10 ml with H_2O.

(3) Add 1 N HCl dropwise until the Ag is completely precipitated as AgCl. Coagulate the precipitate by heating and filter through a small #42 Whatman filter paper in a short-stemmed glass funnel. The filtrate contains the Cd and In fractions. (The AgCl precipitate is worked up separately as described in the procedure for Ag from Cd targets, No. 47-3).

(4) Make the filtrate ammoniacal and add another 3-4 mg Ag as the nitrate solution. Acidify with HNO_3 and add a few drops of 1 N HCl to insure complete precipitation of AgCl. Coagulate the precipitate by heating, filter on #42 paper, and discard.

(5) Adjust the pH of the filtrate to 3.5 with NH_4OH and transfer to a 50 ml separatory funnel.

(6) Extract the In by shaking with three portions of 0.02 M 8-Hydroxyquinoline in CH_3Cl, drawing the organic layers off into a second separatory funnel after each pass. Discard the few drops of mixed solution which remain in the stopcock after separation of layers. (The In is contained in this organic layer.)

The Cd remains in the H_2O layer and is worked up separately as described in the procedure for Cd from Cd targets, No. 48-3.

(7) Treat the organic layers in the second funnel with an equal volume of pH 3.5 HCl solution to remove traces of Cd.

(8) Draw off the organic layer into a beaker, add dilute HCl and boil off the CH_3Cl. Add NH_4OH to precipitate In as the 8-hydroxyquinolate and filter through a #42 Whatman paper disc held in a Gooch crucible or Hirsch funnel. Suck the sample on the paper as dry as possible and then dry the disc carefully under a lamp and mount under tape.

PROCEDURE 2 (Cont'd)

Remarks:

See Scott (Std. Meth. Chem. Anal.) for complete information on the precipitation of AgCl.

See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of In with 8-hydroxyquinoline.

PROCEDURE 3

INDIUM

Source - R. C. Lilly in report AECD-2738, edited by
W. W. Meinke, August 1949.

Target material: Cd (separated isotopes)

Type of bombardment: Deuterons and protons - 60"

Yield: 50-75%

Degree of purification: good - at least factor of 10 from other activities

Time for separation: 10 min.

Equipment required: Small beakers, porcelain filter crucible, filter flasks, Gooch crucible and holders, glass funnel and filter ring, test tube.

Advantages: speed

Procedure:

(1) Dissolve the Cd target material, weighing a few milligrams, in a few drops of hot conc. HNO_3 in a 20 ml beaker. Add 2 mg Ag and 2 mg In as the nitrate solutions. The total volume at this point should be approximately 5 ml.

(2) Add a few drops of methyl orange and neutralize with NH_4OH until the solution is slightly basic (yellow). Coagulate the precipitate for a few seconds on a preheated hot plate.

(3) Filter the sample through a porcelain filter crucible into a 250 ml filter flask, using suction. Wash the precipitate with a small amount of 1% NH_4NO_3 solution.

(4) Place the crucible containing the precipitate on a rubber filter ring in a glass funnel and arrange a test tube in the filter flask in such a way that the tip of the funnel drips into the tube. Dissolve the precipitate in HNO_3 and suck it through the filter into the test tube.

(5) Lift the tube out of the flask and pour the solution into another 20 ml beaker. Repeat the precipitation as in (2) and filter the $In(OH)_3$ through a #42 Whatman filter paper disc held in a Gooch crucible or a Hirsch funnel.

(6) Suck the sample as dry as possible and then pour 1-2 ml acetone through the paper to remove the residual H_2O. When the paper disc is dry, mount on a card under tape.

Remarks:

In practice a segment consisting of approximately 10% of the total was usually cut from the dried paper disc and mounted separately for use in counting the short half lives; the remainder, which was too active to count originally was then used to follow the longer half lives.

PROCEDURE 4

INDIUM

Source - M. Lindner in report AECD-2738, edited by
W. W. Meinke, August 1949.

Target material: Antimony (~ .5 g metal)

Time for separation: 1-2 hours

Type of bombardment: 184" a & D_2

Equipment required: Lusteroid tube, centrifuge, cones, tank H_2S, SO_2

Yield: 50% or greater

Degree of purification: At least factor of 100

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc. HNO_3 dropwise until dissolved (10 min.) Dilute to approximately 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 3 N HCl.

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

(6) Saturate hot with H_2S until Sb_2S_3 precipitation complete.

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

(8) Wash the Cd and In hydroxide with very dilute NaOH, dissolve in HCl. Add 2 mg Sn^{+4} holdback.

(9) Repeat NaOH precipitation, dissolve and make to 15 ml in 2 N HCl.

(10) Add 5 mg Sb^{+++}, 2 mg $TeO_3^{=}$ and saturate with H_2S.

(11) Boil supn. to expel H_2S. Add excess NH_4OH. Centrifuge.

(12) Dissolve the $In(OH)_3$ precipitate in HCl. Add 2 mg Cd^{++}. Repeat NH_4OH treatment.

(13) Dissolve the $In(OH)_3$ precipitate in HCl and plate an aliquot.

PROCEDURE 5

INDIUM

Source - G. Wilkinson in report AECD-2738, edited by
W. W. Meinke, August 1949.

Target material: Uranium ($\sim$ 1 g) Time for separation: $\sim$1 hour

Type of bombardment: 184" (high energy fission) Equipment required: Standard

Yield: 75-80%

Degree of purification: 10^5-10^6 from activities present

Procedure:

(1) To aliquot of target solution add 5 mg of holdback carriers; (Rare Earths, Ba, Sr, Zr, Rb, Cs, Te, Mo and rest of the sulfide group metals) plus 5 mg In and Cd carriers.

(2) Adjust acidity to 0.4 - 0.5 N HCl and saturate with H_2S. Discard precipitate.

(3) Repeat steps 1 and 2 twice.

(4) Add NH_4Ac plus acetic acid, precipitate In and Cd sulfides.

(5) Dissolve precipitate in cold 1 N HCl and repeat steps 1-4 three times or until the acid sulfide fraction is inactive.

(6) Dissolve the In and Cd sulfides from last sulfide precipitation in cold 1 N HCl (only Cd and In sulfides soluble in cold 1 N HCl, Sn and Sb soluble in hot 1 N HCl).

(7) Add R. E., Ba and Sr carriers, make slightly alkaline with NH_4OH. Then add HCl until faintly acid.

(8) Add excess NaAc and boil. Centrifuge off the basic indium acetate. (Cd remains in solution)

(9) Dissolve the precipitate in dilute HCl. Add 5 mg Cd carrier and repeat steps 7 and 8.

PROCEDURE 6

INDIUM

Source - U. Schindewolf and M. Wahlgren in report AECU-3887, edited by W. W. Meinke, November 1958.

Target Material: Meteorite

Type of bombardment: Neutron, 5 min, 100 kw

Yield: 50%

Degree of purification: very good

Advantages:

Time for separation: 30 min.

Equipment required: filter chimney, burner and tripod, miscellaneous beakers, beaker tongs, 250 ml separatory funnel, hydrogen sulfide cylinder, nickel crucible, 7 mm ion exchange column

Procedure:

(1) Fuse 1 g irradiated sample with 8 g sodium peroxide for 2 minutes. (finely ground sample)

(2) Dissolve melt in 50 ml water containing 2 ml carrier solution. CAUTION!!

(3) Add 40 ml 9 N HBr, heat to boiling, cool.

(4) Extract with two 40 ml portions of ether.

(5) Wash combined ether volumes with two 20 ml volumes of 4.5 N HBr.

(6) Strip ether with 30 ml of N HCl solution.

(7) Boil down to about 5 ml; pass over small Dowex-2 anion exchange column.

(8) Scavenge with palladium sulfide, filter.

(9) Buffer with bisulfate, precipitate indium as sulfide.

(10) Pass slowly through filter chimney, air dry.

Chemical yield: weigh as indium sulfide (In_2S_3)

PROCEDURE 7

INDIUM

Source - J. E. Hudgens and L. C. Nelson in Analytical Chemistry 24, 1472 (1952).

ABSTRACT

This work was undertaken to develop a radiochemical procedure for the determination of microgram or submicrogram quantities of indium in materials that might be used in nuclear reactors. A method was developed in which neutron activation with a nuclear reactor and with a radium

beryllium source was used to determine indium concentrations of a few parts per million. The ultimate sensitivity of the method is 10^{-11} gram when the thermal neutron flux of 4 x 10^{12} neutrons per second per square centimeter obtainable in a reactor is used. A rapid solvent extraction method for separating the indium from other sample components was developed. The method is applicable to the determination of indium in a wide variety of sample types.

PROCEDURE

The irradiated sample was dissolved in about 10 ml of concentrated hydrobromic acid, 10 mg of indium as a solution of the bromide and several milligrams of iron as the nitrate were added, and the solution was evaporated just to dryness. The residue was then taken up in 1 M hydrobromic acid, washed into a separatory funnel, and made up to about 8 ml with 1 M hydrobromic acid. Two successive 30-ml portions of isopropyl ether were equilibrated with the acid phase and discarded. Enough concentrated hydrobromic acid (48%) was added to make the hydrobromic acid concentration 4.5 M. The total volume was about 20 ml. A fresh 30-ml portion of isopropyl ether was added and shaken with the aqueous solution for a minute, and the acid phase was separated. This step was repeated and after the second equilibration with ether the acid phase was discarded. The two ether phases were combined and washed with three successive 5-ml portions of 4.5 M hydrobromic acid. The washings were discarded. The ether phase was then equilibrated with three successive 5-ml portions of 5 M hydrochloric acid. The aqueous phases were combined and washed with another fresh 15-ml portion of isopropyl ether. The hydrochloric acid solution was then diluted to 50 ml, 5 grams of ammonium nitrate added, and the solution just neutralized with ammonium hydroxide. The mixture was centrifuged, and the precipitate was washed with water and quantitatively transferred to a 1-inch glass dish. The precipitate was dried under an infrared lamp before the radioactivity determination was made with an end-window Geiger-Müller counter and a commercial scaler. The indium precipitate was then quantitatively transferred to a crucible, ignited at 800 to 850 C, and weighed as In_2O_3. A correction for chemical yield through the procedure was applied where the losses were significant. Total time required to complete the chemical procedure was usually a little more than 1 hour.

PROCEDURE 8

INDIUM

Source - G. Wilkinson and W. E. Grummit, Nucleonics 9,
No. 3, 52-62 (1951).

The U solution, containing Cd and In carriers with 2 mg each of the other sulfide-group elements and Y, La, Ce, Ba, Sr, Zr, Rb, and Cs, was adjusted to 0.5 N HCl and saturated with H_2S. (Cd and In are not precipitated in 0.5 N HCl, although if the Cd concentration exceeds ~ 0.7 mg/ml, precipitation of CdS will occur.) After removal of the sulfide precipitate, the solution was boiled to remove H_2S, and further quantities of As, Ge, Se, Mo, Ru, Rh, Pd, Ag, Sn, Sb, and Te were added and precipitated as before. This step was repeated. Ammonium acetate and acetic acid were added to the filtrate, and In and Cd precipitated by saturating the solution with H_2S. The In and Cd sulfides were dissolved in sufficient cold 1 N HCl to give a concentration of 0.1 mg/ml of each metal. Carriers for Ru, Sn, Sb, Se, Te, Y, La, Ce, Zr, Ba, Sr, and Cs were added, and the separation of In and Cd as sulfides was repeated. This cycle was continued until the acid sulfide group, the rare and alkaline earths, and alkali-metal carriers were recovered inactive. Three cycles were usually required. The final precipitate was again dissolved in cold 1 N HCl. Only Cd and In sulfides were found to be soluble under these conditions; small amounts of Sn, Te, etc., that might follow remained undissolved.

The In and Cd were separated by several methods, including the precipitation of $In(OH)_3$ by NH_4OH, the precipitation of In oxalate or ferro-cyanide in the presence of excess NH_4OH, or the precipitation of

In by K_2CrO_4 from neutral solution.

The best separation was achieved by the precipitation of In basic acetate from dilute acetic acid solution. Cerium, La, Y, Ba, Sr, Zr, Nb, and Cs carriers were added to the acid solution of In and Cd. This solution was made slightly alkaline with NH_4OH and then faintly acid with HCl. Any precipitate, e.g., of Zr and Nb, formed at this stage was removed. Excess solid Na acetate was added to the solution and the mixture boiled for a few minutes and In basic acetate precipitated. This was centrifuged, washed with water, dissolved in dilute acid, and In reprecipitated. The chemical yield of indium was of the order of 50 to 60 per cent.

PROCEDURE 9

INDIUM

Source - A. A. Smales, J. van R. Smit, and H. Irving in
Analyst 82, 539 (1957).

ABSTRACT

Neutron-activation analysis has been applied to the determination of traces of indium, use being made of both the radionuclides indium-114 and indium-116. The ultimate sensitivity with irradiation in the Harwell Pile and use of 49-day indium-114 is 8×10^{-10} g. When there are facilities for chemical processing shortly after irradiation, it is possible to exploit the greater sensitivity of 5×10^{-12} g afforded by the 54-minute isomer indium-116. The radiochemical separations after the addition of carrier were based mainly on precipitations of indium as hydroxide and sulphide, together with stages of solvent extraction. Radiochemically pure indium was finally precipitated and counted as the tris-oxinate; the chemical yield was determined gravimetrically.

It was found to be essential to use dilute aqueous solutions of indium in the standards irradiated simultaneously with the analytical samples to avoid errors due to self-shielding, which were shown to be serious when standards of indium foil were used.

The method has been applied to the determination of indium in the standard rock samples GI and WI, and in a number of separated minerals.

METHOD

REAGENTS-

Dilute standard indium solution - Prepare a solution containing 15 mg of Specpure indium wire in 1 litre of M nitric acid.

Indium carrier solution - Dissolve 1·5 g of pure indium metal in dilute hydrochloric acid and dilute to 500 ml.

1 ml ≡ 3 mg of In.

Copper carrier solution - Prepare a solution of cupric chloride in 0.5 M hydrochloric acid containing 10 mg of copper per ml.

Iron carrier solution - Prepare a solution of ferric chloride in 6 M hydrochloric acid containing 10 mg of iron per ml.

Nickel and barium carrier solutions - Dissolve the appropriate weight of the respective chlorides in water to give solutions containing 10 mg of nickel (or barium) per ml.

Oxine solution, 5 per cent - Dissolve 5 g of 8-hydroxyquinoline in 100 ml of 96 per cent ethanol.

Acetate buffer solution - Dissolve 272 g of trihydrated sodium acetate in distilled water, add 60 g of glacial acetic acid, and dilute to 1 litre.

Sodium peroxide, powdered.
Hydrochloric acid, sp. gr. 1·18.
Perchloric acid, 72 per cent.
Sodium hydroxide solution, 20 per cent.
Hydrobromic acid, 46 to 48 per cent.
Ammonia solution, sp. gr. 0.880.
Sodium sulphite solution - A saturated solution in water.

PROCEDURE FOR INDIUM-114 -

Prepare irradiation ampoules about 5 cm long from silica tubing with a diameter of 5 to 6 mm (or an internal diameter of 4 mm for the standards), each having a constriction near the open end. Grind the sample until it passes through a 300-mesh sieve and weigh out accurately about 0.5 g portions into each ampoule. Prepare standards by weighing out 0.1 to 0.2 ml of the dilute standard indium solution. Seal off the ampoules and pack them into a standard aluminum can with aluminum foil. Each irradiation unit should contain two standards with four or more samples, which should be prepared in duplicate. Irradiate for at least 7 days, and then allow the can to "cool" behind a radiation shield for one-half of the irradiation period.

Remove the ampoules from the can, open them at the constriction, and transfer the solid samples to silica crucibles. To each add 3 to 4 g of powdered sodium peroxide and mix thoroughly. Finally, cover the mixture in each crucible with a thin layer of sodium peroxide and heat in an electric muffle furnace at 480 to 500 C for 10 to 15 minutes. Remove the crucibles from the furnace and quickly cool them by immersing their outside walls in a beaker of water. Detach the cake from each crucible and transfer it to a 150-ml beaker covered with a watch-glass. Dissolve the melt carefully in about 200 ml of water and acidify with hydrochloric acid, sp. gr. 1·18.

Mineral samples that resist the attack by sodium peroxide and samples of pure ilmenite and magnetite were taken up by fusion with four times their weight of potassium hydrogen sulphate.

Stages in the chemical separation that now follows are numbered to facilitate reference in subsequent discussion -

(1) To the acidified solution add an accurately known weight (15 mg) of indium carrier solution. Add 10 mg of nickel carrier solution and boil for 1 minute.

(2) Transfer the solution to a 50-ml centrifuge tube and precipitate the hydroxides by adding an excess of ammonia solution. Spin, and discard the supernatant liquid.

(3) Dissolve the precipitate in 10 ml of 72 per cent perchloric acid and transfer back to the original beaker. Evaporate under an infra-red lamp until copious fumes appear. Add a further 2 ml of perchloric acid and continue heating for 20 minutes.

(4) Take up the residue as completely as possible in hot water and filter into the original centrifuge tube. Wash the precipitate thoroughly with hot water and discard it. To the combined filtrate and washings add sodium hydroxide solution in excess. Spin the precipitated hydroxides in a centrifuge and discard the supernatant liquid. Dissolve the precipitate in dilute hydrochloric acid and add 2 ml of saturated sodium sulphite solution. Add excess of ammonia solution and spin in a centrifuge.

(5) Dissolve the precipitate in 11 ml of 46 to 48 per cent hydrobromic acid (about 8·5 M) and dilute with 9 ml of water to give 20 ml of approximately 4·5 M hydrobromic acid solution. Transfer to a 100-ml separating funnel and extract the indium by shaking with two 25-ml portions of diethyl ether. Run off and reject the aqueous phase. Wash the combined ether phases by shaking with two 5-ml portions of freshly prepared 4·5 M hydrobromic acid. Reject the aqueous washings.

(6) Extract the indium from the ether phase by equilibrating with three successive 5-ml portions of 6 M hydrochloric acid. Discard the ether phase. Wash the combined aqueous extracts once with 15 ml of ether and reject this. To the solution in hydrochloric acid add 10 mg of iron carrier solution and extract with two 15-ml portions of ether. Reject the ether phases. Add a further 10 mg of iron carrier solution to the hydrochloric acid solution and extract with three 15-ml portions of ether, again rejecting the ethereal phases.

(7) To the aqueous phase add ammonia solution until indium hydroxide starts to be precipitated, and then add 10 mg of copper carrier solution, which should give a deep blue colour. Add concentrated hydrochloric acid dropwise until the blue colour fades, and then add 1 ml of hydrochloric acid, sp. gr. 1·18, and dilute to 25 ml. The acidity at this stage should be about 0·5 M. Heat to 60 C and saturate with hydrogen sulphide. Filter off and discard the precipitate. Collect the filtrate and boil it to remove hydrogen sulphide.

(8) To the hot filtrate add 10 mg of copper carrier solution and saturate at 60 C with hydrogen sulphide. Filter off and discard the precipitate.

(9) Repeat step (8) once.

(10) To the filtrate from step (8) add about 2 g of solid ammonium acetate, heat to 70 to 80 C and saturate with hydrogen sulphide. Spin in a centrifuge and reject the supernatant liquid.

(11) Dissolve indium sulphide from the precipitate by adding 12 ml of cold M hydrochloric acid and triturating with a glass rod. Filter off and discard any insoluble residue.

(12) Repeat steps (10) and (11) once.

(13) Boil the solution of indium in hydrochloric acid for 1 minute to expel hydrogen sulphide and then add 10 mg of barium carrier solution. Make the solution ammoniacal and spin the precipitated hydroxides in a centrifuge. Reject the supernatant liquid.

(14) Dissolve the precipitated indium hydroxide in 4 drops of concentrated hydrochloric acid, dilute to 15 ml and add 2 ml of oxine solution. Heat to 50 to 60 C and precipitate indium oxinate by the slow addition of 5 ml of acetate buffer solution. Spin in a centrifuge and wash the precipitate twice with hot 5 per cent ethanol, using a glass rod to break up the precipitate if necessary. Make a slurry of the precipitate with a small amount of water and transfer with a drop-pipette to a tared aluminum counting tray. Dry under an infra-red lamp, cool, and weigh to determine the chemical yield.

At a convenient time open the ampoules containing the irradiated indium standards. Using a drop-pipette drawn out to a point, transfer the indium solution quantitatively to a 100-ml calibrated flask and rinse thoroughly with hot 2 M hydrochloric acid. The final concentration of acid is immaterial. Cool, and dilute to the mark. Transfer a suitable aliquot, depending on the amount of indium expected in the sample, to a 50-ml centrifuge tube and add exactly the same weight of indium carrier (15 mg) as in the chemical separation described above. After thorough mixing, precipitate the indium with an excess of ammonia solution. Spin in a centrifuge and reject the supernatant liquid. Re-dissolve the precipitated indium hydroxide in 4 drops of concentrated hydrochloric acid and then precipitate indium oxinate; mount, dry, and weigh it as described in step (14).

PROCEDURE FOR INDIUM-116 -

Amounts of up to 150 mg of finely powdered sample (less than 300 mesh) are used in this procedure. After introduction of a known weight into a short length of polythene tubing with an internal diameter of 3 to 4 mm, the free end was sealed by being heated in a small flame and squeezed with a pair of tweezers. Liquid samples were prepared as before by weighing out known amounts of dilute indium standard solution into silica ampoules. Since the entire chemical separation and subsequent counting must be carried out with the greatest expedition, only two samples and one standard are packed into an aluminum can and are irradiated for 1 hour, by which time the activity due to indium-116 will have reached about one-half of its saturation value. Samples and standard are processed after "cooling" for 30 to 40 minutes.

The chemical procedure for isolating indium-116 activity is essentially the same as that already described for indium-114. But, since the total weight of sample is smaller, stages (3) and (4) may be omitted. These stages are designed to render insoluble any silica that may accompany the hydroxide precipitate from the preceding stage. When working with larger sample weights, it was found that silicic acid from stage (2) dissolved freely in concentrated hydrobromic acid, but separated at the interface on subsequent dilution and equilibration with ether in stage (5). Under these conditions phase separation was delayed and a clean separation could only be achieved by prolonged centrifugation. A further simplification arises from the smaller contribution made by iron-59 to the total activity when the time of irradiation is short, as is so with the indium-116 procedure. For samples of comparable iron content, the indium-116 procedure permits of a lower decontamination from iron and usually one scavenging with iron carrier is sufficient. With this modification stage (6) would read -

(6) Extract the ether phase by equilibrating with three successive 5-ml portions of 6 M hydrochloric acid. Discard the ether phases. Wash the combined aqueous phases twice with 15 ml of ether. To the hydrochloric acid solution add 10 mg of iron carrier solution and extract with three 15-ml portions of ether, again rejecting the ethereal phases.

With these exceptions the procedures for indium-114 and indium-116 are identical. The irradiated standard is transferred quantitatively as before to a 100-ml calibrated flask and made up to the mark. But two aliquot portions are taken and precipitated with indium carrier. In view of the rapid decay of indium-116, the precipitates of indium oxinate were counted immediately after mounting and the weighing of the dried samples to determine the chemical yield was postponed until after the counting had been completed.

PROCEDURE 10

INDIUM

Source - G. A. Cowan in "Collected Radiochemical Procedures", Los Alamos Report LA-1721, January 1958.

1. Introduction

In its determination in fission-product material, indium first is separated rapidly from cadmium so that a separation time from its parent activity is known accurately. The separation is accomplished by precipitation of indium hydroxide by means of ammonium hydroxide, cadmium remaining in solution as an ammonia complex. The hydroxide is then dissolved and acid-insoluble sulfides are precipitated from a buffered solution (pH 3-4), in the presence of sulfosalicylic acid. Indium is leached from the mixture of sulfides with cold 1<u>M</u> HCl. It is then precipitated as the hydroxide and converted to the bromide by means of 4.5<u>M</u>

hydrogen bromide. The bromide is extracted into ethyl ether and indium is finally precipitated and weighed as the 8-hydroxyquinoline (oxine) derivative. The chemical yield is about 50% and one sample can be run in about 4 hours.

2. Reagents

In carrier: 10 mg In/ml (added as $InCl_3$ in 1.5M HCl)--standardized

Sb carrier: 10 mg Sb/ml (added as $SbCl_3$ in 1M HCl)

Cd carrier: 10 mg Cd/ml (added as $CdCl_2$ in 1M HCl)

HCl: 1M

HCl: 1.5M

HBr: 4.5M

NH_4OH: conc.

H_2S: gas

Buffer solution: (1M $HC_2H_3O_2$ - 2M $NaC_2H_3O_2$)

Sulfosalicylic acid: 5% in H_2O

8-hydroxyquinoline: 5% in 2M $HC_2H_3O_2$

Ethyl ether: saturated with 4.5M HBr.

3. Equipment

Fisher burner

Drying oven

Centrifuge

Block for holding centrifuge tubes

Mounting plates

Forceps

Tongs for Erlenmeyer flasks

Pipets: assorted sizes

125-ml separatory funnels (one per sample)

250-ml Erlenmeyer flasks (one per sample)

100-ml beakers (one per standardization)

Wash bottle

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

Filter chimneys (one per sample)

Filter flasks

60-ml sintered glass crucibles: medium porosity (one per standardization)

No. 41 H Whatman filter circles: 7/8" diameter-weighed

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

Steam bath

Stirring rods.

4. Preparation and Standardization of Carrier

Dissolve 10.0 g of pure In metal in a minimum of HCl and dilute to 1 liter with 1.5M HCl.

Pipet 2.00 ml of the above solution into a 100-ml beaker, and add 20 ml of H_2O, 5 ml of $HC_2H_3O_2$ - $NaC_2H_3O_2$ buffer solution, and 2 ml of 8-hydroxyquinoline solution. Permit the precipitate to settle and add 8-hydroxyquinoline solution dropwise to the supernate until no further precipitation occurs. Filter the precipitate on a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate thoroughly with H_2O and dry at 110° for 1/2 hour. Cool and weigh as $In(C_9H_6NO)_3$ (20.99% In).

Three standardizations, with results agreeing within 0.5%, are run.

5. Procedure

Step 1. To 5 to 20 ml of sample in a 40-ml conical centrifuge tube, add 2.00 ml of In carrier, 2 drops of Cd holdback carrier, and an excess of conc. NH_4OH. Centrifuge the precipitate and discard the supernate.

Step 2. Dissolve the precipitate in 20 ml of 1M HCl and repeat Step 1 two additional times.

Step 3. Dissolve the precipitate in 10 ml of 1M HCl and add 2 ml of 5% sulfosalicylic acid, 5 ml of $HC_2H_3O_2$ - $NaC_2H_3O_2$ buffer solution, and 1 drop of Sb carrier. Saturate the solution with H_2S in the cold. Centrifuge and discard the supernate.

Step 4. Wash the precipitate with 5 ml of diluted (1-10) buffer solution, centrifuge, and discard the supernate.

Step 5. Add 5 ml of 1M HCl and digest just at boiling for 1 min. Centrifuge and transfer the supernate to a clean 40-ml centrifuge tube. Discard the precipitate.

Step 6. Dilute the solution to 10 ml with H_2O and repeat Steps 3-5 three additional times.

Step 7. To the solution containing $InCl_3$ in 1M HCl, add an excess of conc. NH_4OH and centrifuge. Discard the supernate.

Step 8. Dissolve the precipitate in 25 ml of 4.5M HBr, transfer the solution to a 125-ml separatory funnel, and extract $InBr_3$ into 50 ml of ethyl ether which is saturated with 4.5M HBr. Discard the aqueous layer and wash the ether layer twice with 10-ml portions of 4.5M HBr.

Step 9. Draw off the ether into a 250-ml Erlenmeyer flask. Evaporate the ether on a steam bath and take the residue up in 20 ml of 1M HCl. Add 5 ml of buffer solution and 2 ml of 8-hydroxyquinoline reagent. Test for completeness of precipitation by the addition of another drop of reagent to the clear supernate. Filter on a weighed No. 41 H Whatman filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate thoroughly with water and dry at 110° for 1/2 hour. Cool, weigh, and mount. Count immediately in a proportional counter (Note 1).

Notes

1. This procedure has been used for the determination of 4.5h In^{115}, daughter of 58h Cd^{115}.

PROCEDURE 11

INDIUM

Source - "Determination of Palladium, Cadmium, and Indium Activities in Fission", L. E. Glendenin, Paper 265 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951.

Discussion

The separation of indium from the other fission products is based on the precipitation of In_2S_3 with H_2S in $HC_2H_3O_2$ solution. At the low H^+ concentration afforded by $HC_2H_3O_2$, In_2S_3 is completely precipitated, but at H^+ concentrations much higher than 0.05N the precipitation does not occur. The contaminating elements, members of the acid-sulfide group and probably zirconium and niobium, are removed by cycles of PdS scavengings in 0.3M HCl and In_2S_3 precipitations in 0.3M $HC_2H_3O_2$. The indium is finally precipitated, weighed, and mounted as In_2S_3. The decontamination from the other fission activities, as indicated by a separation of indium from a very active concentrate of plutonium fission products, is of the order of 10^6.

Procedure

Step 1. Add 10 to 15 ml of conc. HCl and 20 mg of indium carrier to the sample, and evaporate just to dryness. Take up the residue in 10 ml of 6N $HC_2H_3O_2$, pass in H_2S, centrifuge, and wash the precipitate.

Step 2. Dissolve the In_2S_3 in 0.5 ml of 6N HCl, dilute to 10 ml, add 5 mg of palladium carrier, heat, and precipitate with H_2S. Centrifuge, and discard the PdS.

Step 3. To the supernatant solution add 10 mg of lanthanum carrier and 0.5 ml of 6N $NH_4C_2H_3O_2$. Pass in H_2S, and heat to boiling. Centrifuge. Repeat steps 2 and 3.

Step 4. Filter the In_2S_3, wash with H_2O and C_2H_5OH, dry at 110 C for 10 min, weigh, and mount.

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