



Radiochemistry of Cadmium (1960)

Pages
64

Size
6 x 9

ISBN
0309339618

DeVoe, James R.; Subcommittee on Radiochemistry;
Committee on Nuclear Science; National Research
Council

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The Radiochemistry of Cadmium

By **JAMES R. DeVOE**

*The University of Michigan
Ann Arbor, Michigan*

January 1960

**Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council**

**Printed in USA. Price \$0.75. Available from the Office of Technical
Services, Department of Commerce, Washington 25, D. C.**

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, the problems of stockpiling uncontaminated materials, the 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 Cadmium

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January 1960

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

"Gmelin's Handbuch der Anorganischen Chemie", System Nr. 33, (Verlag Chemie, Gmbh. Weinheim Bergstrasse, 1925).

Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. IV, Longmans, Green and Co., London, (1923), pp. 98-694.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I., "Applied Inorganic Analysis", 2nd ed., Wiley and Sons, New York (1953), p. 254.

Sidgwick, N. V., "The Chemical Elements and Their Compounds", Vol. I, Oxford Press, London (1950), p. 262-285.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF CADMIUM

Rodden, C. J., "Analytical Chemistry of the Manhattan Project", National Nuclear Energy Series, Vol. I, McGraw-Hill Book Company (1950), p. 396.

Finston, H. L., Miskel, I., Ann. Rev. Nucl. Sci., 5, 269-296 (1955). This is a general review of separation procedures and has many references to the separation of specific elements.

III. TABLE OF ISOTOPES OF CADMIUM

Isotope	Half-Life	Type of Decay ^a	Method of Preparation ^{b,c}
Cd ¹⁰⁴	59m	EC	--
Cd ¹⁰⁵	55m	EC, β^+ , γ	Pd ¹⁰² (β, n) Cd ¹⁰⁵ ^d
Cd ¹⁰⁶	6x10 ¹⁶ y	-	1.22%
Cd ¹⁰⁷	6.7h	EC 99% β^+ 0.3%	Cd ¹⁰⁶ (n, γ) Cd ¹⁰⁷
Cd ¹⁰⁸	-	-	0.88%
Cd ¹⁰⁹	470d	EC	Cd ¹⁰⁸ (n, γ) Cd ¹⁰⁹
Cd ¹¹⁰	-	-	12.4%
Cd ^{111m}	48.6m	IT, γ	daughter of In ¹¹¹ (0.01%) Cd ¹¹⁰ (n, γ) Cd ^{111m}
Cd ¹¹²	-	-	24.07%
Cd ^{113m}	-	-	12.26%
Cd ¹¹⁴	-	-	28.86%
Cd ^{115m}	43d	β^- , γ	daughter of Ag ¹¹⁵ (9%) Cd ¹¹⁴ (n, γ) Cd ^{115m} fission products
Cd ¹¹⁵	53h	β^- , γ	daughter of Ag ¹¹⁵ (91%) Cd ¹¹⁴ (n, γ) Cd ¹¹⁵ fission products
Cd ¹¹⁶	10 ¹⁷ y	-	7.58%
Cd ^{117m}	3h	IT, γ	daughter of Ag ¹¹⁷ fission product
Cd ¹¹⁷	50m	β^- , γ	daughter of Ag ¹¹⁷ Cd ¹¹⁶ (n, γ) Cd ¹¹⁷
Cd ¹¹⁸	50m	β^-	fission product
Cd ¹¹⁹	10m	β^-	--

a. For detailed decay and reference to the data in this table see Table of Isotopes, Strominger, D., Hollander, J. M. and Seaborg, G. T., Rev. Mod. Phys., 30, No. 2, Pt. II, (1958).

b. Only a few of the common sources are listed here.

c. This column also lists percent abundance of the stable isotopes.

d. Johnson, F. A., Can. J. Phys., 33, 841 (1955).

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

1. Metallic Cadmium

Cadmium metal has a specific gravity of 8.64¹ at 16.3/4⁰, a melting point of 320⁰ C² and a boiling point of about 766⁰ C.³ It is made commercially from treatment of impure Zn solutions which were used for the electrolytic preparation of Zn. Some Cd is produced by the fractional distillation of zinc smelter dust. Cadmium can be quite easily deposited electrolytically and is one of the purest metals which can be obtained commercially by this means. The standard electrode potential at 25⁰ C is 0.401 volt ($\text{Cd} \rightarrow \text{Cd}^{++} + 2 \bar{e}$).⁴ At room temperature the metal is only slightly tarnished by air or water. It can be ignited to CdO. Cadmium metal dissolves in hot dilute sulfuric and hydrochloric acid. It dissolves most readily in dilute nitric acid. Cadmium has only one stable valence, +2, in aqueous solution.

2. Soluble Salts of Cadmium

All of the common salts of cadmium are soluble in water with the exception of the sulfide, carbonate, oxalate, phosphate, cyanide, ferrocyanide, ferricyanide, and hydroxide. The halides are all soluble in water. The cadmium iodide CdI_2 is one of the few iodides soluble in ethyl alcohol. All cadmium compounds are soluble in excess aqueous halide solution.

3. Insoluble Salts of Cadmium

The insoluble salts are most useful in the gravimetric analysis. Therefore the temperatures at which the ignition should be done will be listed.

Cadmium is precipitated with H_2S in dilute acid or basic solution and is insoluble in $(\text{NH}_4)_2\text{S}_x$. It falls into group II of the qualitative analysis scheme. CdS has a stable weighing form

between 218° C and 420° C.⁵ Cadmium hydrolyzes in aqueous solution above a pH of 5 and is insoluble in excess sodium hydroxide. Cadmium hydroxide, $\text{Cd}(\text{OH})_2$, has a stable weighing form between 89° C and 170° C.⁶ Cadmium forms a $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ which is an insoluble salt in neutral solution and is often used as a stable weighing form.^{7,8} However it is probably not the best form since its temperature range is narrow. It can be weighed after drying between 72° C and 122° C or it can be taken to the pyrophosphate, $\text{Cd}_2\text{P}_2\text{O}_7$, which is completely transformed only above 581° C.⁹ A number of elements also precipitate under these conditions. Cadmium forms a thiourea complex which is precipitated in the presence of Reinecke salt to form the crystalline rose colored precipitate with formula $[\text{Cd}(\text{CH}_4\text{N}_2\text{S})_2][\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]_2$.^{10,11} This forms a stable weighing form up to 167° C.^{11a} Only a few elements precipitate with this reagent. Cadmium oxalate forms a precipitate¹² which in the presence of large excess of oxalate has moderate solubility.¹³ This precipitate yields CdO quantitatively above 770° C.¹⁴ A number of elements form an insoluble oxalate. Cadmium or its ammonium complex can be precipitated with ferrocyanide anion $(\text{Fe}(\text{CN})_6)^{4-}$.¹⁵⁻¹⁷ The precipitate is very insoluble and recently a nephelometric method using this precipitate has been devised.¹⁸ For gravimetry the weighing forms are stable up to 267° C.^{18a} Fe, Mn, Co, Ni, Cu, Zn, Al, Pb, Ca and Mg also form ferrocyanide precipitates. It is possible to coprecipitate cadmium onto many substances. $\text{Fe}(\text{OH})_3$, $\text{In}(\text{OH})_3$, $\text{La}(\text{OH})_3$, LaF_3 , $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ ¹⁹ and many others have been found to carry cadmium from the aqueous solution. Any precipitate which allows chemical interaction with cadmium which is comparable to hydrolysis on a hydrous oxide will carry cadmium. Another example is the removal of cadmium from solution by coprecipitation on AgCl .²⁰ Only silver, mercury, lead, and

thallous thallium are also carried down. Table I lists some of the most common inorganic insoluble compounds.

Table I. INSOLUBLE INORGANIC COMPOUNDS OF CADMIUM

Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
CO_3^-	$\text{Cd}(\text{CO}_3)_2$	Insoluble	Soluble in acids potassium cyanide ammonium salts
CN^-	$\text{Cd}(\text{CN})_2$	1.7 gm/100 ml	Soluble in acids potassium cyanide ammonium hydroxide
$[\text{Fe}(\text{CN})_6]^{-4}$	$\text{Cd}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	Insoluble	Soluble hydrochloric acid
$[\text{Fe}(\text{CN})_6]^{-3}$	$\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$	Insoluble	Soluble in acids and ammonia
OH^-	$\text{Cd}(\text{OH})_2$	0.00026 gms/100 ml	Soluble acids ammonium salts
$\text{MoO}_4^{=}$	CdMoO_4	Insoluble	Soluble acids ammonium hydroxide potassium cyanide
$\text{C}_2\text{O}_4^{=}$	CdC_2O_4	0.00337 gms/100 ml S.P. = 1.5×10^{-8}	Soluble acids excess oxalate
PO_4^{-3}	$\text{Cd}_3(\text{PO}_4)_2$	Insoluble	Soluble acids ammonium salts
P_2O_7	$\text{Cd}_2(\text{P}_2\text{O}_7)$	Insoluble	Soluble acids excess pyrophosphate
$\text{S}^=$	CdS	0.00013 gm/100 ml S.P. = 3.6×10^{-29}	Soluble acids
$(\text{NH}_4)_3\text{PO}_4$	CdNH_4PO_4	Very insoluble	Soluble acids
NH_4ClO_4	$\text{Cd}(\text{NH}_3)_4(\text{ClO}_4)_2$	Insoluble	Soluble acids
AsO_4^{-3}	$\text{Cd}_3(\text{AsO}_4)_2$	Insoluble	Soluble acids ammonium hydroxide
AsO_3^{-3}	$\text{Cd}_3(\text{AsO}_3)_2$	Insoluble	Soluble acids ammonium hydroxide

4. Complex Ions of Cadmium

Cadmium forms a large number of complex ions. Many of the complexes are negatively charged such as the halides, which

allow adsorption of these cadmium ions on an anion exchanger. The equilibrium constants for a number of these complexes are listed in Table II. The complex halides are particularly useful for extraction of the cadmium anions into organic esters. Other complexes such as citrate or tartrate form such strong complexes with cadmium that they prevent hydrolysis of cadmium even in normal solutions of sodium hydroxide. The radiochemical application of these complex ions will be discussed in the section on ion exchange and on the one for extraction. Other complex ions of cadmium which do not appear in Table II are the carbonate, pyrophosphate and perchlorate.

Table II. COMPLEX IONS OF CADMIUM

<u>Complexing Agent</u>	<u>Reaction</u>	<u>Ionic Strength</u>	<u>K</u>	<u>Reference</u>
Cl ⁻	Cd ⁺² + Cl ⁻ → CdCl ⁺	3	38.5	a
		3	35	b
	Cd ⁺² + 2Cl ⁻ → CdCl ₂	3	170	a
		3	115	b
	Cd ⁺² + 3Cl ⁻ → CdCl ₃ ⁻	3	260	a
	3	290	b	
	Cd ⁺² + 4Cl ⁻ → CdCl ₄ ⁻²	3	850	c
Br ⁻	Cd ⁺² + Br ⁻ → CdBr ⁺	3	57	a
		3	58	b
	Cd ⁺² + Br ⁻ → CdBr ₂	3	226	a
		3	275	b
	Cd ⁺² + 3Br ⁻ → CdBr ₃ ⁻	3	2100	a
	3	1600	b	
	Cd ⁺² + 4Br ⁻ → CdBr ₄ ⁻²	3	5000	a
			5400	b
			10 ⁴	c
I ⁻	Cd ⁺² + I ⁻ → CdI ⁺	3	120	a
	Cd ⁺² + 2I ⁻ → CdI ₂	3	500	a
	Cd ⁺² + 3I ⁻ → CdI ₃ ⁻	3	10 ⁵	a
	Cd ⁺² + 4I ⁻ → CdI ₄ ⁻²	3	3 x 10 ⁶	a
		?	2.3 x 10 ⁶	c
SCN ⁻	Cd ⁺² + SCN ⁻ → CdSCN ⁺	3	24.5	a
		2	11	d
	Cd ⁺² + 2SCN ⁻ → Cd(SCN) ₂	3	96	a
		2	56	d
	Cd ⁺² + 3SCN ⁻ → Cd(SCN) ₃ ⁻	3	388	a

Table II. COMPLEX IONS OF CADMIUM (Cont'd.)

Complexing Agent	Reaction	Ionic Strength	K	Reference
	$\text{Cd}^{+2} + 4(\text{SCN})^{-} \rightarrow \text{Cd}(\text{SCN})_4^{-2}$	2	6	d
		2	60	d
NO_3^{-}	$\text{Cd}^{+2} + \text{NO}_3^{-} \rightarrow \text{CdNO}_3^{+}$	3	1.3	a
	$\text{Cd}^{+2} + 2\text{NO}_3^{-} \rightarrow \text{Cd}(\text{NO}_3)_2$	0.05	0.5	e
$\text{SO}_4^{=}$	$\text{Cd}^{+2} + \text{SO}_4^{=} \rightarrow \text{CdSO}_4$	-	8	f
		3	8	a
	$\text{Cd}^{+2} + 2(\text{SO}_4^{=}) \rightarrow \text{Cd}(\text{SO}_4)_2^{-2}$	-	10	f
	$\text{Cd}^{+2} + 3\text{SO}_4 \rightarrow \text{Cd}(\text{SO}_4)_3^{-4}$	-	110	f
CN^{-}	$\text{Cd}^{+2} + \text{CN}^{-} \rightarrow \text{CdCN}^{+1}$	3	3.5×10^5	g
	$\text{Cd}^{+2} + 2\text{CN}^{-} \rightarrow \text{Cd}(\text{CN})_2$	3	4×10^{10}	g
	$\text{Cd}^{+2} + 3\text{CN}^{-} \rightarrow \text{Cd}(\text{CN})_3^{-}$	3	1.8×10^{15}	g
	$\text{Cd}^{+2} + 4\text{CN}^{-} \rightarrow \text{Cd}(\text{CN})_4^{-2}$	3	7×10^{18}	g
$\text{C}_2\text{H}_3\text{O}_2^{-}(\text{Ac}^{-})$	$\text{Cd}^{+2} + \text{Ac}^{-} \rightarrow \text{CdAc}^{+}$	-	60	h
	$\text{CdAc}^{+} + \text{Ac}^{-} \rightarrow \text{Cd}(\text{Ac})_2$	-	10	h

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5. Chelate Complexes of Cadmium

The organic chelate compounds of the metallic cations have very wide application in radiochemistry. These compounds can be used as a basis for gravimetric methods of separation and also for extraction, ion exchange and others. Since the extraction

methods are to be discussed in section 7, consideration is given in this section to the formation of chelate compounds as precipitates and therefore to their use as gravimetric methods.

Cadmium is one of the elements which has benefited most from the introduction of the modern organic reagents. A number of these reagents and their application to gravimetric analysis are listed below. 2-(o-hydroxyphenyl) benzoxazole is a selective precipitant for cadmium with interference from only Ni and Co.²¹⁻²⁴ Salicaldoxime has been used to precipitate cadmium with interference from Pd, Cu, UO_2^{+2} , Ni, Fe and Co.²⁵ There is a large variety of precipitates which are formed with the general structure (organic)₂ (CdX₄) where the X is the bromide or iodide and the organic group is similar to brucine $C_{21}H_{21}O_2N_2(CH_3O)_2$,^{26,27} phenazone,²⁸ or antipyrinylmethane.^{29,30} All of these are believed to have stable weighing forms. For the brucine complex it is between 120° C and 250° C.³¹ Diethyldithiocarbamate precipitates cadmium and interference is limited to Pb, Bi, and Tl if cyanide is added.³² Quinaldic acid³³ is a very good reagent for cadmium because it is easily filtered, but it lacks specificity. It has a stable weighing form between 66 and 197° C. Sodium anthranilate precipitates cadmium with a stable weighing form below 110° C.³⁴⁻³⁶ Some selectivity can be gained by using a tartrate solution when precipitating cadmium with oxine.³⁷ The stable weighing form occurs between 280° and 384° C, and is nearly the most stable oxine known. The insoluble precipitates of cadmium with pyridine such as dipyridinocadmium chloride $[Cd(C_5H_5N)_2]Cl_2$ ³⁸ and dipyridinocadmium thiocyanate³⁹ are quite unstable and decompose at less than 100° C.

Coprecipitants have recently been used to carry traces of cadmium onto a macro organic precipitate. An example of this has been mentioned by Kutznetsov⁴⁰ which co-

precipitates a cadmium iodide complex anion with a precipitate formed with the organic cation, methyl violet and iodide anion.

A number of stability constants for various chelates are listed in Table III. These values were taken from Martell and Calvin^{40a} which is a very good reference to the chemistry of the metal chelate compounds. No effort has been made to list all of the chelate compounds but only a compound representative of the general type of organic structures (e.g. amines, carboxylic acids, etc.) has been listed.

For those elements which have a high stability constant titrimetric methods may be used. An example of this is the analysis of cadmium by titration using sodium ethylenediamine tetraacetate.^{41,42}

An interesting application of the chelate complex is in the formation of the thiourea cation complex of cadmium. By increasing the bulk of the cation a crystalline precipitate can be formed with ammonium reineckate ($\text{NH}_4[\text{Cr}(\text{NH}_2)_2(\text{SCN})_4]$). The exact number of thiourea molecules which coordinate with the cadmium has not been clearly established, although polarographic data indicates that the complex has two molecules of thiourea coordinated with the cadmium cation.⁴³ Prior to this time there has been complexes reported with three and four thiourea molecules coordinated with one cadmium.^{44,45}

Table III. STABILITY CONSTANTS FOR THE CHELATES OF CADMIUM

<u>Chelating Agent</u>	<u>Log K*</u>	<u>Ionic Strength</u>	<u>Reference</u>
Oxalic acid	1.14 pK ₁	0.2	a
HOOC-COOH	3.85 pK ₂	0.2	a
	3.52	0	b
	5.29 (K ₁ K ₂)	0	

Table III. STABILITY CONSTANTS FOR THE CHELATES OF CADMIUM (Cont'd.)

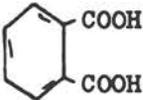
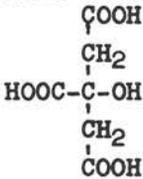
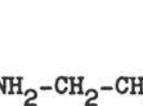
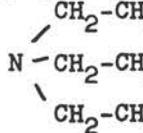
Chelating Agent	Log K*	Ionic Strength	Reference
Malonic acid HOOCCH ₂ COOH	2.69 pK ₁ 5.24 pK ₂ 3.25	0.2 .04	a
o phthalic acid 	3.0 pK ₁ 5.29 pK ₂ 1.07	.01 .03 0.15	c c d
Citric acid 	3.08 pK ₁ 4.39 pK ₂ 5.5 pK ₃ 4.22	0.1 0.1 0.1 0	e e e f
Tartaric acid 	2.88 pK ₁ 4.01 pK ₂ 9.73 (K ₁ K ₂)	0.2 0.2 -	g g h
Ammonia NH ₃	1.9 log K ₁₄	-	i
Ethylenediamine H ₂ NCH ₂ CH ₂ NH ₂	6.98 pK ₁ 9.98 pK ₂ 5.5 10.02 (K ₁ K ₂) 12.18 (K ₁ K ₂ K ₃)	1.0 1.0 0.5 0.5 70.1	j j k l k
Diethylenetriamine NH ₂ -CH ₂ -CH ₂ -NH-CH ₂ -CH ₂ NH ₂	4.61 pK ₁ 9.21 pK ₂ 8.4 13.8 (K ₁ K ₂)	0.5 0.5 0.1 0.1	m m m m
Triethylenetetramine NH ₂ -CH ₂ -CH ₂ -NH 	3.85 pK ₁ 7.00 pK ₂ 10.9 K ₃ 14.0 (K ₁ K ₃ :2)**	0.5 0.5 1.5 1.5	n n o o
β,β',β''-Triaminotriethylamine 	8.79 pK ₂ 9.84 pK ₃ 10.29 pK ₄ 12.3	0.5 0.5 0.5 0.1	p p p q

Table III. STABILITY CONSTANTS FOR THE CHELATES OF CADMIUM (Cont'd.)

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- p. Prue, J. and Schwarzenbach, G., Helv. Chim. Acta, 33, 963 (1950).
- q. Ackermann, H., Prue, J. and Schwarzenbach, G., Nature, 163, 723 (1949).
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- s. Krumholz, H., Nature, 163, 724 (1949).
- t. Schwarzenbach, G. and Freitag, E., Helv. Chim. Acta, 34, 1492-1502 (1951).
- u. Schwarzenbach, G. and Ackermann, H., Helv. Chim. Acta, 30, 1798 (1947).

Table III. STABILITY CONSTANTS FOR THE CHELATES OF CADMIUM (Cont'd.)

- v. Schwarzenbach, G. and Freitag, E., *Helv. Chim. Acta*, 34, 1503 (1951).
- w. Schwarzenbach, G., Suter, H. and Lutz, K., *Helv. Chim. Acta*, 23, 1191 (1940).
- x. Von Uiter, R., Douglas, R. and Fernelius, C., U. S. Atomic Energy Commission, Report NYO-727, May 2, 1951.

6. Extraction of the Thenoyl Trifluoroacetone (TTA)
Complex of Cadmium into Organic Solvents

To this date there has been little evidence that cadmium forms a stable complex with TTA which can be extracted into organic solvents. Experimental attempts to extract cadmium in this laboratory have shown that from a pH of 1 to 6 the amount of cadmium extracted into 0.25 M TTA in benzene (equal volumes) was negligible after 10 minutes of vigorous agitation. At a pH of 8 the extraction seemed to be about 5-10%. This however is very close to the highest pH under which TTA can be used, and the cadmium may be hydrolyzing giving some intersurface adsorption of the hydroxide.

7. Extraction of Cadmium into Organic Solvents

a) Ion association system of solvent extraction.

This type of extraction has a number of mechanisms and many equilibria are involved between the species of ions. In general it involves the solvation of a complex cation or anion by a water immiscible liquid.

The complex chlorides,⁴⁶ bromides and fluorides of cadmium⁴⁷ do not in general extract into organic solvents. The complex iodides 6.9 N in HI do extract into diethyl ether.⁴⁸ Since HI is somewhat unstable a convenient method of maintaining the iodide concentration is with the use of 1.5 N H_2SO_4 with KI.⁴⁹ These methods are somewhat specific, with only Sn, Hg, Sb, Bi, Zn and In interfering. A good review and discussion of the

analytical chemical applications of the complex iodide extraction is given by Bouilloux.⁵⁰

Another ion association system which is not very selective is the extraction of cadmium into n-butyl phosphate (mixture of di-n butyl and mono-n-butyl phosphate).⁵¹ Other elements which extract are Cs, Sr, La, Ce⁽⁺³⁾, Ag, Fe, Se⁽⁺⁴⁾, Te⁽⁺⁴⁾, Sb⁽⁺³⁾, Sb⁽⁺⁵⁾, As⁽⁺⁵⁾, Pd, Ru, Rh and Nb. Other complex ions such as the nitrate, perchlorate cyanide, SCN, etc. are not known to extract into organic solvents by an ion association mechanism.

b) Chelate system of solvent extraction.

The other general type of solvent extraction involves the chelation of the metallic cation in aqueous solution followed by solvation of the organic chelate by the organic solvent. The most used example of this for cadmium is the extraction with dithizone. A general discussion on the uses of dithizone and particularly the chemistry of the cadmium dithizonate is given by Sandell,^{52,53} Dwantscheff,⁵⁴ and the textbook on analytical chemistry by Charlot and Bezier.⁵⁵ The general extraction of a group of elements with dithizone at different pH is shown in figure 1.⁵⁶

Saltzman⁵⁷ extracted the cadmium cyanide complex from alkaline solution into a dithizone solution in CHCl_3 . The cadmium was then back extracted into tartaric acid. Sandell^{57a} has found that cadmium can be back extracted into as weakly acidic a solution as 0.01 N HCl. It is preferable to use CHCl_3 as the solvent for dithizone rather than CCl_4 since the dithizone is more soluble and stable in CHCl_3 . An interesting adaptation of the method involves passing the chloroform solution of the dithizonates through an alumina column. By adjusting the polarity of the eluant one can separate selectively the various dithizonates which adhere to the column.⁵⁸

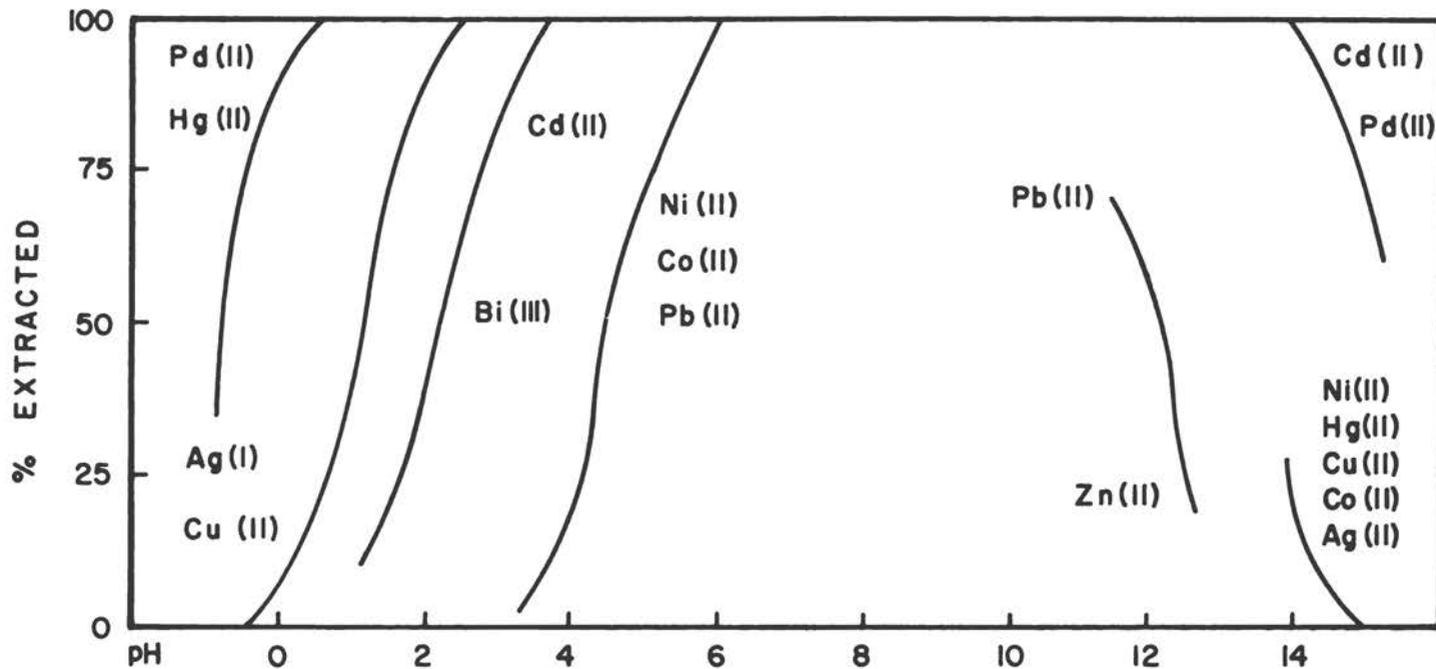


Figure 1 Variation of degree of extraction of dithizonates by carbon tetrachloride, with pH. (Taken from Charlot and Bezier⁵⁵)

Other methods which make use of the extraction of the chelate compound are pyridine in CHCl_3 ,⁵⁹ diethyldithiocarbamate in CCl_4 , sodium malonate,⁶⁰ acetylacetonate and di- β -naphthylthiocarbozone.⁶¹ There are undoubtedly a number of other chelates which are listed in Table III which could be used in a solvent extraction system.

A good treatment of the application of solvent extraction to analytical chemistry is given in a book by Morrison and Freiser.⁶²

8. Ion Exchange Behavior of Cadmium

There are a few very good general references on the ion exchange properties of the elements. A very good bibliography which is segmented into the behavior of the elements as well as many organic classes of compounds is that of Osborn.⁶³ There also is a very good list of references on the theory of ion exchange. This review was made to include all papers up to June 1953. Satisfactory texts on ion exchange are those of Samuelson⁶⁴ and Nachod.⁶⁵ A more recent review of latest developments in ion exchange was done by Kraus and Nelson.⁶⁶ Other new developments include the gradient elution method which continuously changes the concentration of the eluting substance. Another approach is to synthesize an ion exchange resin which has a chelate compound attached to the molecule.⁶⁷ This increases the selectivity of the elution step by introducing another reagent. A similar procedure designed for the separation of cadmium uses cellulose acetate impregnated with dithizone in CHCl_3 .⁶⁸

The usual cation exchangers are the sulfonated phenolic resins (Amberlite IR-100) or the sulfonated hydrocarbon chain or the divinyl benzenes (Amberlite IR-120) (Dowex 50). In addition one can use filter paper, cellulose acetate, alumina, or even

some ionic precipitates as effective cation exchangers. The proton on the acid form will exchange with various cations depending upon the electronegativity and size of the cation. Dowex 50 is the most popular because of its increased stability over the other ion exchange resins. Various eluting agents have been used for cadmium depending upon the form of the cation. For example, the complex ammonium ion is eluted with ammonium citrate⁶⁹ and the complex oxalate is eluted with 1 N HCl.⁷⁰ Cadmium can be separated from an aqueous solution of low ionic strength from the alkali metals with Dowex 50 after elution of the cadmium with 0.70 M HCl.⁷¹ Bonner and Smith⁷² list a selectivity scale for the monovalent and divalent cations on Dowex 50. This selectivity scale is based upon the arbitrary index that the affinity of Li for Dowex 50 is 1. The values appear in Tables IV and V. Koch^{72a} investigated the elution order of divalent cations on Dowex 50. His results are shown in figures 2 and 3. This should aid the experimenter in determining elution order. Cadmium has been satisfactorily separated from uranium with Amberlite IR-120. The uranium is eluted with 0.5 N oxalic acid and the cadmium is eluted with 1 N HCl.⁷³

Some of the more unstable cation exchangers have been used. Riches⁷⁴ suggested the separation of cations Cd, Cu, Mn, Ni and Zn from plant material containing moderately high concentration of $(\text{NH}_4)_3\text{PO}_4$ (0.1 N) using Amberlite 100 to retain the cation. They are then eluted with 1 N HCl.

Yoshino and Kojima⁷⁵ were able to separate Zn from Cd by elution from a cation exchanger (Dowex 50) with different concentrations of chloride ion.

An alumina column has separated the following system containing cadmium: Cu, Cd; Cd, Po; Zn, Cd, Fe; Sb, Cd, Zn.⁷⁶ A surprisingly rapid (2 min.) paper chromatographic separation of

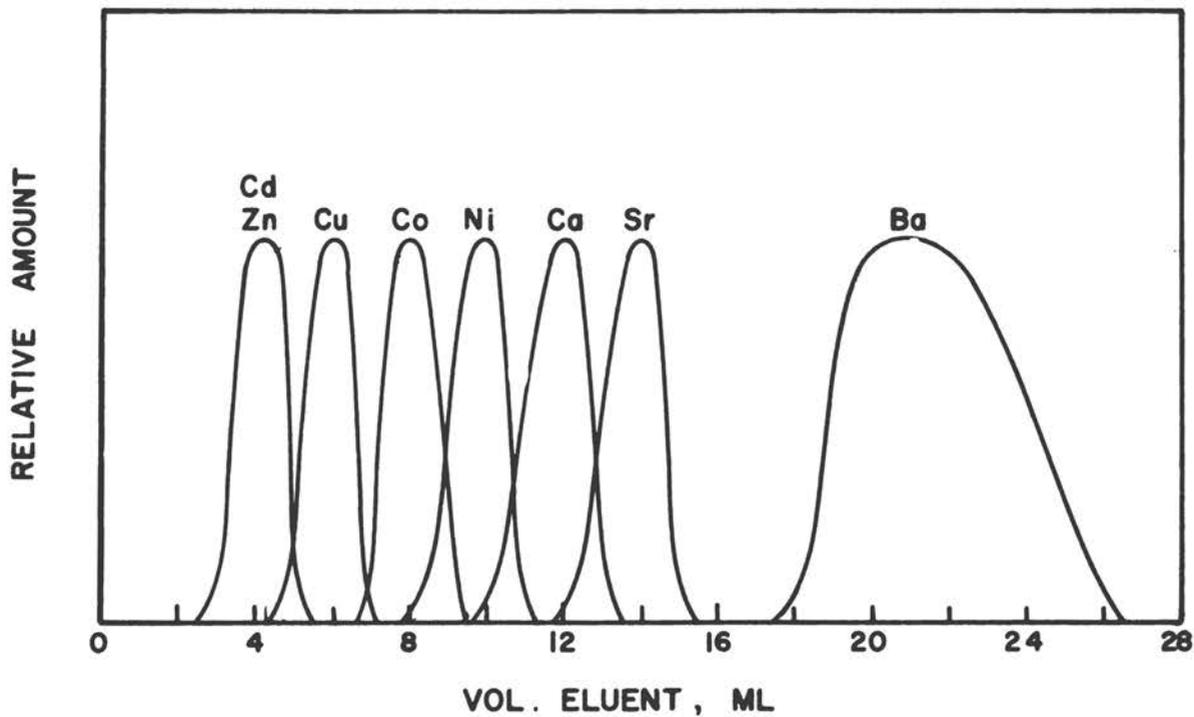


Figure 2 Elution curves for some of the divalent metal ions; 3.1 M HCl used as eluent; ion exchange resin, Dowex 50x4, 200-400 mesh. (Taken from UCRL 2531^{72a}.)

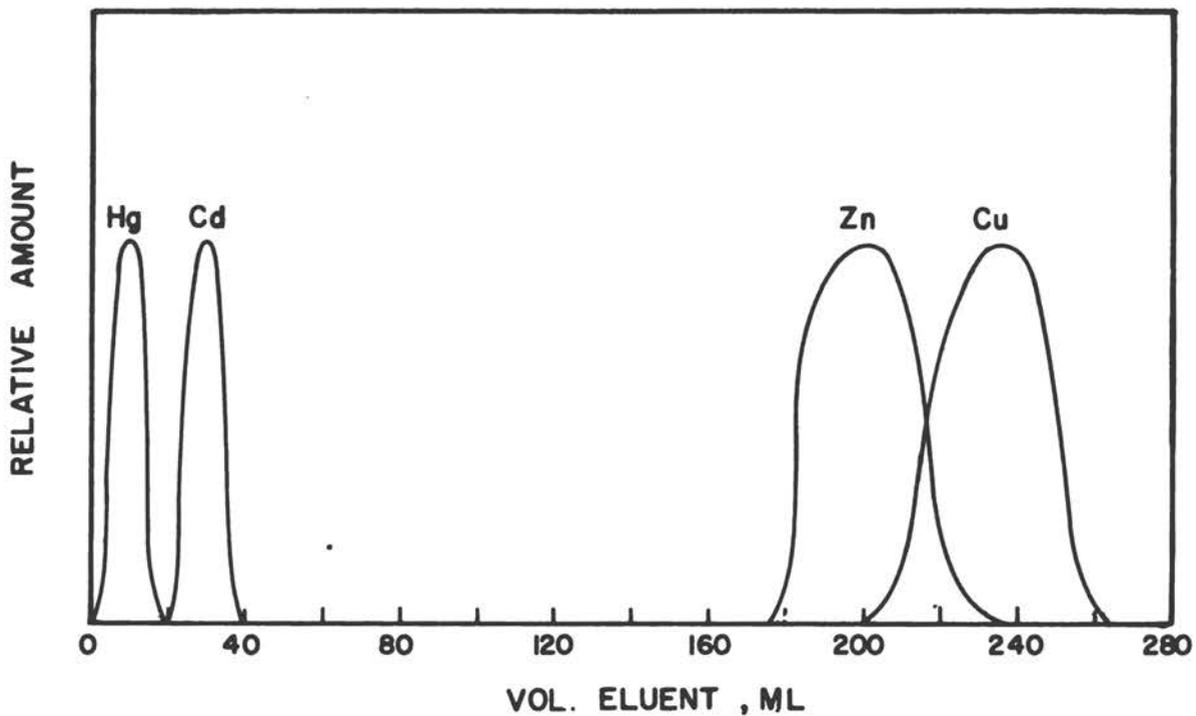


Figure 3 Elution curves for some of the divalent metal ions. 0.4 M HCl used as eluent; ion exchange resin, Dowex 50x4, 200-400 mesh.

(Taken from UCRL 2531^{72a}.)

Table IV. REVISED SELECTIVITY SCALE
FOR UNIVALENT IONS ON DOWEX 50

	4% DVB	8% DVB	16% DVB
Li	1.00	1.00	1.00
H	1.32	1.27	1.47
Na	1.58	1.98	2.37
NH ₄	1.90	2.55	3.34
K	2.27	2.90	4.50
Rb	2.46	3.16	4.62
Cs	2.67	3.25	4.66
Ag	4.73	8.51	22.9
Tl	6.71	12.4	28.5

Table V. SELECTIVITY SCALE FOR
DIVALENT IONS ON DOWEX 50

	4% DVB	8% DVB	16% DVB
UO ₂	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Zn	3.13	3.47	3.78
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Cd	3.37	3.88	4.95
Ni	3.45	3.93	4.06
Ca	4.15	5.16	7.27
Sr	4.70	6.51	10.1
Pb	6.56	9.91	18.0
Ba	7.47	11.5	20.8

cadmium from about 20 contaminating elements has been reported by Warren and Fink.⁷⁷

Kozak and Walton gained partial separation of Cu, Zn, Ni, Cd, Ag and Au on a sulfonated coal cation exchanger.⁷⁸

The effect of a high ionic strength on a cation exchanger is not always predictable. For instance, a very strong anion complex such as AuCl_4^- in a high chloride concentration shows very strong adsorption of the anion on a Dowex 50 cation exchanger.⁷⁹

Anion exchange is more useful with cadmium than cation exchange, because cadmium forms many stable anion complexes. In general, anion exchange is more useful than cation exchange for the following reasons:

1. High ionic strength is an advantage because the complex anion is the interacting species.
2. In order to work with some cations in aqueous solution they must be complexed to prevent hydrolysis, these complexes are usually anions.
3. The amount of reagent in the eluting medium is small. Usually water or a very dilute solution of the complexing agent is used.

The best anion exchange resins are of the strongly basic type like the quarternary ammonium salts (usually chloride) of polystyrene divinylbenzene (Dowex 1 and 2, or Amberlite IRA-400). The most often used method of separating cadmium from the other elements is the use of the chloride complex with Dowex 1 or 2⁸⁰ or Amberlite IRA-400.⁸¹ Kraus and Nelson⁸² have an extensive review of the behavior of most all of the elements in the periodic table with Dowex 2 in hydrochloric acid media. Figure 4 shows that it is possible to gain some separation of Cd from Zn (very difficult to do by other methods) in the region of 0.01 N HCl

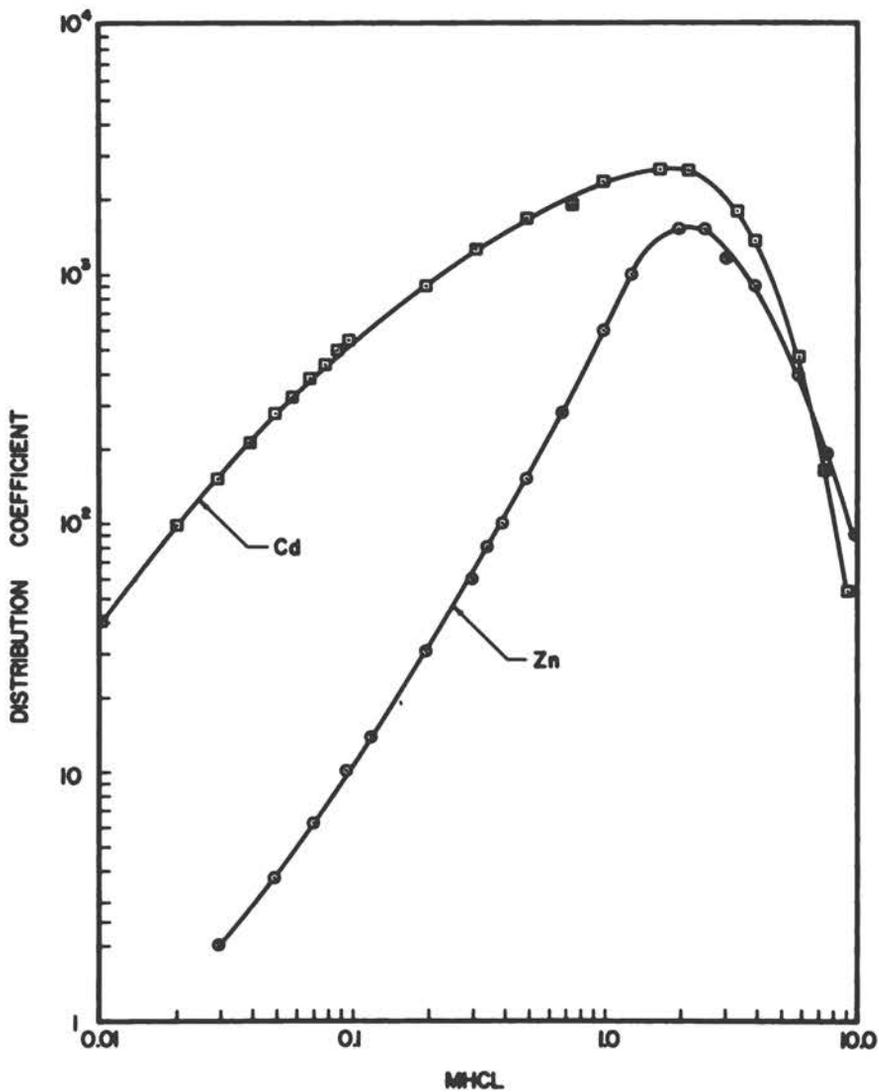


Figure 4 Anion exchange adsorption of Zn(II) and Cd(II). (Taken from Kraus and Nelson⁸³)

eluant.⁸³ Kallman et al.⁸⁴ shows the possibility of this separation. Hicks et al.^{84a} have adsorbed many elements on a Dowex 2 anion exchanger in 12 M HCl and then eluted selectively by altering the species and concentration of the eluant. Cadmium was found to elute in 3 M HClO₄ along with Po and Sb⁺³ or ⁺⁵.⁸⁵ Recently the complex iodide has been used. This is a stronger complex than the chloride and gains separation with less interference from other ions.^{86,87}

It is possible that other complex anions of Cd would find applicability in ion exchange separations; however none have been reported. The use of chelating agents as an ion adjunct to the ion exchange resin to gain selectivity has not been developed sufficiently to allow adequate evaluation of its importance.

V. Dissolution of Cadmium Containing Materials

Most minerals containing cadmium can be readily dissolved by attack with hydrochloric acid, hydrochloric acid followed by nitric acid, or nitric acid alone.⁸⁸ The insoluble residue which ordinarily contains no cadmium can be decomposed by fusion with sodium carbonate followed by solution of the melt in acid. Another attack is discussed by Crouch and Cook⁸⁹ which involves a fusion in a nickel crucible with a mixture of 2 gm potassium nitrate, 1 gm potassium carbonate and 1 gm potassium hydroxide at 500° C for 2 hours. This does not effect complete solution in many cases and use is made of this fact to gain some separation by changing the reagents used to leach the residue. Once the material is broken down into various fractions of lixivated solution containing predictable elements depending upon the type leaching reagent, the general separations (as listed in this document) are used to complete separation of the individual elements.

A very useful procedure for effecting solution of minerals and organic substances including tissue involves the fusion in sodium peroxide and its subsequent solution in acid.⁹⁰ The reaction is carried out in a nickel crucible. Macro amounts of the crucible are dissolved, but this does not in general interfere with the subsequent separations. By using this technique very rapid fusions are accomplished (less than 2 min.) when crushed rock or organic materials are used. Occasionally one finds a sample which combusts with explosive violence and adequate safety precautions (such as the use of heavy plastic shielding) must be taken.

VI. Counting Techniques of the Cadmium Nuclides

The number of radioactive nuclides of cadmium is quite large and their radiations are representative of many types of decay. There is of course very little in the literature on the counting techniques of those nuclides which are not often encountered. Beaufait and Lukens⁹¹ have compiled excellent information on the counting procedures for some of the common nuclides for each element.

Since $\text{Cd}^{115\text{m}}$ is the longest lived, and has both β^- (98%) and γ (2%) emission, it makes a suitable tracer and can be counted in either a scintillation well or Geiger Müller counter. The absolute counting efficiency of the standard well counter (NaI crystal dimensions 1 3/4" dia. x 2" thick, well 3/4" dia. x 1 1/2" deep) is about 10%, and of the Geiger Müller with the sample 1 cm from the window is about 7%. A gamma ray spectrum of $\text{Cd}^{115\text{m}}$ and Cd^{115} are shown in figures 5 and 6.⁹²

If one has Cd^{115} it is desirable to delay counting about 16 hours to allow the $\text{In}^{115\text{m}}$ daughter to grow into equilibrium. It has been found by Cuninghame et al.⁹³ that there is a measurable self absorption of a cadmium 8-hydroxyquinolate precipitate when

using a proportional counter with Cd^{115} . When a scintillation well counter is used for a strong β^- emitter such as $\text{Cd}^{115\text{m}}$, the Bremsstrahlung is very great and since the counting efficiency of the scintillator is greater for Bremsstrahlung than the proportional or Geiger Müller (G/M) counter, the self absorption effect is not as apparent. For very precise absolute counting, however, the G/M counter corrected for self absorption should be used since Cd^{115} and $\text{Cd}^{115\text{m}}$ are primarily β^- emitters. The same effect is even more apparent in $\text{Cd}^{113\text{m}}$ since it decays with lower β^- energy. Cd^{109} decays by electron capture with accompanying characteristic x-rays. In addition a gamma ray of 0.087 Mev. has been measured. It does not decay by β^- and therefore the use of G/M type counters is not as efficient as the use of scintillation or x-ray counters. The same applies to the measurement of Cd^{117} and $\text{Cd}^{117\text{m}}$ which are primarily gamma emitters.

VII. Collected Radiochemical Separation Procedures for Cadmium

The radiochemical separation procedures which have been used in the past can be subdivided according to the type of mixture from which the separation is to be made. References to other separations of the same type which are not discussed in detail here are:

1. Separations of cadmium from the fission products.⁹⁴⁻⁹⁸
2. Separations of cadmium from Cd metal targets.⁹⁹⁻¹⁰²
3. Separations of cadmium from Ag metal targets.^{103,104}
4. Separations of cadmium from Th metal targets.¹⁰⁵

In the following pages are listed several of the better detailed procedures for each of the categories listed above.

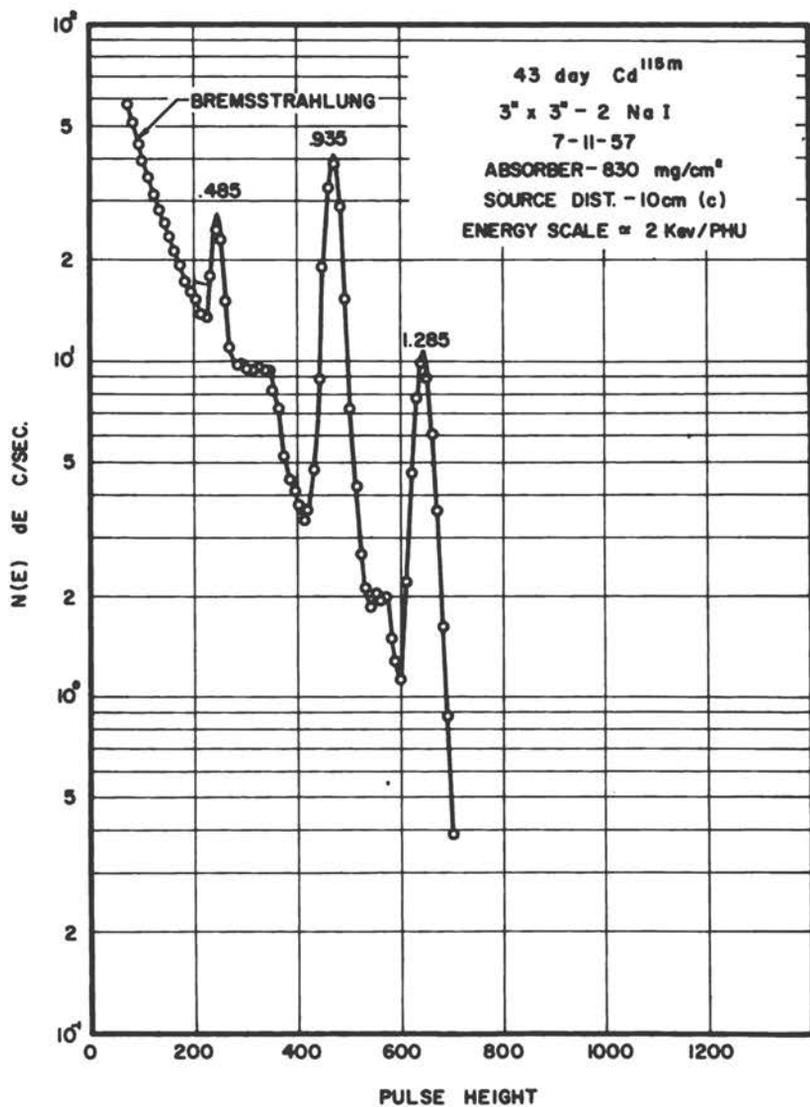


Figure 5 Gamma ray spectrum of $Cd^{115}-In^{115}$.
 (Taken from IDO 16408 ⁹²)

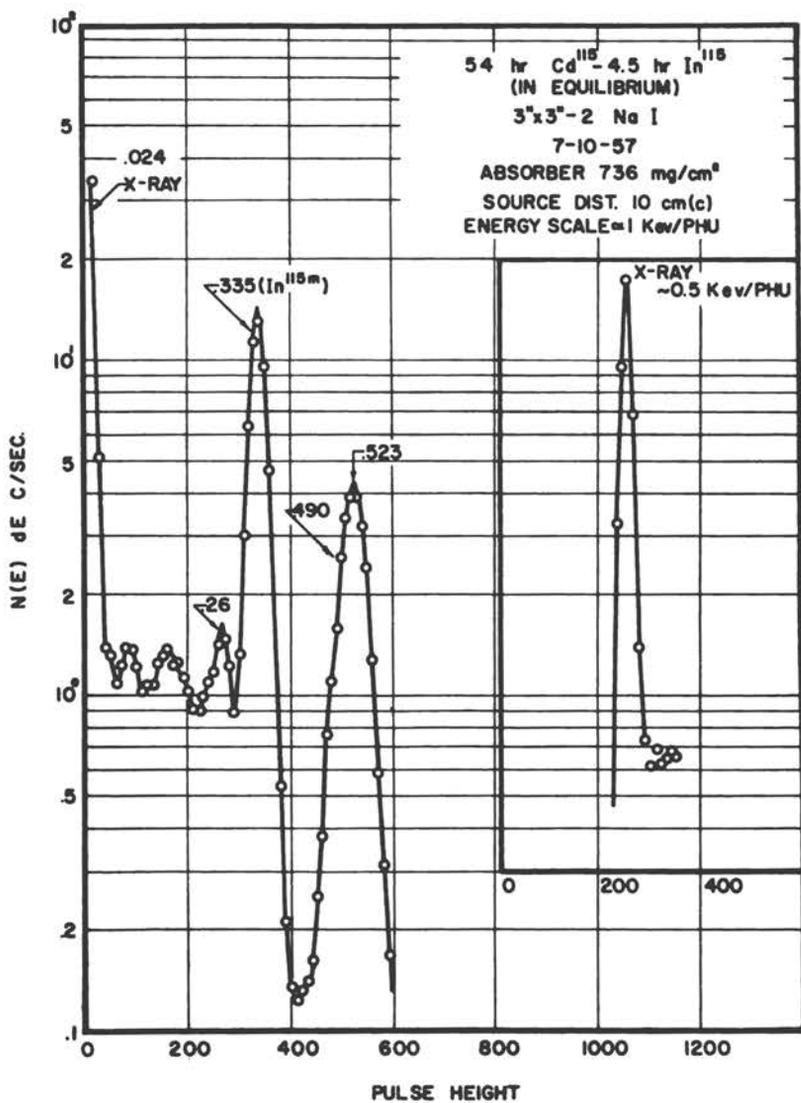


Figure 6 Gamma ray spectrum of Cd^{115m}.
 (Taken from IDO 16408 ⁹²)

PROCEDURE 1 (Cont'd.)

Gold	0.4%	Selenium	0.01%
Indium	0.5%	Silver	2%
Iodine	0.06%	Tantalum	0.6%
Iridium	0.1%	Thallium	91%
Mercury	0.1%	Tin	0.3%
Nickel	0.1%	Zinc	64%
Palladium	0.1%	Zirconium	0.1%
Ruthenium	0.03%		

2. Dithizone is known to react with a great many of the heavy metals, but cadmium is almost unique in being able to form a stable dithizonate in strongly basic solution.

3. Of the twenty-three elements listed above only silver, copper, thallium and zinc contaminate the separation. Presence of 1 M ammonium hydroxide in the original solution satisfactorily complexes the silver preventing contamination, but contamination by the other three elements is not affected. When the basicity is increased to 0.5 M sodium hydroxide, the copper contamination is reduced to about 0.1%. The increased basic strength often reduces the strength of the dithizonate bond. This is probably caused by increased solubility of the dithizone in the basic aqueous layer, thereby displacing the equilibrium toward dissociation of the dithizonate. Unfortunately the yield of cadmium is also reduced to about 50% by this step.

The contamination of thallium can be conveniently removed by utilizing a displacement reaction.¹⁰⁶ An equal volume of a solution made up with 0.1 gm of cobalt nitrate, 5.0 gm sodium acid tartrate, and 4.0 gm sodium acid carbonate in one liter of water is agitated with a chloroform solution of the cadmium and thallos dithizonate. The cobalt displaces the thallium to form

PROCEDURE 2 (Cont'd.)

3. Percent of foreign ion carried with cadmium:

Antimony	4.6%	Mercury	36%
Barium-Lanthanum	0.03%	Ruthenium	0.12%
Cerium	0.01%	Selenium	0.01%
Cesium	0.007%	Silver	89%
Chromium	0.02%	Tantalum	0.005%
Cobalt	0.007%	Thallium	0.007%
Indium	0.3%	Tin	0.3%
Iodine	0.1%	Zinc	81%
Iridium	0.015%	Zirconium	0.03%

The impurities elute in the first 6 free volumes, while the cadmium does not elute until 9 free volumes have been collected.

4. Ion exchange can be used to separate zinc, mercury and silver from cadmium by replacing the ammonium hydroxide eluant with distilled water. In this modified procedure the yield of cadmium was found to be about 55%, with a contamination of 1.0, 0.5 and 0.3% for zinc, mercury and silver respectively.

5. Special care must be taken in the case of thallium to insure that it is all present in the +1 state. This is accomplished by heating the solution with 0.1 M sodium bisulfite.

PROCEDURE 3

Source - DeVoe, J. R., Meinke, W. W., Anal. Chem.,
31, 1428 (1959)

Precipitation

Element separated: Cadmium Time for sep'n: 30 min.

Target material: Misc. activities Equipment required: standard

Yield: ~ 78%

Degree of purification: Decontamination factor up to 3×10^3
 per cycle depending upon elements present

PROCEDURE 3 (Cont'd.)

Advantages: Separates from zinc

1. Procedure

Step 1. To the original solution add 10 mg of carrier of each contaminating element. Mix to secure exchange in a 15 ml centrifuge cone.

Step 2. Add 10 mg of cadmium carrier and 2 ml of thiourea (5 gms/100 ml water). Add 5 ml of 2 M hydrochloric acid and dilute to a total volume of 10 ml.

Step 3. While stirring add 2.5 ml of Reinecke salt solution (4 gms/100 ml water). $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4] \cdot \text{H}_2\text{O}$. Available Eastman Kodak Co.

Step 4. Continue stirring for 5 minutes and centrifuge for 5 minutes.

Step 5. Remove the supernate and wash with 10 ml of a 1% (by weight) thiourea solution in 1 N hydrochloric acid. Stir for 5 minutes.

Step 6. Filter the solution onto a paper disc, mount and count or centrifuge for 5 minutes, remove the supernate and slurry the precipitate into a culture tube for counting in a scintillation well counter.

2. Remarks

1. The original solution can be up to 1 M in hydrochloric acid. Small amounts of perchloric, nitric or sulfuric acid (<.1 N) do not interfere.

2. Percent of foreign ion carried with cadmium (one cycle):

Antimony	3%	Chromium	0.2%
Barium-Lanthanum	0.06%	Cobalt	0.05%
Cerium	.03%	Indium	0.1%
Cesium	0.8%	Iodine	0.7%

PROCEDURE 3 (Cont'd.)

Iridium	0.08%	Tantalum	0.06%
Mercury	46%	Thallium	99%
Ruthenium	0.28%	Tin	0.83%
Selenium	93%	Zinc	0.6%
Silver	99%	Zirconium	0.04%

Silver and thallium undoubtedly precipitate as the chloride. The use of nitric acid for these elements does not, however, improve the separation because they, along with mercury, also form insoluble Reineckates. Selenium is found to be reduced by the thiourea to the metallic state. Removal of thiourea will lower the contamination of selenium, but at the same time the overall contamination may increase because of the loss of crystallinity in the precipitate.

With thiourea the cadmium precipitate is rose in color and is very granular and crystalline. Ammonium Reineckate when dissolved in distilled water, slowly decomposes on standing to give the greenish blue chromium ammonium complex. Thus a solution of the ammonium Reineckate (5 ml. of 4 gm/100 ml) was unable to precipitate 10 mg. of cadmium in 5 ml. of water 72 hours after preparation. The precipitation was quantitative, however, if the reagent was used during the first 24 hours after preparation and if a 10% excess of reagent was used.

PROCEDURE 4

Source - DeVoe, J. R., Thesis, University of Michigan,
Feb. 1960; Submitted Anal. Chem. 1959

Vacuum Distillation of Metals

Element separated: Cadmium	Time for sep'n: 30 min.
Target material: Misc. activities	Equipment required: Distillation apparatus which consists of an evacuated chamber into which a liquid nitrogen cooled cold finger protrudes to collect the vapor ejected from a long cylindrical carbon rod heated by induction.
Yield: 74%	(For details see source.)
Degree of purification: Up to 10^4 depending upon elements present	
Advantages: Selective, particularly from those elements which contaminate chemically	

1. Procedure

Step 1. To a solution which is 0.1 to 0.2 M in either HCl or HNO_3 with the radioactive contaminants present, add 1 mg of inactive Cd to give a total volume of 2 ml.

Step 2. Insert a platinum wire anode and a copper foil (1/2 cm wide by 10 mils thick) cathode into the solution.

Step 3. Allow current to pass at 6 Volts (negligible current) for 20 minutes.

Step 4. Remove the copper foil and wash in H_2O and acetone. Cut out the deposited area on the foil and place in a scintillation well counter to measure the contamination in the electrolysis step.

Step 5. Place the foil in the furnace of the distillation apparatus and heat to 180°C for 5 min. after equilibrium pressure (6×10^{-5} mm Hg) is obtained.

Step 6. The area of the teflon film collector upon which the cadmium condensed is cut away and placed in a tube for counting in a scintillation well counter.

PROCEDURE 4 (Cont'd.)

2. Remarks

1. Percent of foreign ion carried with cadmium:

<u>Element</u>	<u>Amount</u>			
	<u>mg.</u>	<u>Electrolysis</u>	<u>Distillation</u>	<u>Overall</u>
Ag ¹¹⁰	0.032	40	0.7	0.28
Ce-Pr ¹⁴⁴	C.F.	33	0.01	0.003
Cs ¹³⁴	0.01	0.1	3	0.003
Co ⁶⁰	0.007	26	0.1	0.03
Ir ¹⁹²	0.006	33	0.03	0.01
Se ⁷⁵	0.014	100	0.05	0.05
Ru-Rh ¹⁰⁶	0.008*	20	0.05	0.01
Tl ²⁰⁴	0.36	66	2.5	1.6
Zn ⁶⁵	0.36	22	1.3	0.29
Zr-Nb ⁹⁵	0.03	1.2	0.01	0.00012

* Solution of chloride converted to sulfate so that final concentration is 0.1 N H₂SO₄.

PROCEDURE 5

Source - Beaufait, L. S., Lukens, H. R., U. S. Atomic Energy Commission, Rept NP-5057 (March 1952)

Precipitation

Element separated: Cadmium Equipment required: standard

Target material: general

1. Procedure

Step 1. To the solution containing the cadmium activity in a volume of 10-15 ml (in a 40-ml heavy-walled glass centrifuge tube), add cadmium carrier. Stir thoroughly and adjust the pH to 7 with NH₄OH. Saturate the solution with H₂S, centrifuge

PROCEDURE 5 (Cont'd,)

and wash the CdS once with 5 ml of water. Discard the supernate and wash solution.

Step 2. Dissolve the CdS with 1 ml of 6 N HCl. Boil off the H₂S and dilute to 8 ml. Add 5 mg of Fe⁺⁺⁺, stir, and then precipitate Fe(OH)₃ with the addition of 6 N NH₄OH. Centrifuge and wash once with 5 ml of water containing three drops of NH₄OH. Combine the supernate and wash solution. Discard the Fe(OH)₃ precipitate.

Step 3. Acidify the combined supernate and wash solution with HCl, add 5 mg of Fe⁺⁺⁺, stir and precipitate Fe(OH)₃ with the addition of 6 N NH₄OH. Centrifuge and wash as in step 2. Combine the wash solution with the supernate in a 50-ml lusteroid tube. Discard the Fe(OH)₃ precipitate.

Step 4. Adjust the solution with the dropwise addition of HCl to a pH of 1 and add 10 mg of La⁺⁺⁺ carrier. Stir and add 0.5 ml of HF. Stir thoroughly, centrifuge, and decant the supernate into a clean 40-ml glass tube. Neutralize the solution with NH₄OH and saturate with H₂S. Centrifuge the CdS and wash once with 5 ml of water containing 1 drop of HCl. Discard the supernate and wash solution.

Step 5. Dissolve the CdS with 4 ml of 6 N HCl. Boil the solution to expel the H₂S and dilute to 10 ml with water. Add 5 ml of Ag⁺ carrier and centrifuge. Add 10 mg of Pd⁺⁺ carrier, stir, heat the solution to 70° C and precipitate PdS with H₂S. (Note 1). Add a pinch of filter aid pulp, stir thoroughly, and centrifuge. Add 10 mg of Sb carrier, stir, heat the solution to 70° C and precipitate Sb₂S₃ with H₂S (Note 1). Centrifuge and wash the Sb₂S₃ once with 5 ml of 3 N HCl. Combine the supernate and wash solution.

PROCEDURE 5 (Cont'd.)

Step 6. Repeat the Pd scavenge with the addition of 10 mg of Pd^{++} carrier and using the conditions set forth in step 5.

Step 7. Filter the combined supernates from step 6 through a funnel containing a Whatman No. 42 filter paper and neutralize to pH 7 with the dropwise addition of NH_4OH . Saturate the solution with H_2S and centrifuge. Wash the CdS precipitate once with 5 ml of water. Discard the supernate and the wash solution.

Step 8. Dissolve the CdS in 1 ml of HCl and boil off the H_2S . Filter the solution (with water washing) through a funnel containing a Whatman No. 42 filter paper; do not allow the final volume of the filtrate to exceed 15 ml. Dilute the volume of the filtrate to 15 ml with water if necessary. Add 1.5 ml of 3 N NH_4Cl and adjust the pH to 7 by the dropwise addition of 6 N NH_4OH . Add 1.5 ml of 1.5 N $(\text{NH}_4)_2\text{HPO}_4$ and digest in a hot-water bath for fifteen minutes. Maintain a pH of 7 throughout the digestion by the addition of NH_4OH or HCl if necessary.

Step 9. Prepare a Whatman No. 42 paper disc by washing with water and drying in an oven at $90-100^\circ\text{C}$ for ten minutes. Cool the paper for ten minutes in a desiccator and weigh. Repeat this procedure until the weighings agree to within 0.1 mg.

Step 10. Filter the precipitate through the prepared filter paper disc. Wash with five 5-ml portions of water. Dry at $90-100^\circ\text{C}$ to a constant weight as in step 9. Weigh as $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$.

Step 11. Mount, and after 16 hours count (Note 2). See Volume I, Section 1, "Counting Instructions" for Cadmium and $\text{Cd}^{115\text{m}}$ Growth Curve, Section 2.

2. Notes

1. The solution should be 2-3 N in HCl to prevent CdS from precipitating.

PROCEDURE 5 (Cont'd.)

2. Cd-115 (In-115) transient equilibrium is in effect after 16 hours.

PROCEDURE 6

Source - Wilkinson, G., Grummit, W. E., Nucleonics,
9 (3), 52-62 (1951)

Precipitation

Element separated: Cadmium	Time for sep'n: ?
Target material: General	Equipment required: Standard
Yield: 50-60%	Degree of purification: ?

1. Procedure

Step 1. Dissolve oxide in fuming nitric acid. Convert to chloride, add carriers of Cd, In, all other sulfide group elements, X, La, Ce, Ba, Sr, Zr, Rb and Cs. Adjust acidity to 0.5 N HCl. Precipitate with H_2S . Remove ppt.

Step 2. Boil to expel H_2S and add carrier of As, Ge, Se, Mo, Ra, Rh, Pd, Ag, Sn, Sb and Te and reprecipitate and remove ppt as before.

Step 3. Add ammonium acetate and acetic acid to the filtrate and ppt CdS and InS_3 with H_2S . Dissolve in cold 1 N HCl sufficient to give .1 mg/ml of each metal.

Step 4. Add carrier of Ru, Sn, Sb, Se, Te, V, La, Ce, Zr, Ba, Sr and Cs and separate In and Cd sulfides by pptn.

Step 5. Dissolve the Cd and In sulfides in 1 N HCl. Repeat steps 4 and 5 until there is no activity in the precipitates.

Step 6. To the 1 N HCl solution of Cd and In carriers of Ce, La, V, Ba, Sr, Zr, Nb and Cs were added. The solution is made slightly alkaline with ammonia and then faintly acid with HCl.

PROCEDURE 6 (Cont'd.)

Step 7. Excess solid sodium acetate was added to the solution and the mixture boiled for a few minutes. This precipitates the indium basic acetate. The precipitate is dissolved in dilute acid and is reprecipitated.

Step 8. The cadmium is recovered from the filtrate by precipitating the sulfide in 0.2 N acid with carriers La, Ce, X, Zr, Ba, Sr and Cs present.

Step 9. Redissolve and precipitate the cadmium with either allyliodidehexamine (5% aq. soln.) or with phenyltrimethylammonium iodide (2% aq. soln. containing 5% KI) in the presence of rare earth. Zr, Ba, Sr, Cs and In hold back carriers.

2. Remarks

1. In step 6 any precipitate of Zr or Nb, etc. was removed at this stage.

2. In step 9 Ag, Sb, and Pd interfere with the separation by precipitating their iodides.

PROCEDURE 7

Source - Hicks, H. G., U. S. Atomic Energy Commission,
Report UCRL 4377 (Aug. 1954)

Precipitation, Ion Exchange

Element separated: Cd ¹¹⁵	Time for sep'n: 4 hours
Target material: Uranium	Equipment required: Standard
Yield: 70%	Type of bdbt: neutron
Degree of purification: 10 ¹¹ atoms of Cd ¹¹⁵ from 10 ¹⁵ fission showed no detectable contamination when decay was followed over 3 half lives.	

1. Procedure

Step 1. To an acid solution of the activity, add 10 mg Cd⁺⁺. Add several milligrams of Fe⁺⁺⁺, Mo⁺⁶, and one drop of NaNO₂. Make basic with NH₄OH.

PROCEDURE 7 (Cont'd.)

Step 2. Centrifuge and discard precipitate. Reacidify supernatant, add several mg Fe^{+++} and repeat step 1.

Step 3. Discard precipitate and decant supernatant into a 125-ml Erlenmeyer flask. Boil to remove NH_3 and add NaOH pellets until $\text{Cd}(\text{OH})_2$ precipitates. Wash precipitate twice with water.

Step 4. Dissolve precipitate in 2 M HCl and add Pd and Sb carriers. Saturate with H_2S and discard precipitate.

Step 5. Boil H_2S from the supernatant and pass solution through a Dowex A-2 resin column 5 mm x 10 cm. Wash column with 10 ml 0.1 M HCl. Discard effluent.

Step 6. Through the column pass 15 ml 1.5 M H_2SO_4 , collecting the eluate in a 40-ml centrifuge cone. Transfer eluate to a hot bath and dilute to 30 ml with water.

Step 7. Saturate with H_2S while hot and digest precipitate for several minutes.

Step 8. Repeat steps 4 through 7.

Step 9. Wash precipitate twice with water, twice with acetone, dry, and weigh as CdS.

PROCEDURE 8

Source - Lee and Cook, U. S. Atomic Energy Commission,
Rept AERE, C/R-430

Precipitation-Distillation and Electrodeposition

Element separated: Cadmium	Time for sep'n: ~ 2 hours
Target material: UO_2SO_4	Equipment required: Standard
Yield: ?	Type of bbd: neutron
Degree of purification: ?	

1. Procedure

Step 1. Dissolve the target in H_2O ; add 10 mg of carriers

PROCEDURE 8 (Cont'd.)

Ru, Rh, Te, Ag, Sb, Sn, and Cd. Total solution should be 2-3 N in HCl.

Step 2. Precipitate Ag, Ru, Sb, Te and Rh with H_2S . Make filtrate basic with NaOH and then add just enough HCl to dissolve uranium hydroxide.

Step 3. Precipitate Cd, Sn and remaining Sb with H_2S .

Step 4. Dissolve the sulfide precipitates in aqua regia and convert to sulfates by evaporating to SO_3 fumes after adding conc. H_2SO_4 .

Step 5. Selectively deposit on a copper plated platinum cathode the antimony (at -0.25V to -0.40V) and tin (at -0.55 V to -0.70V).

Step 6. Make the solution ammoniacal before removing the cathodes.

Step 7. Readjust the solution to acid by evaporating the ammonia and adding HCl dropwise.

Step 8. Electrolyze the cadmium onto a copper plated platinum cathode at -0.80V to -0.9V.

2. Remarks

1. In step 2 if a cloudy filtrate occurs heat with a dilute $KClO_3$ soln.

2. This separation is satisfactory for Sn and Sb also if selective potential is used.

3. The ammoniacal soln. in step 6 prevents the Sn from dissolving in the HCl.

PROCEDURE 9

Source - Maxwell et al., U. S. Atomic Energy Commission,
Rept UCRL 404 (Aug. 1949)

Extraction

Element separated: Cadmium Time for sep'n: 4-5 hrs.
Target material: Silver metal Equipment required: Standard
Yield: 80-95% Type of bbd: 60" D₂
Degree of purification: At least factor of 100
Advantages: Carrier-free. Suitable for use in biological systems.

1. Procedure

Step 1. Dissolve the silver turnings in a minimum volume of 16 N HNO₃ and evaporate solution to dryness on a steam bath.

Step 2. Dissolve in 25 ml H₂O and add excess NH₄CNS to complex the silver.

Step 3. Adjust the solution to pH 5 with sodium acetate and extract the cadmium activity with chloroform containing 5% pyridine.

To remove traces of silver:

Step 4. Evaporate chloroform phase to dryness on a steam bath.

Step 5. Redissolve in 2-3 ml of 1% H₂SO₄ and extract with 0.005% dithizone in chloroform.

2. Remarks

1. The target was a 1/4-inch thick block of spectrographically-pure silver (obtained from Johnson Mathey and Co. -- no Cd was detected by spec. analysis) soldered to a water-cooled copper plate. The bombarded surface of the silver was removed from the target by milling off to a depth of 1/8 inch.

2. This procedure, originally developed for the separation of micro amounts of cadmium (H. Fischer and G. Leopoldi, Mikro-

PROCEDURE 9 (Cont'd.)

chim Acta, 1, 30 (1937) quantitatively extracted Cd^{109} from solutions containing presumably less than 10^{-8} grams available cadmium.

3. The final solution of Cd^{109} contained less than one microgram of silver.

4. Radioactive palladium also formed in the bombardment, is not extracted with cadmium by this procedure.

PROCEDURE 10

Source - Meinke, W. W., U. S. Atomic Energy Commission,
Rept UCRL 432 (Aug. 1949)

Extraction, Precipitation

Element separated: Cadmium

Time for sep'n: 2-3 hours

Target material: Cd
(separated isotopes)

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

Type of bdbt: Deuterons and
protons - 60"

Yield: ~ 90%

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

Advantages: Good separation

1. Procedure

Step 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 .

Step 2. Add 3-4 mg In and 3-4 mg Ag as the nitrate sol'ns and dilute to ~ 10 ml with H_2O .

Step 3. Add 1 N HCl dropwise until the Ag is completely pptd as AgCl . Coagulate the ppt by heating and filter through

PROCEDURE 10 (Cont'd.)

a small No. 42 Whatman filter paper in a short-stemmed glass funnel. The filtrate contains the Cd and In fractions. (The AgCl ppt is worked up separately as described in the procedure for Ag from Cd targets, No. 47-3).

Step 4. Make the filtrate ammoniacal and add another 3-4 mg Ag as the nitrate soln. Acidify with HNO_3 and add a few drops of 1 N HCl to insure complete pptn of AgCl. Coagulate the ppt by heating, filter on No. 42 paper, and discard.

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

Step 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 soln which remain in the stopcock after separation of layers. (The In is contained in this organic layer and is worked up separately as described in the procedure for In from Cd targets, No. 49-1).

Step 7. Add 3-4 mg In as the nitrate soln to the H_2O layer remaining in the first funnel. Repeat the extractions as outlined in step 6 above, but this time discard the three organic layers containing the scavenger In.

Step 8. Draw the H_2O layer into a beaker, boil off residual CH_3Cl , and add NH_4OH to ppt Cd as the 8-hydroxyquinolate. Filter through a No. 42 Whatman paper disc held in a Gooch crucible or Hirsch funnel. Suck the sample on the paper as dry as possible and then complete the drying under a heat lamp before mounting under tape.

PROCEDURE 10 (Cont'd.)

2. Remarks

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

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

PROCEDURE 11

Source - Meinke, W. W., U. S. Atomic Energy Commission,
Rept UCRL 432 (Aug. 1949)

Precipitation

Element separated: Cadmium	Time for sep'n: ~ 2 hours
Target material: Sb (~ .5 gm metal)	Equipment required:
Type of bbd: 184" α and D ₂	Lusteroid tubes, centrifuge, cones, tank H ₂ S, SO ₂
Yield: 50% or greater	
Degree of purification: At least factor of 100.	

1. Procedure

Step 1. To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc. HNO₃ dropwise until dissolved (10 min.) Dilute to ~ 20 ml.

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

Step 3. Divide supernatant into two equal parts.

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

Step 5. Boil the supn. to expel SO₂, add 5 ml H₂O.

Step 6. Saturate hot with H₂S until Sb₂S₃ pptn complete.

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

PROCEDURE 11 (Cont'd.)

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

Step 9. Repeat NaOH pptn, dissolve and make to 15 ml in 2 N HCl.

Step 10. Add 5 mg Sb^{+++} , 2 mg $\text{TeO}_3^=$ and saturate with H_2S .

Step 11. Boil supn. to expel H_2S . Add excess NH_4OH .

Centrifuge.

Step 12. To the supn. containing the Cd $(\text{NH}_3)_4^{++}$ complex add 2 mg In^{+++} . Centrifuge off the $\text{In}(\text{OH})_3$ ppt.

Step 13. Saturate supn. with H_2S . Centrifuge CdS ppt.

Step 14. Dissolve CdS in HCl.

Step 15. Dilute an aliquot of solution to 15 ml. Add 11 ml 3 M NH_4Cl , 1 ml 1.5 M $(\text{NH}_4)_2\text{HPO}_4$ and weigh the $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ppt formed.

PROCEDURE 12

Source - Meinke, W. W., U. S. Atomic Energy Commission,
Rept UCRL 432 (Aug. 1949)

Precipitation

Element separated: Cadmium Time for sep'n: ~ 2 hrs.

Target material: ~ 1 g Bi metal Equipment required: Centri-

Type of bbd: 184" all particles fuge, tubes, H_2S tank,
110° oven

Yield: ~ 70%

Degree of purification: Decontamination factor $>10^4$ from fission and spallation products.

Advantages: Good yield of pure Cd

1. Procedure

Step 1. To aliquot of HNO_3 soln of target add 10 mg Cd and make basic with NH_3 , centrifuge out $\text{Bi}(\text{OH})_3$.

Step 2. Add 10 ml concentrated HCl to supernatant and

PROCEDURE 12 (Cont'd.)

evaporate to dryness. Take up in 20 ml 0.2 N HCl and saturate with H_2S . Wash CdS with H_2S water.

Step 3. Dissolve CdS in 1 ml 6 N HCl, boil out H_2S , dilute to 10 ml, add 5 mg Fe^{+3} and 6 N NH_4OH^- dropwise until $Fe(OH)_3$ precipitation begins. Redissolve 1-2 drops HCl, heat, add 4-5 drops 6 N CH_3COONH_4 , centrifuge out basic ferric acetate precipitate.

Step 4. Add 10-15 drops 6 N HCl to supernatant and precipitate CdS.

Step 5. Dissolve CdS in HCl and expel H_2S , add several mg In and precipitate with NH_3 .

Step 6. Re-acidify and precipitate CdS.

Step 7. Dissolve CdS in 2 ml 6 N HCl, dilute to 10 ml, add 10 mg Pd^{+2} , heat, and saturate with H_2S .

Step 8. Add 5 mg Sb^{+3} to supernatant and scavenge with Sb_2S_3 .

Step 9. To supernatant add excess NH_4OH and saturate with H_2S .

Step 10. Dissolve CdS in a few drops of HCl, expel H_2S , dilute to 15 ml, add 2 ml 3 M HCl, boil, add 2 ml 1 M $(NH_4)_2HPO_4$, and digest hot 15 min. Filter, wash with H_2O , dry 10 min. at $110^\circ C$. Weigh as $CdNH_4PO_4 \cdot H_2O$ (21.66 mg per 10 mg Cd).

PROCEDURE 13

Source - Nervik, W. E., U. S. Atomic Energy Commission
Rept UCRL 2542 (Sept. 1954)

Precipitation, Ion Exchange

Element separated:	Cadmium	Time for sep'n:	?
Target material:	Ta	Equipment required:	standard
Yield:	?	Type of bbd:	p(340 Mev)
Degree of purification:	Purification factor $\sim 10^4$		

PROCEDURE 13 (Cont'd.)

1. Procedure

Step 1. Dissolve the Ta foil in concentrated HF-HNO₃ (1/1) in a lusteroid tube and add Cd and Ce carriers.

Step 2. Centrifuge the rare earth fluorides.

Step 3. Make the centrifugate 18 N in H₂SO₄, extract Ta with di-isopropyl ketone. Evaporate the aqueous layer to dryness.

Step 4. Dissolve the residue in water; add Fe carrier and make soln basic with NH₄OH. Centrifuge.

Step 5. Precipitate CdS with H₂S. Centrifuge and dissolve ppt. in 2 NHCl. Add Cu carrier; precipitate the sulfide and centrifuge.

Step 6. Add Zn carrier and boil the centrifugate. Pass through a column of Dowex A-2 anion exchanger; wash resin with 0.1 N HCl.

Step 7. Elute the cadmium with 1.5 N H₂SO₄.

Step 8. Precipitate CdS with H₂S from the eluant. Repeat the anion exchange step without carrier.

Step 9. Adjust the final eluant (1.5 N H₂SO₄) to pH 4 with NH₄OH. Boil. Add (NH₄)₂HPO₄. Centrifuge. Wash with H₂O and ethanol. Dry at 110° C and weigh as Cd(NH₄)PO₄·H₂O.

2. Remarks

1. In step 6 volatilize H₂S.
2. In step 6 the cadmium is adsorbed.
3. In step 6 the zinc is a hold back carrier.

PROCEDURE 14

Source - Glendenin, L. E., National Nuclear Energy Series IV,
Vol. 9, McGraw-Hill Co., New York (1951), p. 1575

Precipitation

Element separated: Cadmium Time for sep'n: ?
Target material: plutonium Equipment required: standard
Yield: -- Type of bdbt: neutron
Degree of purification: Decontamination factor 10^6 from remain-
ing fission product activity

1. Procedure

Step 1. Add 10 ml of conc. HCl and 20 mg of cadmium carrier to the sample, and evaporate just to dryness. Take up the residue in 20 ml of 0.2 M HCl and saturate with H₂S. Centrifuge, and wash the CdS precipitate.

Step 2. Dissolve the precipitate in 1 ml of 6 M HCl, dilute to 10 ml, and add 5 mg of iron carrier and 6 N NH₄OH in drops until Fe(OH)₃ just begins to precipitate. Dissolve the precipitate with 1 or 2 drops of HCl, heat to boiling, and add 4 or 5 drops of 6 M NH₄C₂H₃O₂. Centrifuge, and discard the precipitate.

Step 3. Add 10 to 15 drops of 6 M HCl to the solution and pass in H₂S. Centrifuge, and wash the CdS precipitate.

Step 4. Repeat steps 2 and 3. Dissolve the CdS in 2 ml of 6 M HCl and dilute to 10 ml. Add 10 mg of palladium carrier, heat, pass in H₂S, and centrifuge. Discard the PdS precipitate, add 10 mg of palladium carrier to the solution, and repeat the precipitation of PdS.

Step 5. Add 2 ml of 6 N NH₄OH to the solution and pass in H₂S. Centrifuge, and wash the CdS.

Step 6. Dissolve the CdS precipitate in a few drops of HCl, heat to expel H₂S, dilute to 15 ml, add 1.5 ml of 3 N NH₄Cl, and heat to boiling. Add 1.5 ml of 1.5 N (NH₄)₂HPO₄ and digest hot

PROCEDURE 14 (Cont'd.)

for 15 min. Filter, wash the CdNH_4PO_4 precipitate with H_2O , dry at 110°C for 10 min., weigh as $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, and mount.

2. Remarks

1. The separation of cadmium from the other fission products is based on precipitation of CdS with H_2S in dilute acid solution. The contaminating elements, members of the acid-sulfide group and probably zirconium and niobium (columbium), are removed by basic ferric acetate $[\text{FeOH}(\text{C}_2\text{H}_3\text{O}_2)_2]$ and PdS scavenging cycles. Precipitation of $\text{FeOH}(\text{C}_2\text{H}_3\text{O}_2)_2$ is an excellent scavenging operation, the precipitate carrying a great number of the fission elements.¹⁰⁷ The PdS scavenging precipitation is made in 1 M HCl solution (in which CdS does not precipitate) and serves to remove many contaminants of the acid-sulfide group. The cadmium is finally precipitated, weighed, and mounted as $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$. This procedure is similar to that developed independently by Metcalf.¹⁰⁸

In a separation of ^{115}Cd by this procedure from a very active concentrate of plutonium fission products, a sample of the cadmium activity was obtained in about 99 per cent purity, as shown by a decay curve.¹⁰⁹ Since the ^{115}Cd comprised only 0.005 per cent of the total fission-product activity in the concentrate at the time of the cadmium separation, a decontamination factor of more than 10^6 was indicated.

PROCEDURE 15

Source - Meinke, W. W., U. S. Atomic Energy Commission,
Rept Newton UCRL 432 (Aug. 1949)

Precipitation

Element separated:	Cadmium	Yield:	~ 50%
Target material:	Thorium metal (.1-1 gm)	Time for sep'n:	2 hrs.

PROCEDURE 15 (Cont'd.)

Equipment required: Standard, tank H₂S Type of bbd: 60" α's
Degree of purification: ~ 10⁵ from fission products

1. Procedure

The metal dissolved in conc. HCl + a few drops .2 M solution (NH₄)₂SiF₆ to clear up black residue. The HCl is diluted to 2 N and an aliquot taken.

Step 1. Add 10 mg cadmium carrier. Dilute to 0.2 N HCl, pass in H₂S, ppt CdS. Wash with H₂S water.

Step 2. Dissolve CdS in 1 ml 6 N HCl. Boil out H₂S. Dilute to 10 ml. Add 5 mg Fe⁺³, 5 mg La⁺³, 5 mg In⁺³, add NH₄OH. Precipitate Fe(OH)₃. Centrifuge. Add more Fe⁺³ and scavenge again, centrifuging down on top of first.

Step 3. Pass H₂S into supernate, ppt CdS.

Step 4. Dissolve CdS in 1 ml 6 N HCl, boil, dilute to 10 ml, heat, add Ag⁺, ppt AgCl, digest a few min., centrifuge.

Step 5. Add NH₄OH until alkaline, pass in H₂S, ppt CdS.

Step 6. Dissolve Cd in 2 ml 6 N HCl. Dil to 10 ml. Add 10 ml Pd⁺², heat and saturate with H₂S, ppt PdS. Repeat sulfide scavenging with 5 mg Sb.

Step 7. To supernate add 2 ml 6 N NH₄OH saturate H₂S. Ppt CdS.

Step 8. Dissolve CdS in a few drops HCl. Boil to expel H₂S. Dilute to 15 ml. Add 1.5 ml 3 M NH₄Cl, boil, add 1.5 ml 1.5 M (NH₄)₂HPO₄ and digest hot 15 minutes. Filter. Wash with H₂O, dry 10 min. at 110°. Weigh as Cd(NH₄)PO₄·H₂O.

2. Remarks

1. 10 mg Cd = 21.63 mg CdNH₄PO₄·H₂O (M.W. = 243.45).
2. This method has been described previously (Phys. Rev., 75, 17 (1949)).

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