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## Recent Work

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SOME NOTES ON RADIOCHEMICAL SEPARATION METHODS

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## SOME NOTES ON RADIOCHEMICAL SEPARATION METHODS

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June 9, 1953

In the following pages are collected some notes on chemical separation methods of relatively recent origin which show promise for radiochemical separation of interest to nuclear chemists or have already been so used. The list is not complete in any sense and is offered merely in the hope that some members of this Conference may find some useful suggestions. In general, methods covered in one of the basic references cited below are not mentioned in these notes.

## GENERAL REFERENCES

"Radiochemical Studies: The Fission Products," Volume 9, National Nuclear Energy Series. Coryell and Sugarman, editors, McGraw-Hill Book Company.

"Radioactivity Applied to Chemistry." Wahl and Bonner, Wiley, New York.

"Analytical Chemistry of the Manhattan Project," Volume 8, National Nuclear Energy Series. Rodden, editor.

"Chemical Procedures Used in Bombardment Work at Berkeley." W. W. Meinke, AECD-2738; Addenda No. 1 and 2, AECD-2750 and AECD-3084.

"Production and Isolation of Carrier-Free Radioisotopes." W. M. Garrison and J. G. Hamilton, UCRL-1067-Rev.

Nuclear Science Abstracts.

For the heavy elements considerable information may be found in:

"The Transuranium Elements: Research Papers," Volume 14B, National Nuclear Energy Series. Seaborg, Katz and Manning, editors.

The forthcoming volume 14A of the National Nuclear Energy Series entitled "The Actinide Elements" is presently in proof and should appear late in 1953. This volume contains chapters on the chemistry of several of the heavy elements. Radiochemists in particular may be interested in chapter 15 entitled "The Radiochemical Separation of the Actinide Elements" by E. K. Hyde. This contains a comprehensive review of separations methods for elements 89 through 98.

## RARE GASES

### Fixation of Emanation or Xenon Activity on Foils or Wires for Counting Purposes

Studies of Hyde and Momyer have shown that emanation activities can be readily affixed to metallic surfaces by introducing gaseous activity to glow discharge tube consisting of two electrodes sealed into a glass vessel. Collector foil is fastened to negative electrode, or wire electrode can serve as collector. Inert carrier gas is introduced to raise pressure to 100-1000 micron range. Potential of 400-800 volts causes formation of glow discharge. Gas is ionized and collected on negative electrode. Foil or wire can then be removed from tube and counted by all methods typical for nongaseous samples. Collection efficiency is 5-10 percent and activity does not diffuse off over period of weeks unless temperature of sample is raised above room temperature. Used by Momyer and Hyde to study  $Em^{208-209-210-211-212-221}$ . Methods and results detailed in UCRL-2060. Also used by Mathur and Hyde in a study of xenon radioisotopes (unpublished).

## ZIRCONIUM-HAFNIUM-TITANIUM

### TTA Extraction.

Very high extraction coefficients into organic phase of zirconium-TTA complex. The high coefficients even at high acidities result in excellent purification from all but a very few other elements.

Connick and McVey, J. Am. Chem. Soc. 71, 3182 (1949).

### Anion Exchange Studies.

Zirconium forms negative complexes in strong hydrochloric acid or in mixed HCl-HF solutions and these are strongly adsorbed by anion exchange resins. Excellent method of separation from ions not forming negative complexes (e.g., thorium(IV)). With proper choice of conditions niobium-zirconium and even zirconium-hafnium separations can be made.

Kraus and Moore, J. Am. Chem. Soc. 73, 9 (1951).

Huffman and Lilly, J. Am. Chem. Soc. 71, 4146 (1949).

Huffman, Iddings and Lilly, J. Am. Chem. Soc. 73, 4474 (1951).

Radiochemical application given by Hyde and O'Kelley, Phys. Rev. 82, 944 (1951).

Anion exchange of oxalate complexes of niobium and zirconium discussed by Wacker and Baldwin, ORNL-637.

Titanium forms negative complexes in  $\text{HCl} > 9 \text{ M}$ . Strongly adsorbed by Dowex-1 at  $12 \text{ M HCl}$ . Good titanium-vanadium separation achieved by adsorption of titanium(IV) on Dowex-1 since vanadium(IV) does not adsorb (Kraus).

#### Cation Exchange.

Recent studies in England by Lister, J. Chem. Soc. 3123 (1951); see also AERE-C/R-703. Elution effects of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , oxalic acid. Hafnium-zirconium separation on 1 gram scale in one pass using  $\text{H}_2\text{SO}_4$ .

#### Radiocolloidal Behavior.

"Preparation of Carrier-Free Radiozirconium from Pile Irradiated Uranium." Roake, AECD-3201.

#### Some Recent General References on Zirconium Chemistry.

"Some Aspects of the Solution Chemistry of Zirconium." Lister and McDonald, AERE-C/R-801.

"Zirconium Ions in Aqueous Solutions." Dewell and Voight, Iowa State College ISC-146.

"Recent Advances in Chemistry of Zirconium and Hafnium." Larson, J. Chem. Education 28, 529 (1951).

### NIOBIUM

#### Older Methods Described in Sugarman and Coryell.

Chloroform extraction of cupferride complex of tracer niobium from acid solution.

Precipitation of phosphate.

Specific precipitation of  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  from strongly acid solution.

Soluble complex of niobium with oxalate.

Coprecipitation on thorium iodate.

Elution from cation exchange resin with HF.

Coprecipitation on  $\text{MnO}_2$ .

Separation of niobium and zirconium by fusion with  $\text{K}_2\text{CO}_3$  to form soluble  $\text{K}_8\text{Nb}_6\text{O}_{19}$ .

## New Procedures.

### Anion Exchange.

Negative complexes form in HCl, HF, and oxalic acid solutions and are strongly adsorbed by anion exchange resins. See references in ZIRCONIUM section. ("Separation of Niobium and Tantalum with Anion Exchange Resins." Kraus and Moore, J. Am. Chem. Soc. 71, 3855 (1949).)

### Solvent Extraction Procedure.

#### Separation of Tantalum and Niobium by Solvent Extraction.

Stevenson and Hicks, UCRL-2009. Tantalum and niobium are separated by extraction into di-isopropyl ketone from mineral acid-HF aqueous phases. (Initial observation by W. Nervik, unpublished.) Extraction of tantalum is the greater ranging up to extraction coefficient of 20 for 4.5 M H<sub>2</sub>SO<sub>4</sub>-0.4 M HF system. Other systems studied were HCl-HNO<sub>3</sub>-HF and HClO<sub>4</sub>-HF.

Extraction of the following ions was appreciable under some or all conditions: elemental halogens, iron(III), gallium(III), antimony(V), arsenic(III), selenium(VI) and tellurium(VI). Slight extraction of antimony(III), arsenic(V) and tellurium(IV).

It is significant that silicon(IV), tin(IV), titanium(IV), manganese(II), zirconium(IV) and hafnium(IV) do not extract.

Very useful as radiochemical method for tantalum.

#### Solvent Extraction of Niobium from Concentrated Hydrochloric Acid into Di-isopropyl Ketone. Hicks and Stevenson, unpublished.

High extraction coefficients at 10-12 M. Can re-extract at 6 M HCl. Sharp separation from zirconium.

#### Solvent Extraction of Thiocyanate Complex.

"Colorimetric Determination of Niobium Using Thiocyanate."  
Allen, Lam-Zecha, Lord and Hume, Anal. Chem. 24, 1169 (1952).)

#### Solvent Extraction Method for the Separation of Niobium and Tantalum.

G. W. Leddicotte and F. L. Moore, J. Am. Chem. Soc. 74, 1618 (1952).

Quantitative extraction of niobium from ~8 M HCl with a solution of methyldioctylamine in xylene. Extraction of tantalum is negligible. Niobium backextracted into dilute mineral acid.

Solvent Extraction Separation of Niobium and Tantalum.

"A Study of the Separation of Tantalum from Niobium and its Application to Quantitative Analysis." Burstall, Swain, Williams and Wood. J. Chem. Soc. 1497 (1952).

The method is based on their extraction in turn as fluorides into ethyl methyl ketone in the presence of cellulose adsorbent.

Precipitation Procedure.

Determination of radioniobium in the presence of soluble orthophosphates. Hahn and Burros, ORNL-831; Anal. Chem. 23, 1713 (1951).

VANADIUM

Thiocyanate Complexes.

Furman and Gaines, J. Am. Chem. Soc. 73, 4528 (1951). "Thiocyanate Complexes of Vanadium(III) and Vanadium(IV)."

Solubility of thiocyanate complex in organic solvents.

Rosenheimer, Hilyheimer and Wolff, Z. Anorg. Chem. 201, 162 (1931).

Unpublished studies, M.I.T.

Anion Exchange Behavior.

Kraus and Co-workers at ORNL.

Stevenson at UCRL.

Vanadium(V) is adsorbed at very high (10-12 M) HCl concentration as are niobium(V) and tantalum(V). Reduction by resin to vanadium(IV) is ready. (This reduction also occurs on cation exchange resins as observed by Salmon and Tietze, J. Chem. Soc. 2324 (1952).) Vanadium(IV) is not adsorbed at any concentration of HCl by Dowex-1 and hence is readily separated from niobium, tantalum and titanium.



## Other Isolation Methods.

### Separation of Vanadium from Iron Target Bombarded with 340 Mev Protons.

Rudstam, Folger and Stevenson, UCRL-1586. Separated as sulfide from ammoniacal solution. Sulfide dissolved in concentrated  $\text{HNO}_3$ , scavenged with  $\text{MnO}_2$  ( $\text{KClO}_3$  and fuming  $\text{HNO}_3$ ) and then with  $\text{Y}(\text{OH})_3$  in  $\text{NH}_4\text{OH}$  solution. Vanadium sulfide again precipitated. Sulfide dissolved and the solution buffered with acetate-acetic acid. Chromium hold back agent added. Vanadium oxidized by  $\text{H}_2\text{O}_2$ .  $\text{Pb}(\text{VO}_3)_2$  precipitated. Precipitate dissolved in 2 M  $\text{HNO}_3$ , and lead removed as  $\text{PbS}$ . The solution then buffered with acetate-acetic acid and oxidized and  $\text{Pb}(\text{VO}_3)_2$  again brought down. Washed, dried, weighed.

"Preparation and Isolation of  $\text{V}^{48}$  from Titanium." Haymond, Maxwell, Garrison and Hamilton, AECU-623. The titanium powder was dissolved in  $\text{H}_2\text{SO}_4$  and evaporated to dryness. Fifty grams  $\text{Na}_2\text{CO}_3$  and 0.1 gram  $\text{NaNO}_3$  were added and mixture fused at  $300^\circ\text{C}$  for 30 minutes.  $\text{V}^{48}$  as vanadate was extracted from the insoluble titanium oxide by cold water. Ten milligrams each of calcium and scandium were added and precipitated from 1 M  $\text{Na}_2\text{CO}_3$ . The supernate containing the  $\text{V}^{48}$  was neutralized with 12 M  $\text{HCl}$  and evaporated to dryness. The vanadium activity was separated from most of the  $\text{NaCl}$  by extraction with approximately 5 ml of 12 M  $\text{HCl}$ .

Solvent extraction of vanadium(V) has been noted in a number of organic solvents.

Cupferride of vanadium is insoluble in acid solutions and can be extracted into chloroform.

For some further suggestions on vanadium chemistry consult,

Chapter 19, Analytical Chemistry of the Manhattan Project, Volume 8, National Nuclear Energy Series.

## ALKALI METALS

### Carrier-Free Method for Isolation of Cesium or Francium.

Hyde, J. Am. Chem. Soc. 74, 4181 (1952). Depends on coprecipitation of tracer alkali with free silicotungstic acid which is soluble in dilute  $\text{HCl}$  but not in saturated  $\text{HCl}$ . Tracer alkali then separated from carrier by quick cation exchange method. No separation of cesium and francium. Rubidium and cesium are separated.

### Ion Exchange of Alkali Elements.

"Ion Exchange Separation of Alkali Metals." Cohn and Kohn, J. Am. Chem. Soc. 70, 1986 (1948).

"The Separation of Sodium and Potassium by Organic Ion Exchangers." Kayas, Compt. Rendu 228, 1002 (1949); see also, J. Chim. Phys. 47, 408 (1950).

"Chromatographic Separation of Francium." Perey and Adloff, Compt. Rendu 236, 1163 (1953).

"Determination of Sodium and Potassium Employing Ion Exchange Separations." Beukenkamp and Reiman, Anal. Chem. 22, 582 (1950).

"Separation of Alkali Ions Using Ion Exchangers and a Complex Ion." Buser, Helv. Chim Acta 34, 1635 (1951). Used uramildiacetic acid as complexing agent. Lithium-sodium and sodium-potassium separations stressed.

"Isolation of Fission Product Cs<sup>137</sup> by Ion Exchange." Parker and Lantz, AECD-2160.

"Reaction of Cesium in Trace Amounts with Ion Exchange Resins." Miller and Kline, J. Am. Chem. Soc. 73, 2741 (1953).

### Other Methods of Alkali Element Separation.

"Separation of Alkali Elements by Partition Chromatography." Miller and Magee, J. Chem. Soc. 383 (1951).

"The Isolation of Radiochemically Pure 2.6 Year Sodium From Deuteron Bombarded NaK Alloy. Motta, NAA-SR-106, North American Aviation Corporation Report.

"The Recovery of Cs<sup>137</sup> from ORNL Radiochemical Waste." Gresky, ORNL-742. Based on coprecipitation with potassium alum.

"Separation of Na<sup>22</sup> from Magnesium Cyclotron Targets." Irvine and Clarke, J. Chem. Phys. 16, 686 (1948).

### ARSENIC-ANTIMONY

#### Solvent Extraction.

"The Separation of Sb(V) from Sb(III) by Extraction into Isopropyl Ether." Edwards and Voight, AECU-192. Best extraction of Sb(V) in range 6.5-8.5 M HCl.

Extraction of antimony and arsenic into di-isopropyl ketone from 6 M HF-6 M HCl was noted by Hicks and Stevenson, UCRL-2009. Sb(V) extracts well; backextracts into water. Sb(III) extracts slightly. As(III) extracts well. As(V) extracts less than As(III).

#### Anion Exchange Behavior.

As(III), As(V) not adsorbed from 12 M HCl.  
Sb(III), Sb(V) strongly adsorbed at all HCl concentrations above 0.1 M. Slow elution below 0.1 M HCl. Hicks, Stevenson, Gilbert (unpublished results).

#### LEAD-BISMUTH-POLONIUM

#### Separations Based on Classical Electrodeposition and Carrier Methods.

Novey, Phys. Rev. 89, 673 (1953).

Wahl and Bonner, Phys. Rev. 85, 572 (1952).

Neumann, Phys. Rev. 78, 192 (1950).

Novey, Engelkemeir and Levy, Paper 9, p. 116 in volume 9, "Radiochemical Studies: The Fission Products," National Nuclear Energy Series.

#### Simple Anion Exchange Separation of RaDEF.

Hyde and Raby, unpublished procedure.

Adjust acidity to 2 M HCl. Pass through short column Dowex-1 resin and rinse with 2 M HCl. Lead(II) passes through. Bismuth(III) and polonium(IV) adhere. Pass concentrated HCl through column to desorb bismuth(III). Finally, pass concentrated HNO<sub>3</sub> through column to desorb polonium(IV). HCl concentration ranges in which adsorption is very marked are for lead(II) 4.5-7.0 M, for bismuth(III) 0-6 M, and for polonium(IV) all concentrations.

#### Radiocolloid Adsorption Methods.

"Preparation and Isolation of Carrier-Free Bi<sup>204-206</sup> from Lead." Gile, Garrison and Hamilton, UCRL-1017. Based on quantitative adsorption of bismuth as radiocolloid on filter paper from 10 percent NaOH.

### Solvent Extraction.

Polonium is readily extracted into tributyl phosphate from 6 M HCl, or 2 N H<sub>2</sub>SO<sub>4</sub>. Bismuth and lead do not extract.

Procedures by Karraker and Barton in Meinke's "Chemical Procedures," AECD-2738.

Karraker and Templeton, Phys. Rev. 81, 510 (1951).

Barton, Ghiorso and Perlman, Phys. Rev. 82, 13 (1951).

Hall, UCRL-1460.

Peppard, unpublished results.

### GALLIUM, INDIUM AND THALLIUM

#### Anion Exchange.

Gallium and indium are strongly adsorbed from hydrochloric acid solution. They can be desorbed with HCl < 3 M. Thallium(III) is adsorbed strongly from HCl of any concentration. It is so difficult to desorb in (III) state that elution is effected by reduction.

Unpublished thallium procedure by Hicks and Lindner, CR and D, Livermore, California. Adsorb thallium(III) from 12 M HCl. Rinse with 1 M H<sub>2</sub>SO<sub>4</sub>. Pass 1 M H<sub>2</sub>SO<sub>4</sub> saturated with SO<sub>2</sub> through column to reduce thallium(III) to thallium(I). Thallium(I) elutes quickly.

#### Solvent Extraction of 8-Hydroxyquinolates.

Moeller and Cohen, Anal. Chem. 22, 686 (1950).

Feigl and Baumfeld, Anal. Chim Acta 3, 83 (1949).

#### Ether Extraction Behavior of Gallium Indium and Thallium From HBr, HI and HCl Solutions.

See, Irvine and Rossotti, Analyst 77, 801 (1952).

#### Solvent Extraction of Gallium into Tributyl Phosphate.

K<sub>d</sub>'s > 1000. M.I.T. group, Irvine, unpublished.

"Carrier-Free Separation of Radioactive Indium from Cadmium." Jacobi, *Helv. Phys. Acta* 22, 66 (1949).

Radioactive indium is carried on  $Mg(OH)_2$  to separate it from cadmium. It is then electrolytically deposited carrier-free from weak  $H_2SO_4$  onto small piece of mica.

#### PHOSPHORUS

Isolation of  $P^{32}$  from Sulfur Targets.

Principal method is the extraction of phosphorus from molten sulfur by boiling nitric acid. See Cohn, MDDC-518 (1946).

Variants and extensions of this method are given by:

Jensen, Nichols, Clement and Pohn, *Phys. Rev.* 85, 119 (1952).

Kenny and Spragg, AERE-C/R-485 (1950); *J. Chem. Soc. Suppl.* 2, S326 (1949).

#### BERYLLIUM

"Thenoyltrifluoroacetone as a Complexing Agent for the Isolation and Purification of Carrier-Free Radioberyllium." Bolomey and Wish, AECD-2665.

#### SCANDIUM

Extraction of Thiocyanate Complex into Organic Phase.

Fischer and Bock, *Z. Anorg. allgem. Chem.* 249, 146-197 (1942).

Peppard and co-workers at ANL separate scandium from rare earths, thorium and other elements with thiocyanate extraction method. Good extraction of scandium by 2 M solution of HCNS in ether from aqueous solution 2 M HCl. See ANL reports.

Extraction of Scandium into Tributyl Phosphate.

Peppard et al. found distribution coefficient into organic phase of 32 from 6.4 M HCl allowing clean separation from rare earths. *J. Phys. Chem.* 57, 294 (1953).

Extraction of Scandium into TTA.

Broido in AECD-2616 studied extraction of scandium into TTA-benzene and the separation of scandium from rare earths by this method.

RARE EARTHS

Solvent Extraction of Rare Earths--Tributyl Phosphate-Mineral Acid Systems.

"Fractionation of Trivalent Rare Earths." Peppard, Faris, Gray and Mason, AECD-3327 (January 17, 1952); J. Phys. Chem. 57, 294 (1953). HCl-TBP systems. HNO<sub>3</sub>-TBP systems. Separation of rare earths as a group. Fractionation of rare earths.

Quantity Separation of Rare Earths by Liquid-Liquid Extraction.

"The First Kilogram of GdO<sub>2</sub>." Weaver, Kappelmann and Topp, ORNL-1408.

"Extraction of Neodymium and Samarium Nitrates." Topp, ORNL-1409.

Ion Exchange Separations.

New work on separation of rare earths using citrate as eluting agent covered in numerous papers.

Use of ethylenediamine tetra-acetic acid as eluting agent--representative papers:

Vickery, J. Chem. Soc. 1817 (1951) and 4357-63 (1952).

Wheelwright, Spedding and Schwarzenbach, ISC-279.

Marsh, J. Chem. Soc. 3057 (1951).

Schwarzenbach, Helv. Chim Acta 34, 1503 (1951).

ZINC-CADMIUM-MERCURY

Standard Methods.

Precipitation ZnHg(SCN)<sub>4</sub>.

Precipitation ZnS, CdS.

Precipitation CsNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O.

Precipitation of 8-hydroxyquinolate.

Precipitation Hg<sub>2</sub>Cl<sub>2</sub>.

New Work.

Thiocyanate complexes in excess of reagent.

Cyanide complexes.

D. Terwilliger has studied separation of mercury from mixture of lead and bismuth. Mixture adsorbed on Dowex-50. Mercury eluted quickly with 0.3 M HCl. No elution of bismuth or lead until acidity is raised.

Kraus et al. Zinc, cadmium, and mercury form strong negative chloride complexes. In proper system zinc(II) and cadmium(II) can be separated from each other. (ORNL-1153)

## COPPER

### Standard Methods.

Precipitation CuS.

Precipitation CuCNS.

Reduction to metal.

### Recent Methods.

Haymond, et al., J. Chem. Phys. 18, 901 (1950), extract Cu<sup>64,67</sup> carrier-free from a dissolved zinc target by adjusting pH to 1.0-1.2 and extracting dithiozonate complex into CCl<sub>4</sub>.

Nervik, Folger and Stevenson (unpublished) extract copper as dithizone complex into organic phase using other complexing agents in aqueous phase to reduce extraction of interfering ions.

Anion exchange. Strong adsorption of copper chloride complexes by Dowex-A1 or A2 resins. Can be desorbed in dilute HCl solutions.

Extraction of copper by acetylacetone and the separation of copper and zinc are discussed by Steinbach and Freiser, NYO-3070, Pittsburgh University report.

## SILVER

### Methods of Separation of Silver from Palladium.

Haymond, et al., J. Chem. Phys. 18, 391 (1950). Authors isolate Ag<sup>105</sup> carrier-free from palladium targets by coprecipitation on Hg<sub>2</sub>Cl<sub>2</sub>. The Hg<sub>2</sub>Cl<sub>2</sub> is removed by volatilization.

Griess and Rogers, AECD-2299, separate Ag<sup>111</sup> from palladium by electrolysis from 1 M NaOH-0.1 M NaCN solution using platinum electrodes and a cathode potential of -1.21 volts.

Slater (unpublished) removes silver from palladium by reducing Ag<sup>+</sup> to metallic state with ascorbic acid.

Schwertzer and Nehls, J. Am. Chem. Soc. 74, 6186-9 (1952). Use radiocolloidal behavior of silver to effect separation of silver from palladium.

Could employ anion exchange from HCl solutions. Silver complexes are adsorbed from 12 M HCl. Can be desorbed below 9 M HCl. Palladium complexes adsorb at all concentrations HCl. Cannot be desorbed by HCl or H<sub>2</sub>O. NH<sub>4</sub>OH solutions will desorb palladium. Hicks, Stevenson, Gilbert (unpublished results).

#### IRON-COBALT-NICKEL

##### Principal Older Methods.

Extraction of ferric chloride into ether and other organic solvents.

Precipitation of nickel as dimethyl glyoximate.

Precipitation nickel sulfide.

Precipitation of potassium cobaltinitrite.

##### Newer Methods.

Extraction of chelate complexes.

Kenny, Maton and Spragg, Nature 165, 483 (1950), extracted ferric acetyl acetonate into xylene to separate Fe<sup>59</sup> from cobalt target.

TTA extraction of iron.

Anion exchange from hydrochloric acid.

Separation of cobalt(II) and nickel(II). Nickel(II) does not form negative complexes. Cobalt(II) is strongly adsorbed on Dowex-2 in HCl > 6 M.

Orth and Street, unpublished data.

Moore and Kraus, J. Am. Chem. Soc. 74, 843 (1952).

Adsorption behavior of iron(III).

Kraus, J. Am. Chem. Soc. 72, 5792 (1950).



### Solvent extraction.

Extraction of the thiocyanate complex of cobalt into ether, ethyl acetate and other solvents. McCallum and Hoskovsky, J. Chem. Phys. 16, 255 (1948).

## ACTINIUM

### TTA Extraction.

Extraction by 0.25 M solution TTA in benzene is negligible below pH 3 but rises rapidly to 100 percent extraction at pH 5.5. See Hagemann, J. Am. Chem. Soc. 72, 768 (1950).

See also, Hall and Templeton UCRL-957.

For application to target problem see Depocas and Harvey, Phys. Rev. 85, 499 (1952).

### Ion Exchange Methods.

Separation by ion exchange of traces of  $\text{Ac}^{227}$  from a large amount of lanthanum. Tsong, J. chim Phys. 47, 805 (1950).

Uses 5 percent ammonium citrate at pH 5.5. Amberlite IR-100 resin.

### Solvent Extraction of Actinium.

Readily extracted into tributyl phosphate from saturated  $\text{NH}_4\text{NO}_3$ -0.3 M  $\text{HNO}_3$ . See Peppard et al., J. Am. Chem. Soc. 74, 6081 (1952).

Extraction from saturated aluminum nitrate-1 N  $\text{HNO}_3$  is also very high.

## THORIUM

### General Reference on Radiochemical Methods.

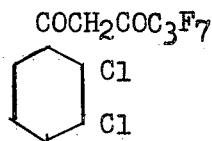
See chapter 15 of forthcoming volume 14A, "The Actinide Elements," of the National Nuclear Energy Series.

### Extraction of Chelate Complexes.

Strong extraction of thorium(IV) above pH 1.5 into TTA-benzene. See Hagemann, J. Am. Chem. Soc. 72, 768 (1950).

Use of TTA extraction of thorium as a tool in the study of complexing of thorium discussed by Stoughton and co-workers in a series of reports. For example, AECD-2429, ORNL-468 and AECD-3305. Similar studies carried out by Zebroski, Alter and Heumann, J. Am. Chem. Soc. 73, 5646 (1951).

A recently introduced chelating agent, Dagmar, is useful for thorium:



or corresponding 3,4 dichloro compound. (Dow Chemical Company, Pittsburg, California.) Dagmar has a higher solubility for the metal chelate in the organic phase than TTA. Useful property in extractions of larger amounts of material.

#### Solvent Extraction.

Extraction of thorium by various organic solvents. Ames Group.

High extractability from nitrate systems into tributyl phosphate and dibutoxytetraethyleneglycol. Employed, for example, by Peppard and co-workers at ANL to extract ionium from uranium-process wastes.

#### Ion Exchange.

A large number of papers on ion exchange behavior of thorium are available but only a few will be mentioned here. The general comment may be made that cation exchange is admirably suited to thorium. This tetrapositive ion is adsorbed strongly and may be thoroughly scrubbed of lower valent contaminants. On the other hand, a number of complexing agents form very strong complexes with thorium and may be used to strip it rapidly from a cation resin.

Thorium forms no prominent negative complexes so that anionic contaminants may be removed with anion resin as for example zirconium.

Complexing agents useful in eluting thorium.

Citric acid.  
Oxalic acid.  
Hydrofluoric acid.  
Carbonate.  
Sulfate.  
Lactic acid.

"Ion Exchange Equilibria Involving Fission Products and Thorium in Uranyl Nitrate." Schubert, AECD-3273.

"Preparation of Carrier-Free  $UX_1$ ." Dyrssen, Svensk Kem Tid. 62, 153 (1950).

Extracts uranium with ether. Dilutes aqueous phase containing  $UX_1$  with 0.1 M HCl and adsorbs on cation resin. Washes  $UO_2^{++}$  and other contaminants with 2 M HCl. Desorbs  $UX_1$  with 0.5 M oxalic acid.

Elution of thorium and rare earths from IR-110H and Dowex-50 using such eluting agents as ammonium citrate, ethylenediamine tetra-acetic acid, ammonium oxalate, ammonium carbonate and hydrochloric acid. Taylor, NP-1434.

#### PROTACTINIUM

##### General References.

See chapters in forthcoming volume 14A, "The Actinide Elements," National Nuclear Energy Series.

Meinke, "Chemical Procedures," AECD-2738.

Papers in volume 14B, National Nuclear Energy Series.

Elson, et al., AECD-2896.

Elson, et al., J. Am. Chem. Soc. 73, 4974 (1951).

##### Coprecipitation Methods.

Coprecipitation on zirconium phosphate.

Pre-war researches of A. V. Grosse and co-workers.

Gofman and Seaborg, National Nuclear Energy Series, volume 14B, paper 19.14.

Kraus and Garen, Oak Ridge Progress Reports.

Coprecipitation on zirconium iodate.

Stoughton )  
Kraus and Van Winkle ) classified progress reports.

Coprecipitation on BaZrF<sub>6</sub>.

See Crane in Meinke's "Berkeley Procedures," AECD-2738.

Coprecipitation on MnO<sub>2</sub>.

Effect of varying conditions studied by Katzin and Stoughton.

Ion Exchange.

Anion exchange.

Kraus and Moore, J. Am. Chem. Soc. 72, 4293 (1950) showed that protactinium in HCl is strongly adsorbed on Dowex-1.

Separation from thorium effected by adsorption at 8 M HCl and thorough rinsing of resin with 8 M HCl. Thorium does not form negative chloride complexes. Protactinium is stripped from column with 1-4 M HCl.

Kraus and Moore, J. Am. Chem. Soc. 73, 2900 (1951) studied anion exchange of protactinium in HCl-HF mixtures and the separation of niobium-tantalum-protactinium.

Cation exchange.

Can be adsorbed on cation resins and eluted with ammonium oxalate or sulfate.

Solvent Extraction.

M. J. Wolf established high extractability of protactinium into di-isopropyl ketone and similar solvents from pure HNO<sub>3</sub> solutions and from mixed HNO<sub>3</sub>-nitrate salt solutions.

Overholt, Steahly and others introduced di-isopropyl carbinol as protactinium solvent.

Kraus and Van Winkle recommended extraction into di-isopropyl ketone from strong hydrochloric acid solutions particularly for macro amounts of protactinium.

Aluminum ion is useful as salting agent and for tying up fluoride ion which interferes with extraction.

Elson, et al. have reported extraction of protactinium into tributyl phosphate from a nitrate salted system. J. Am. Chem. Soc. 73, 4974 (1951).

TTA Extraction.

Excellent method of purification. Protactinium extracted into TTA-benzene from strongly acidic solutions in contradistinction to all but a very few ions such as zirconium. For application see Meinke, "Berkeley Procedures," AECD-2738.

ELECTRODEPOSITION OF FISSION ELEMENTS

Lee and Cook in AERE-C/R-430 describe electrodeposition of tin, antimony, tellurium, cadmium and several other elements.

Rogers in Anal. Chem. 22, 1386 (1950) describes some practical considerations in tracer separations by electrodeposition.

M.I. T. group, unpublished results.

Anion Exchange From HCl Solutions--General Survey.

Hicks, Stevenson, Gilbert, California Research and Development Corporation, Livermore, California (unpublished results) carried out a general survey of anion exchange behavior of the elements.

Each element in 12 M HCl solution was passed through a Dowex-A2 resin column and the observation made whether the element adsorbed or not. For those elements which did adsorb, HCl of decreasing normality was tried as eluting agent. Results were as follows:

Elements which did not adsorb from 12 M HCl.

All alkali elements.

All alkaline earth elements.

Al	Mn(II)
Sc	Ni(II)
Y	As(III)
Rare earths	As(V)
Ac	Se(II)
Ti(III)	Se(IV)
V(II-III-IV)	Tl(I)
Cr(III)	Pb(II)

Elements which adsorbed at 12 M HCl, but were removed with 6-9 M HCl.

Te(IV)	Ag
V(V)	Ta(V)

Elements not desorbed with HCl > 6 M which were desorbed with 3-6 M HCl.

Zr(IV)	Cu(I, II)
Nb(V)	Ge
Fe(III)	Hf(IV)
Co(II)	

Elements not desorbed with HCl > 3 M which were desorbed with 1-3 M HCl.

Zn(II)	Sn(IV)
Ga(III)	Te
Mo	Au(I) (desorbed with mixed HI-HCl solution)
In	

Elements not desorbed with HCl > 1 M which were desorbed with 0.1-1.0 M HCl.

Pt(II)

Elements not desorbed above 0.1 M HCl which desorbed slowly with 0.01-0.1 M HCl or H<sub>2</sub>O.

Sn(II)	Hg(II)
Sb(III, V)	Bi(III)

Elements which adsorbed at all concentrations HCl and were not desorbed by H<sub>2</sub>O.

Tc  
Ru, Rh, Pd (can be desorbed with NH<sub>4</sub>OH)  
Re, Os, Ir  
Cd (can be desorbed with 1.5 M H<sub>2</sub>SO<sub>4</sub>)  
Tl(III) (can be desorbed by reduction to Tl(I))  
Po  
W (can be desorbed with 1 M NaOH)  
Au(III)