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*Collected Radiochemical and  
Geochemical Procedures  
Fifth Edition*

**For Reference**

**Not to be taken from this room**

LOS ALAMOS NATL. LAB. LIBS.



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**Los Alamos**

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Edited by Jody H. Heiken, INC Division*

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*Collected Radiochemical and  
Geochemical Procedures*

*Fifth Edition*

*Compiled and Edited by  
Jacob Kleinberg*

*Individuals responsible for developing procedures are named at the  
heading of each procedure.*

LOS ALAMOS NATIONAL LABORATORY



3 9338 00159 2921

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## ABSTRACT

This revision of LA-1721, 4th Ed., *Collected Radiochemical Procedures*, reflects the activities of two groups in the Isotope and Nuclear Chemistry Division of the Los Alamos National Laboratory: INC-11, Nuclear and Radiochemistry; and INC-7, Isotope Geochemistry. The procedures fall into five categories: I. Separation of Radionuclides from Uranium, Fission-Product Solutions, and Nuclear Debris; II. Separation of Products from Irradiated Targets; III. Preparation of Samples for Mass Spectrometric Analysis; IV. Dissolution Procedures; and V. Geochemical Procedures. With one exception, the first category of procedures is ordered by the positions of the elements in the Periodic Table, with separate parts on the Representative Elements (the A groups); the *d*-Transition Elements (the B groups and the Transition Triads); and the Lanthanides (Rare Earths) and Actinides (the 4f- and 5f-Transition Elements). The members of Group IIIB—scandium, yttrium, and lanthanum—are included with the lanthanides, elements they resemble closely in chemistry and with which they occur in nature. The procedures dealing with the isolation of products from irradiated targets are arranged by target element.

## PREFACE

This revision of LA-1721, 4th Ed., *Collected Radiochemical Procedures*, reflects the activities of two groups in the Isotope and Nuclear Chemistry Division of the Los Alamos National Laboratory: INC-11, Nuclear and Radiochemistry; and INC-7, Isotope Geochemistry. In line with the material in the revision, its title is *Collected Radiochemical and Geochemical Procedures, 5th Ed.*

The procedures fall into five categories: I. Separation of Radionuclides from Uranium, Fission-Product Solutions, and Nuclear Debris; II. Separation of Products from Irradiated Targets; III. Preparation of Samples for Mass Spectrometric Analysis; IV. Dissolution Procedures; and V. Geochemical Procedures. With one exception, the first category of procedures is ordered by the positions of the elements in the Periodic Table, with separate parts on the Representative Elements (the A groups); the *d*-Transition Elements (the B groups and the Transition Triads); and the Lanthanides (Rare Earths) and Actinides (the 4f- and 5f-Transition Elements). The members of Group IIIB—scandium, yttrium, and lanthanum—are included with the lanthanides, elements they resemble closely in chemistry and with which they occur in nature. The procedures dealing with the isolation of products from irradiated targets are arranged by target element.

In the procedures, all chemicals used are of the highest purity available and only for special cases are sources listed. All filter papers that are ignited are of the ashless variety.

A number of the procedures included in the 4th Edition, which are clearly of limited usefulness or have been superseded by better ones, have been deleted. A list of those deleted is given after the **CONTENTS**.

The compilers of this revision thank both the developers of the procedures for their willing cooperation and the word processors of INC-11 for the typing of the manuscript. We particularly appreciate the patient and thorough work of Carla E. Lowe, who has coordinated this effort. Merlyn E. Holmes was responsible for the initial compilation of the procedures and made helpful suggestions. Jody Heiken, INC Division Editor, saw the manuscript through its final editing and the various other stages of publication and we express our appreciation to her.

Representative elements		d-Block elements										Representative elements							Noble gases							
I (1) $ns^1$		Group numbers										III (13) $ns^2 np^1$							VII (17) $ns^2 np^5$	(18) $ns^2 np^6$						
H 1 $1s^1$ 1.0079												B 5 $2s^2 2p^1$ 10.81							C 6 $2s^2 2p^2$ 12.011	N 7 $2s^2 2p^3$ 14.0067	O 8 $2s^2 2p^4$ 15.9994	F 9 $2s^2 2p^5$ 18.998403	Ne 10 $2s^2 2p^6$ 20.179			
Li 3 $2s^2$ 6.941												Al 13 $3s^2 3p^1$ 26.98154							Si 14 $3s^2 3p^2$ 28.0855	P 15 $3s^2 3p^3$ 30.97376	S 16 $3s^2 3p^4$ 32.06	Cl 17 $3s^2 3p^5$ 35.453	Ar 18 $3s^2 3p^6$ 39.948			
Na 11 $3s^1$ 22.98977												Ga 31 $4s^2 4p^1$ 69.72							Ge 32 $4s^2 4p^2$ 72.59	As 33 $4s^2 4p^3$ 74.9216	Se 34 $4s^2 4p^4$ 78.96	Br 35 $4s^2 4p^5$ 79.904	Kr 36 $4s^2 4p^6$ 83.80			
K 19 $4s^1$ 39.0983												In 49 $5s^2 5p^1$ 114.82							Sn 50 $5s^2 5p^2$ 118.69	Sb 51 $5s^2 5p^3$ 121.75	Te 52 $5s^2 5p^4$ 127.60	I 53 $5s^2 5p^5$ 126.9045	Xe 54 $5s^2 5p^6$ 131.29			
Ca 20 $4s^2$ 40.08												Tl 81 $6s^2 6p^1$ 204.383							Pb 82 $6s^2 6p^2$ 207.2	Bi 83 $6s^2 6p^3$ 208.9804	Po 84 $6s^2 6p^4$ (209)	At 85 $6s^2 6p^5$ (210)	Rn 86 $6s^2 6p^6$ (222)			
Sc 21 $3d^1 4s^2$ 44.9559												Au 79 $5d^{10} 6s^1$ 196.9665							Hg 80 $5d^{10} 6s^2$ 200.59							
Ti 22 $3d^2 4s^2$ 47.88												Pt 78 $5d^9 6s^1$ 195.09							Ir 77 $5d^7 6s^2$ 192.22							
V 23 $3d^3 4s^2$ 50.9415												Os 76 $5d^6 6s^2$ 190.2							Re 75 $5d^5 6s^2$ 186.207							
Cr 24 $3d^5 4s^1$ 51.996												Ru 44 $4d^7 5s^1$ 101.07							Rh 45 $4d^8 5s^1$ 102.9055							
Mn 25 $3d^5 4s^2$ 54.9380												Pd 46 $4d^{10}$ 106.42							Ag 47 $4d^9 5s^1$ 107.868							
Fe 26 $3d^6 4s^2$ 55.847												Cd 48 $4d^{10} 5s^2$ 112.41							Ni 28 $3d^8 4s^2$ 58.69							
Co 27 $3d^7 4s^2$ 58.9332												Zn 30 $3d^{10} 4s^2$ 65.38							Cu 29 $3d^9 4s^1$ 63.546							
Ni 28 $3d^8 4s^2$ 58.69												Ga 31 $4s^2 4p^1$ 69.72							Mn 25 $3d^5 4s^2$ 54.9380							
Cu 29 $3d^9 4s^1$ 63.546												Ge 32 $4s^2 4p^2$ 72.59							Cr 24 $3d^5 4s^1$ 51.996							
Zn 30 $3d^{10} 4s^2$ 65.38												As 33 $4s^2 4p^3$ 74.9216							Fe 26 $3d^6 4s^2$ 55.847							
Ga 31 $4s^2 4p^1$ 69.72												Se 34 $4s^2 4p^4$ 78.96							Co 27 $3d^7 4s^2$ 58.9332							
Ge 32 $4s^2 4p^2$ 72.59												Br 35 $4s^2 4p^5$ 79.904							Ni 28 $3d^8 4s^2$ 58.69							
As 33 $4s^2 4p^3$ 74.9216												Kr 36 $4s^2 4p^6$ 83.80							Cu 29 $3d^9 4s^1$ 63.546							
Se 34 $4s^2 4p^4$ 78.96												Rb 37 $5s^1$ 85.4678							Zn 30 $3d^{10} 4s^2$ 65.38							
Br 35 $4s^2 4p^5$ 79.904												Sr 38 $5s^2$ 87.62							Ga 31 $4s^2 4p^1$ 69.72							
Kr 36 $4s^2 4p^6$ 83.80												Y 39 $4d^1 5s^2$ 88.9059							Ge 32 $4s^2 4p^2$ 72.59							
Rb 37 $5s^1$ 85.4678												Zr 40 $4d^2 5s^2$ 91.22							As 33 $4s^2 4p^3$ 74.9216							
Sr 38 $5s^2$ 87.62												Nb 41 $4d^4 5s^1$ 92.9064							Se 34 $4s^2 4p^4$ 78.96							
Y 39 $4d^1 5s^2$ 88.9059												Mo 42 $4d^5 5s^1$ 95.94							Br 35 $4s^2 4p^5$ 79.904							
Zr 40 $4d^2 5s^2$ 91.22												Tc 43 $4d^5 5s^1$ (98)							Kr 36 $4s^2 4p^6$ 83.80							
Nb 41 $4d^4 5s^1$ 92.9064												Ru 44 $4d^7 5s^1$ 101.07							Rb 37 $5s^1$ 85.4678							
Mo 42 $4d^5 5s^1$ 95.94												Rh 45 $4d^8 5s^1$ 102.9055							Sr 38 $5s^2$ 87.62							
Tc 43 $4d^5 5s^1$ (98)												Pd 46 $4d^{10}$ 106.42							Y 39 $4d^1 5s^2$ 88.9059							
Ru 44 $4d^7 5s^1$ 101.07												Ag 47 $4d^9 5s^1$ 107.868							Zr 40 $4d^2 5s^2$ 91.22							
Rh 45 $4d^8 5s^1$ 102.9055												Cd 48 $4d^{10} 5s^2$ 112.41							Nb 41 $4d^4 5s^1$ 92.9064							
Pd 46 $4d^{10}$ 106.42												In 49 $5s^2 5p^1$ 114.82							Mo 42 $4d^5 5s^1$ 95.94							
Ag 47 $4d^9 5s^1$ 107.868												Sn 50 $5s^2 5p^2$ 118.69							Tc 43 $4d^5 5s^1$ (98)							
Cd 48 $4d^{10} 5s^2$ 112.41												Sb 51 $5s^2 5p^3$ 121.75							Ru 44 $4d^7 5s^1$ 101.07							
In 49 $5s^2 5p^1$ 114.82												Te 52 $5s^2 5p^4$ 127.60							Rh 45 $4d^8 5s^1$ 102.9055							
Sn 50 $5s^2 5p^2$ 118.69												I 53 $5s^2 5p^5$ 126.9045							Pd 46 $4d^{10}$ 106.42							
Sb 51 $5s^2 5p^3$ 121.75												Xe 54 $5s^2 5p^6$ 131.29							Ag 47 $4d^9 5s^1$ 107.868							
Te 52 $5s^2 5p^4$ 127.60												Fr 87 $7s^1$ (223)							Cd 48 $4d^{10} 5s^2$ 112.41							
I 53 $5s^2 5p^5$ 126.9045												Ra 88 $7s^2$ 226.0254							In 49 $5s^2 5p^1$ 114.82							
Xe 54 $5s^2 5p^6$ 131.29												Ac <sup>b</sup> 89 $6d^1 7s^2$ 227.0278							Sn 50 $5s^2 5p^2$ 118.69							
Fr 87 $7s^1$ (223)												Unq 104 $6d^1 7s^2$ (261)							Sb 51 $5s^2 5p^3$ 121.75							
Ra 88 $7s^2$ 226.0254												Unp 105 $6d^2 7s^2$ (262)							Te 52 $5s^2 5p^4$ 127.60							
Ac <sup>b</sup> 89 $6d^1 7s^2$ 227.0278												Unh 106 $6d^4 7s^2$ (263)							I 53 $5s^2 5p^5$ 126.9045							
Unq 104 $6d^1 7s^2$ (261)												Uns 107 $6d^1 7s^2$ (262)							Xe 54 $5s^2 5p^6$ 131.29							
Unp 105 $6d^2 7s^2$ (262)												Uno 108 $6d^9 7s^2$ (265)							Fr 87 $7s^1$ (223)							
Unh 106 $6d^4 7s^2$ (263)												Une 109 $6d^7 7s^2$ (266)							Ra 88 $7s^2$ 226.0254							
Uns 107 $6d^1 7s^2$ (262)																			Ac <sup>b</sup> 89 $6d^1 7s^2$ 227.0278							
Uno 108 $6d^9 7s^2$ (265)																			Unq 104 $6d^1 7s^2$ (261)							
Une 109 $6d^7 7s^2$ (266)																			Unp 105 $6d^2 7s^2$ (262)							

f-Block elements

<sup>a</sup> Lanthanides ~

<sup>b</sup> Actinides ~

Ce 58 $4f^1 5d^1 6s^2$ 140.12	Pr 59 $4f^3 5d^0 6s^2$ 140.9077	Nd 60 $4f^4 5d^0 6s^2$ 144.24	Pm 61 $4f^5 5d^0 6s^2$ (145)	Sm 62 $4f^6 5d^0 6s^2$ 150.36	Eu 63 $4f^7 5d^0 6s^2$ 151.96	Gd 64 $4f^7 5d^1 6s^2$ 157.25	Tb 65 $4f^9 5d^0 6s^2$ 158.9254	Dy 66 $4f^{10} 5d^0 6s^2$ 162.50	Ho 67 $4f^{11} 5d^0 6s^2$ 164.9304	Er 68 $4f^{12} 5d^0 6s^2$ 167.26	Tm 69 $4f^{13} 5d^0 6s^2$ 168.9342	Yb 70 $4f^{14} 5d^0 6s^2$ 173.04	Lu 71 $4f^{14} 5d^1 6s^2$ 174.967
Th 90 $5f^10 6d^1 7s^2$ 232.0381	Pa 91 $5f^2 6d^1 7s^2$ 231.0359	U 92 $5f^3 6d^1 7s^2$ 238.0289	Np 93 $5f^4 6d^1 7s^2$ 237.0482	Pu 94 $5f^6 6d^0 7s^2$ (244)	Am 95 $5f^7 6d^0 7s^2$ (243)	Cm 96 $5f^7 6d^1 7s^2$ (247)	Bk 97 $5f^9 6d^0 7s^2$ (247)	Cf 98 $5f^{10} 6d^0 7s^2$ (251)	Es 99 $5f^{11} 6d^0 7s^2$ (252)	Fm 100 $5f^{12} 6d^0 7s^2$ (257)	Md 101 $5f^{13} 6d^0 7s^2$ (258)	No 102 $5f^{14} 6d^0 7s^2$ (259)	Lr 103 $5f^{14} 6d^1 7s^2$ (260)

Symbol

H	1	Atomic number
$1s^1$		Outer configuration
1.0079		Atomic mass

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The following procedures from *Collected Radiochemical Procedures*, LA-1721, 4th Ed, have not been included in this revision:

Separation of Milligram Amounts of Cobalt and Manganese from 100 grams of Iron

Standardization of Europium Solutions by Titration with EDTA

Extraction of Plutonium from Phosphoric Acid Solutions by Octylphosphoric Acid

Separation of Element 104 from Fission Products

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Procedures for Quality Control in Counting Radioactive Nuclides

Separation of Scandium from Large Amounts of Titanium Metal

Separation of Yttrium from Zirconium (two procedures)

Separation of Milligrams of Strontium and Zirconium from 100 grams of Yttrium

Separation of Lead from Uranium and the Transuranic Elements

Separation of Milligrams of Zirconium Metal from Ten Grams of Molybdenum Metal

Preparation of Uranium and Plutonium for Mass Spectrometric Analysis; Addendum (Replaced by a new procedure in the revision)

Preparation of Plutonium for Mass Spectrometric Analysis (the less detailed of the two procedures in the 4th Ed)

Analysis of Tritium in Water Samples

Beryllium (p. 27 of the 4th Ed)

Separation of Radioberyllium from Plutonium

$^{230}\text{Th}$ (ionium)

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I. Separation of Radionuclides from Uranium, Fission-Product Solutions and Nuclear Debris

Representative Elements

d-Transition Elements

f-Transition Elements (The Lanthanides and Actinides)

## SODIUM

B. R. Erdal

### 1. Introduction

This procedure for the separation of sodium from all other nuclides produced in nuclear reactions is based primarily on an observation by F. Girardi and E. Sabbioni. These investigators found that in conc HCl only sodium and tantalum, among 60 elements tested, were retained on hydrated antimony(V) oxide,  $\text{Sb}_2\text{O}_5 \cdot \text{XH}_2\text{O}$  (HAP). The sodium is recovered from the HAP by reduction of the antimony(V) with conc HI, extraction of antimony(III) into 4-methyl-2-pentanone (hexone) from HCl medium, and then passage of the aqueous phase through a Dowex AG 1 anion resin column. The sodium is finally converted to NaCl.

The chemical yield is ~75%. A decontamination factor of greater than  $10^4$  has been found for all  $^{235}\text{U}$  thermal-neutron fission products.

### 2. Reagents

Sodium carrier: 5 mg sodium/ml, added as NaCl in 6M HCl; standardized by atomic absorption spectroscopy

Potassium carrier: 5 mg potassium/ml, added as KCl in 6M HCl

Rubidium carrier: 5 mg rubidium/ml, added as RbCl in 6M HCl

Cesium carrier: 5 mg cesium/ml, added as CsCl in 6M HCl

Tellurium carrier: 5 mg tellurium/ml, added as  $\text{K}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$  in 6M HCl

Copper carrier: 5 mg copper/ml, added as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 6M HCl

HCl: conc; 6M

HI: conc (47%)

4-methyl-2-pentanone (hexone)

$\text{H}_2\text{S}$ : gas

HAP:  $\text{Sb}_2\text{O}_5 \cdot \text{XH}_2\text{O}$ ; see below for preparation

Anion-exchange resin: Dowex AG 1-X8, 100 to 200 mesh, thoroughly washed with 6M HCl

1-butanol

Butanol-HCl reagent: 1-butanol saturated with HCl gas

Diethyl ether

### 3. Preparation of HAP

Four hundred and seventy milliliters of  $\text{SbCl}_5$  are diluted to 2 l with  $\text{H}_2\text{O}$ , and the solution is permitted to hydrolyze overnight with stirring. The resulting hydrated oxide is filtered through a large Büchner funnel and washed thoroughly first with 6M HCl and then with  $\text{H}_2\text{O}$ . The material is dried under reduced pressure for several hours, powdered, and dried in an oven at  $270^\circ\text{C}$  for ~5 h. The yellow material is then powdered and sieved. That portion of the oxide having a mesh size between 60 and 170 is used in the procedure.

### 4. Procedure

*Step 1.* To a 40-ml glass centrifuge tube, add 1 ml of standard sodium carrier, an aliquot of the sample, two drops each of potassium, rubidium, cesium, tellurium, and copper carriers; dilute to 5 ml with  $\text{H}_2\text{O}$ . (The HCl concentration should be ~1M.) Saturate the solution with  $\text{H}_2\text{S}$ , digest, and filter under suction through a glass frit of medium porosity, collecting the filtrate in a 50-ml erlenmeyer flask.

*Step 2.* Evaporate the solution to dryness and cool. Dissolve the residue in 0.5 ml of  $\text{H}_2\text{O}$  (Note 1), add 10 ml of conc HCl, and transfer the solution to a clean glass centrifuge tube. Add 300 mg of HAP, mix by swirling for ~5 min, centrifuge, and discard the supernate. Wash the HAP three times with 10-ml portions of conc HCl, each time swirling for ~5 min, centrifuge, and discard the supernate.

*Step 3.* Add 3 ml of conc HI to the HAP and mix until the HAP is well dispersed. Heat for ~2 min on a steam bath, add 1 ml of conc HI, and reheat for ~2 min. Add 6 ml of 6M HCl,

heat for  $\sim 2$  min on a steam bath, and transfer the solution to a 60-ml separatory funnel. Add 20 ml of hexone, shake for  $\sim 1$  min, transfer the aqueous (lower) phase to a clean 60-ml separatory funnel, and discard the organic phase. Extract the aqueous phase with 10 ml of hexone as before and discard the organic phase.

*Step 4.* Transfer the aqueous phase to a clean 40-ml glass centrifuge tube, add 3 ml of  $H_2O$ , and saturate the solution with  $H_2S$ . Filter under suction through a glass frit of fine porosity, collecting the filtrate in a 50-ml erlenmeyer flask. Evaporate the solution to dryness, add 1 ml of conc HCl, and again evaporate to dryness. Repeat the addition of HCl and evaporation.

*Step 5.* Dissolve the residue in a minimum of 6M HCl and transfer the solution to the top of a 10-cm by 4-mm Dowex AG 1-X8, 100 to 200 mesh, anion-exchange resin column. Add 10 ml of 6M HCl to the column and collect the eluate in a 50-ml erlenmeyer flask. Evaporate the solution to dryness.

*Step 6.* To the residue, add 0.5 ml of conc HCl, 5 ml of 1-butanol, and  $\sim 2$  ml of butanol-HCl reagent. Permit the mixture to stand for  $\sim 5$  min, add 8 to 10 ml of diethyl ether, and filter through a synthetic filter paper (Note 2). Wash the precipitate on the filter with diethyl ether, dry under suction and mount for counting.

### Notes

1. The acidity should be kept as high as possible ( $\sim 10M$ ) in *Step 2* to prevent adsorption of rubidium on HAP. Some adsorption of that element occurs from solutions 6M in HCl.

2. Fluoride Metrical VF-6 filter paper [source: Gelman Instrument Co., P.O. Box 1448, Ann Arbor, MI 48106] wet with methanol has been used for mounting. The paper can be washed with methanol and ether and weighed before use without problems arising from humidity.

### REFERENCE

1. F. Girardi and E. Sabbioni, J. Radioanal. Chem. 1, 169 (1968).

(October 1989)

# RUBIDIUM

E. J. Lang

## 1. Introduction

In this procedure for the analysis of radio-rubidium in solutions obtained from underground nuclear debris, alkali metals are first precipitated as perchlorates in an ethanolic medium. Following  $\text{Fe}(\text{OH})_3$  scavengings, rubidium is precipitated as the phospho-9-molybdate, a step that serves effectively to decontaminate the element from potassium. Molybdenum is then removed by precipitation as  $\text{MoS}_3$  from slightly acidic solution. Rubidium perchlorate is again formed, and the element is separated from cesium by adsorption of the latter on a thallium(I) phospho-12-tungstate (TPT) exchange column. The effluent is treated with aqua regia to oxidize thallium to the +3 state, the solution is evaporated to dryness, and any  $\text{NH}_4^+$  ion present is removed by heating the residue. After the thallium is separated by adsorption on an anion-exchange resin from a solution 1M in HCl, rubidium is finally precipitated as the perchlorate. The chemical yield is 50 to 60%.

## 2. Reagents

Rubidium carrier: 10.0 mg rubidium/ml, added as analytical reagent grade RbCl

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1M HCl

HCl: 1M; conc

$\text{HClO}_4$ : conc

$\text{HNO}_3$ : 3M; 6M; conc

Aqua regia: 3:1 V/V conc HCl: conc  $\text{HNO}_3$

$\text{NH}_4\text{OH}$ : conc

NaOH: 6M

$\text{H}_2\text{S}$ : gas

Ethanol: absolute

9-molybdophosphoric acid solution: 5 g of 12-molybdophosphoric acid, gently heated to  $\sim 400$  to  $450^\circ\text{C}$  (color will change through orange to green). Cool. Leach with  $\sim 10$  ml  $\text{H}_2\text{O}$ . Filter, oxidize greenish solution to yellow

solution with bromine water. Make up to  $\sim 20$  ml with 6M  $\text{HNO}_3$ .

TPT exchanger: To 180 ml of a 0.0015M  $\text{TlNO}_3$  solution in 0.4M  $\text{HNO}_3$ , add 50 ml of a solution containing 2% by weight of 12-tungstophosphoric acid ( $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ ) in 0.4M  $\text{HNO}_3$ . Evaporate the mixture containing precipitated thallium(I) phospho-12-tungstate until the volume is  $\sim 10$  ml. Add 2.5 g of filter paper pulp and shake thoroughly.

Anion-exchange resin: Dowex AG 1-X10, 50 to 100 mesh, stored in 6M HCl

## 3. Procedure

*Step 1.* To 2.0 ml of rubidium carrier in a 125-ml erlenmeyer flask, add an aliquot of the sample, 5 ml of conc  $\text{HNO}_3$ , and 8 ml of conc  $\text{HClO}_4$ . Heat until dense  $\text{HClO}_4$  fumes appear and then cool.

*Step 2.* Transfer the solution to a clean 40-ml glass centrifuge tube. Wash the erlenmeyer flask with two 10-ml portions of absolute ethanol and add the washings to the centrifuge tube. With vigorous stirring, cool the contents of the tube for  $\sim 15$  min in an ice bath. Centrifuge and discard the supernate. Add 20 ml of absolute ethanol to the  $\text{RbClO}_4$  precipitate and, with stirring, cool in an ice bath for 15 min. Centrifuge and discard the supernate. Repeat the ethanol wash.

*Step 3.* To the precipitate add 20 ml of  $\text{H}_2\text{O}$  in 1 drop of conc HCl and stir to effect solution. Neglect any residue. Add 5 drops of iron carrier and then conc  $\text{NH}_4\text{OH}$  dropwise until precipitation occurs. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. Repeat the  $\text{Fe}(\text{OH})_3$  scavenge and transfer the supernate to a clean 125-ml erlenmeyer flask.

*Step 4.* Evaporate the solution to dryness, add 5 ml of 3M  $\text{HNO}_3$ , and transfer to a clean centrifuge tube. Wash the erlenmeyer flask twice with 10-ml portions of 3M  $\text{HNO}_3$  and add the washings to the

centrifuge tube. Add 10 ml of freshly prepared 9-molybdophosphoric acid solution, heat to boiling, and let the mixture stand until precipitation of rubidium is complete. Centrifuge and discard the supernate. Wash the precipitate with one 10-ml portion of 3M HNO<sub>3</sub>. Discard the washing.

*Step 5.* Dissolve the precipitate in a minimum amount of 6M NaOH, heating if necessary. Dilute to 20 ml with H<sub>2</sub>O and make barely acidic with 6M HNO<sub>3</sub> and then barely alkaline with 6M NaOH. Saturate the solution with H<sub>2</sub>S, heat to boiling, add 1 drop of conc HNO<sub>3</sub>, and heat to coagulate the MoS<sub>3</sub> precipitate. Centrifuge and transfer the supernate to a clean 125-ml erlenmeyer flask.

*Step 6.* Heat the supernate to dryness. Add 2 ml of 3M HNO<sub>3</sub> to dissolve the residue and transfer the solution to an 8-mm by 5-cm TPT exchange column that has been prepared by washing with 3M HNO<sub>3</sub> under pressure (6 to 8 drops per min) until the effluent is clear. Wash the erlenmeyer flask with two 2-ml portions of 3M HNO<sub>3</sub> and add the washings to the column. By means of air pressure, force the solution through the column at a rate of 6 to 8 drops per min. Collect the effluent in a clean 125-ml erlenmeyer flask. Wash the TPT column with a 5-ml portion of 3M HNO<sub>3</sub> and pass the wash through the column. Repeat the washing. Combine all effluents. (Note)

*Step 7.* Evaporate the solution to dryness, add 5 ml of aqua regia, and take to dryness again. Heat the residue to decompose any ammonium salts present. Cool, add 2 ml of 1M HCl, and put the solution on a Dowex AG 1-X10 anion-exchange resin column, 8-mm by 5-cm, which has been washed with two 5-ml portions of 1M HCl. Rinse the erlenmeyer flask with 2 ml of 1M HCl and add the rinsings to the column. Repeat the washing. Permit the solution and the rinsings to run sequentially through the column under gravity and collect the effluents in a clean 125-ml erlenmeyer flask. (Thallium is adsorbed on the column.)

*Step 8.* To the solution add 5 ml of conc HNO<sub>3</sub> and 8 ml of conc HClO<sub>4</sub>, and evaporate until dense HClO<sub>4</sub> fumes appear. Cool and transfer the solution to a clean centrifuge tube. Wash the erlenmeyer flask with two 10-ml portions of absolute ethanol and add the washings to the centrifuge tube. Cool, with vigorous stirring, in an ice bath for 15 min. Centrifuge and discard the supernate. To the RbClO<sub>4</sub> precipitate, add 20 ml of absolute ethanol and, with stirring, repeat the cooling process. Centrifuge and discard the supernate. Repeat the ethanol wash, but this time filter the precipitate onto a weighed filter circle. Dry the precipitate for 5 min at 110°C. Cool, weigh, and mount for counting.

#### Note

Radiochemically pure cesium, which is strongly adsorbed on the TPT column, can be eluted with 0.15M TINO<sub>3</sub>.

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# CESIUM I

P. B. Elkin

## 1. Introduction

In the separation of cesium from other fission-product activity, a preliminary precipitation of the element as the silicotungstate is carried out. This step gives a decontamination factor of 100 to 200 and is a specific separation of cesium from  $\text{NH}_4^+$  ion, rubidium, and the other alkali metals that may interfere in the determination of cesium as the perchlorate. The silicotungstate is dissolved in alkali and  $\text{CsClO}_4$  precipitated from  $\text{HClO}_4$  medium with absolute ethanol. The initial perchlorate precipitation is followed by two  $\text{Fe}(\text{OH})_3$  scavengings and two additional perchlorate precipitations. Cesium is finally filtered as the perchlorate, which is dried, weighed, and mounted for counting. The chemical yield is 60 to 70%.

## 2. Reagents

Cesium carrier: 10 mg cesium/ml, added as  $\text{CsCl}$  in  $\text{H}_2\text{O}$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

$\text{HCl}$ : 6M; conc

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : 70%

$\text{NaOH}$ : 6M; pellets

$\text{NH}_4\text{OH}$ : 6M

Silicotungstic acid: solid

Ethanol: absolute

Phenolphthalein indicator solution: 1% in 90% ethanol

## 3. Preparation and Standardization of Carrier

Dissolve 12.7 g of  $\text{CsCl}$  in  $\text{H}_2\text{O}$  and dilute to 1 l with  $\text{H}_2\text{O}$ .

Pipette 5 ml of the above carrier solution into a 125-ml erlenmeyer flask and add 3 ml of conc

$\text{HNO}_3$  and 5 ml of  $\text{HClO}_4$ . Boil until dense white fumes appear, cool to room temperature, and add 15 ml of absolute ethanol. Cool for 15 min in an ice bath. Filter on a weighed filter and wash three times with 3-ml portions of absolute ethanol. Dry at  $110^\circ\text{C}$  for 15 min, cool, and weigh as  $\text{CsClO}_4$ .

Four standardizations, with results agreeing within 0.5%, were run.

## 4. Procedure

*Step 1.* To 5 ml of cesium carrier solution in a 40-ml glass centrifuge tube, add an aliquot of sample and make up to a volume of 40 ml, the final solution being 6M in  $\text{HCl}$ . [If the active solution contains  $\text{HNO}_3$ , evaporate (with carrier) to dryness and take up with 40 ml of 6M  $\text{HCl}$ .]

*Step 2.* Add ~2 g of silicotungstic acid dissolved in 2 ml of  $\text{H}_2\text{O}$  and let stand for at least 1 h (preferably overnight). Centrifuge, discard the supernate, and wash the precipitate twice with 10-ml portions of 6M  $\text{HCl}$ .

*Step 3.* Dissolve the cesium precipitate by boiling with 2 ml of  $\text{H}_2\text{O}$  and adding two pellets of  $\text{NaOH}$  (~0.24 g). Add  $\text{H}_2\text{O}$ , if necessary, to prevent boiling to dryness. Pour into 20 ml of hot  $\text{HCl}$  in a 125-ml erlenmeyer flask and boil. Add 0.5 ml of conc  $\text{HNO}_3$  and continue to boil. Add 10 ml of  $\text{HClO}_4$  and boil until white fumes appear. Cool and add 10 ml of  $\text{H}_2\text{O}$ , heat almost to boiling, and centrifuge in a 40-ml tube (Note 1).

*Step 4.* Pour the supernate into a 50-ml erlenmeyer flask, add 1 ml of conc  $\text{HNO}_3$ , and boil until white fumes appear. Cool to room temperature and transfer to a 40-ml centrifuge tube, using 30 ml of absolute ethanol to aid in the transfer. Cool in an ice bath. Stir, let stand for 15 min, and centrifuge. Immediately pour the supernate into a sink drain that is being flushed with running water. Wash the precipitate twice with 10-ml portions of absolute ethanol (Note 2).

*Step 5.* Dissolve the precipitate in 10 ml of H<sub>2</sub>O, heat to boiling, add 0.5 ml of iron carrier, 2 drops of phenolphthalein indicator, and 6M NH<sub>4</sub>OH dropwise until the solution is alkaline. Centrifuge and transfer the supernate to a 40-ml centrifuge tube.

*Step 6.* Add 0.5 ml of iron carrier and again precipitate Fe(OH)<sub>3</sub>. Centrifuge and pour the supernate into a 50-ml erlenmeyer flask.

*Step 7.* Boil and remove NH<sub>3</sub> by adding 2 drops of 6M NaOH.

*Step 8.* Add 0.5 ml of conc HNO<sub>3</sub> and 5 ml of HClO<sub>4</sub>. Boil until white fumes appear. Cool and transfer to a 40-ml centrifuge tube, using 15 ml of absolute ethanol. Cool in an ice bath. Let stand for 15 min, centrifuge, dispose of the supernate as before (*Step 4*), and wash the precipitate twice with 10-ml portions of anhydrous ethanol.

*Step 9.* Dissolve the precipitate in 2 ml of H<sub>2</sub>O, heating if necessary, and transfer to a 50-ml erlenmeyer flask. Wash the centrifuge tube with 2 ml of H<sub>2</sub>O and transfer washing to the 50-ml erlenmeyer flask. Heat to boiling to remove ethanol (1 min). Repeat *Step 8*, making sure to remove HClO<sub>4</sub> thoroughly by washing twice with ethanol.

*Step 10.* Slurry the precipitate in 5 ml of absolute ethanol and filter on weighed filter paper. Use absolute ethanol to complete transfer. Dry at 110°C for 15 min. Cool for 10 min, weigh, and mount. Count immediately (Note 3).

## Notes

1. It is necessary to heat at this stage to ensure rapid and complete dissolution of CsClO<sub>4</sub>. Silica and tungstic oxide (WO<sub>3</sub>) remain behind.

2. The CsClO<sub>4</sub> must be washed thoroughly with absolute ethanol to remove NaClO<sub>4</sub> that has coprecipitated.

3. If 13.7-d <sup>136</sup>Cs is to be determined in the presence of 33-y <sup>137</sup>Cs, gamma-counting with a scintillation counter is advantageous because there are 2 γ's per disintegration for <sup>136</sup>Cs and only one for <sup>137</sup>Cs. A 400-mg Al/cm<sup>2</sup> absorber will stop most of the betas that are emitted by both isotopes of cesium. The most practicable way of resolving the two components, <sup>136</sup>Cs and <sup>137</sup>Cs, is by a least squares determination.

(October 1989)

## CESIUM II

B. E. Cushing

### 1. Introduction

In this procedure, cesium is first precipitated as the silicotungstate. Dissolution of the precipitate is followed by a  $\text{Fe}(\text{OH})_3$  scavenge, and then the cesium is precipitated as the dipicrylamine. This salt is dissolved in 4-methyl-2-pentanone (hexone) and the cesium is extracted by means of 2M HCl. Cesium is finally precipitated as the perchlorate, in which form it is weighed and counted. The chemical yield approximates 70%.

### 2. Reagents

Cesium carrier: 10 mg cesium/ml, added as CsCl in  $\text{H}_2\text{O}$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

$\text{HClO}_4$ : 3M; conc

HCl: 2M; 6M; conc

$\text{HNO}_3$ : conc

NaOH: pellets

Silicotungstic acid: 1 g/ml  $\text{H}_2\text{O}$

Sodium dipicrylamine solution: Stir 25 g of dipicrylamine with 500 ml of  $\text{H}_2\text{O}$  and add 6M NaOH until solution is complete. Allow the solution to stand for several hours and filter.

Ethanol: absolute

4-methyl-2-pentanone (hexone)

Thymol blue indicator solution: Mix 100 mg of thymol blue with 2 ml of 0.1M NaOH and dilute to 100 ml with  $\text{H}_2\text{O}$ .

### 3. Preparation and Standardization of Carrier

Make up an aqueous solution containing 12.7 g of CsCl per liter. Pipette 5 ml of the solution into a 125-ml erlenmeyer flask and add 1 ml of conc  $\text{HNO}_3$  and 5 ml of conc  $\text{HClO}_4$ . Boil until dense white fumes appear, cool to room temperature, and add 15 ml of absolute ethanol. Cool for 15 min in an ice bath. Filter on a weighed filter paper and

wash three times with 3-ml portions of absolute ethanol. Dry at 100°C for 15 min, cool, and weigh as  $\text{CsClO}_4$ .

Four standardizations gave results agreeing within 0.5%, were run.

### 4. Procedure

*Step 1.* To the sample in a 40-ml glass centrifuge tube, add 2 ml of cesium carrier and make the solution 6M in HCl by the addition of the conc acid. Add 2 ml of silicotungstic acid solution, stir, and let the mixture stand for 5 to 10 min. Centrifuge, discard the supernate, and wash the precipitate with 10 ml of 6M HCl.

*Step 2.* Add 2 ml of  $\text{H}_2\text{O}$  to the precipitate, heat to boiling, and then add three pellets of NaOH to dissolve the precipitate.

*Step 3.* Pour the alkaline solution into 20 ml of hot 3M  $\text{HClO}_4$  in a 125-ml erlenmeyer flask. Boil over a burner until the volume is reduced to about 10 ml. Transfer to a 40-ml centrifuge tube and again heat to boiling. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate that consists of silica and tungsten(VI) oxide.

*Step 4.* Add 5 drops of iron carrier, heat, and precipitate  $\text{Fe}(\text{OH})_3$  by adding NaOH pellets singly. Add a few drops of thymol blue indicator and continue to add NaOH until the solution turns blue. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

*Step 5.* Cool the solution in an ice-water bath and add 10 ml of sodium dipicrylamine solution with constant stirring. Continue to stir for 15 min and then place the tube in a refrigerator for at least 30 min.

*Step 6.* Filter through a sintered glass crucible of fine porosity. Wash at 110°C.

*Step 7.* Dissolve the dry precipitate in about 20 ml of 4-methyl-2-pentanone, place the solution in a 60-ml separatory funnel, and add 20 ml of 2M HCl. Shake the funnel vigorously for 1 min and permit the aqueous layer to run into a 125-ml erlenmeyer flask. Extract the 4-methyl-2-pentanone solution twice more with 20-ml portions of 2M HCl and combine the aqueous extracts.

*Step 8.* To the aqueous extracts add 1 ml of conc HNO<sub>3</sub> and evaporate the solution to ~10 ml. Add 5 ml of conc HClO<sub>4</sub> and boil until dense white fumes are evolved.

*Step 9.* Cool and transfer to a 40-ml centrifuge tube using 20 ml of absolute ethanol to effect complete transfer. Cool in an ice bath, let stand for 15 min and centrifuge. Wash the precipitate twice with 10-ml portions of absolute ethanol.

*Step 10.* Slurry the precipitate in 5 ml of absolute ethanol and filter onto a weighed filter paper. Use absolute ethanol to complete the transfer of the CsClO<sub>4</sub> precipitate. Wash the precipitate several times with 5-ml portions of the alcohol. Dry at 110°C for 15 min, cool for 10 min, weigh, and mount. Count immediately.

(October 1989)

# BERYLLIUM I

R. J. Prestwood

## 1. Introduction

This procedure is suitable for the determination of radioberyllium in fission-product solutions containing macro quantities of other metal ions. The procedure consists of the extraction into  $\text{CCl}_4$  of the beryllium-acetylacetonate complex from a solution of EDTA at a pH of 7.7 (Note 1), followed by an anion-exchange column separation, a NaOH scavenge, fluoride scavenges, and mounting as  $\text{BaBeF}_4$ . The chemical yield is  $\sim 90\%$ . Beryllium run on  $10^{14}$  fissions 4 d old gave less than 1  $\beta$  count/min. Another sample, consisting of a mixture of  $^7\text{Be}$ ,  $10^{14}$  old fission products, and  $2 \times 10^{14}$  fresh fission products in 100 ml of 4M HCl, resulted in pure  $^7\text{Be}$ .

## 2. Reagents

Beryllium carrier: 2.5 mg beryllium/ml, added as  $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

Zirconium, lanthanum, and scandium carriers: 10 mg metal/ml, added as nitrate or chloride

Tellurium carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_4$  in  $\text{H}_2\text{O}$

HCl: conc, 6M

$\text{HNO}_3$ : conc

HF: conc

$\text{NH}_4\text{OH}$ : conc

NaOH: 10M

$\text{BaCl}_2$ : 1.0M

EDTA: 0.2M solution of the disodium salt of ethylenediaminetetraacetic acid

Dowex AG 1-X8 anion-exchange column: 50 to 100 mesh, 8 mm by 4 cm, pretreated with conc HCl

Methyl red indicator solution: 0.1% in ethanol

Acetylacetonate (3,4-pentanedione): solution made by shaking 15 ml with 100 ml  $\text{H}_2\text{O}$

Wash solution: The wash solution for the extraction is made up as follows: 15 ml acetylacetonate, 100 ml 0.2M EDTA, and 300 ml  $\text{H}_2\text{O}$ ;  $\text{NH}_4\text{OH}$  added until the pH

reaches 7.7. Kept in tightly closed plastic bottle

$\text{CCl}_4$

pH meter

## 3. Procedure

*Step 1.* Add in order into a beaker of suitable size: 2 ml beryllium carrier, the sample to be analyzed, an equal volume of EDTA or 10 ml EDTA (whichever is larger), and 10 ml of acetylacetonate solution. Mix thoroughly. Add conc  $\text{NH}_4\text{OH}$  until the pH equals  $7.7 \pm 0.1$ . (Use the pH meter to get an accurate pH reading.) Transfer the solution to a separatory funnel of appropriate size. A water rinse may be used on the beaker because it does not change the pH.

*Step 2.* Add 8 ml  $\text{CCl}_4$  and shake 1 min. Transfer the  $\text{CCl}_4$  layer to 60-ml separatory funnel. Extract twice more with 8 ml of  $\text{CCl}_4$ ; add each portion to the same 60-ml separatory funnel. Discard the  $\text{H}_2\text{O}$  layer. To the 24 ml of  $\text{CCl}_4$  add 20 ml of wash solution (see Reagents). Shake 1 min and let stand several minutes. Transfer the  $\text{CCl}_4$  to a clean separatory funnel.

*Step 3.* Add 10 ml of 6M HCl to the  $\text{CCl}_4$  and shake for  $\sim 30$  s. Drain the  $\text{CCl}_4$  into a clean 60-ml separatory funnel and then drain the 10 ml of 6M HCl containing the beryllium into a 125-ml erlenmeyer flask. Add 5 ml of 6M HCl to the  $\text{CCl}_4$  in the separatory funnel, shake 30 s and discard the  $\text{CCl}_4$ . Drain the 5 ml of 6M HCl into the 125-ml erlenmeyer containing the first 10-ml portion of 6M HCl.

*Step 4.* Add 1 drop each of zirconium and tellurium carriers, then boil the 6M HCl down almost to dryness, adding a few drops of conc  $\text{HNO}_3$  if the solution starts to turn dark because of the organic material present. Add  $\sim 2$  ml of conc HCl and boil down again almost to dryness. Cool. Add 2 to 3 ml of conc HCl and swirl to dissolve the contents of the erlenmeyer. Pass through  $\sim 2$  in. of

Dowex AG 1-8X resin, 50 to 100 mesh, prepared as described in Note 2. Wash the erlenmeyer with 2-ml portions of conc HCl and pass through the column. Collect all effluents in a 40-ml plastic centrifuge cone. Heat in a steam bath carefully while stirring to drive off some of the excess HCl gas. Add 5 ml of 0.2M EDTA and 10 ml of H<sub>2</sub>O. Add excess NH<sub>4</sub>OH and put in an ice bath for ~30 min or until all the beryllium has precipitated as Be(OH)<sub>2</sub>. Centrifuge and discard the supernate if it is clear. If not, replace in the ice bath and centrifuge again.

*Step 5.* Dissolve the Be(OH)<sub>2</sub> in 10 drops of conc HCl and add 1 drop of zirconium carrier. Make the volume ~15 ml with H<sub>2</sub>O and add 3 to 4 ml 10M NaOH. Mix thoroughly and centrifuge the Zr(OH)<sub>4</sub>. Transfer the supernate to a clean plastic centrifuge cone and discard the Zr(OH)<sub>4</sub>.

*Step 6.* To the supernate add 2 drops of methyl red solution and conc HCl until the solution is acidic. Precipitate Be(OH)<sub>2</sub> by adding NH<sub>4</sub>OH. Centrifuge and discard the supernate. Dissolve the Be(OH)<sub>2</sub> with 10 drops of conc HCl and dilute to 15 ml with H<sub>2</sub>O. Add 4 drops of lanthanum carrier and 25 drops of conc HF. Mix thoroughly and centrifuge; then transfer the supernate to a clean plastic tube.

*Step 7.* Add NH<sub>4</sub>OH until the solution is neutral. Add 1 more drop and 4 drops of lanthanum carrier. Centrifuge and pour the supernate into a clean plastic tube. Add 5 ml of conc HCl and 10 drops of scandium carrier. Heat for 5 min on the steam bath, let stand several minutes, centrifuge, transfer the supernate to a clean plastic tube, and discard the ScF<sub>3</sub>.

*Step 8.* Put sample in a steam bath until hot and add 1.5 ml of 1M BaCl<sub>2</sub>. Digest in the steam bath for 2 min, let stand a few minutes more, then centrifuge. Discard the supernate, wash the precipitate with 15 ml of H<sub>2</sub>O, centrifuge, and discard the wash. Transfer the precipitate with H<sub>2</sub>O to the Millipore filter system (Note 3). Filter

the sample, wash with H<sub>2</sub>O, allow to remain on the filter assembly with suction applied for ~20 min, then disassemble and dry at 110°C for 5 min.

## Notes

1. The extraction is very specific for beryllium, and the only activities observed after this step were <sup>132</sup>Te-<sup>132</sup>I and <sup>95</sup>Zr-<sup>95</sup>Nb. The anion-exchange column removes both tellurium and zirconium.

2. To prepare the resin column for use (a) place a small plug of glass wool in the tip of the column, (b) add enough resin slurry to obtain a bed height of 4 to 5 cm, and (c) allow the acid to drain off. (The column is fabricated by fusing a 15-ml conical centrifuge tube to an 8-cm length of 1-cm tubing drawn to a tip.)

3. The Millipore filter system consists of the 25-mm, 0.8-μm pore, designation AAWP 025 00 Millipore filter clamped on top of a Whatman No. 42 filter paper mounted on a regular Millipore sintered glass filter and suction flask. After the filtering, the chimney is left clamped in place and air is sucked through until the precipitate and papers are dry; this prevents the Millipore filter paper from sticking to the chimney when it is removed. Because the Whatman filter is used as a backing, the two filters may be removed as a unit and dried and weighed together. A Millipore filter with a precipitate on it is difficult to handle—hence the double papers. A pair of similar filters is treated the same as the sample and used as a tare in the balance. After being weighed, the Millipore filter is treated with 4 or 5 drops of 6% rubber cement in benzene, separated from the Whatman filter, dried, and mounted for counting.

(October 1989)

## BERYLLIUM II

R. J. Prestwood

### 1. Introduction

The beryllium procedure that precedes this generally works well, but occasionally the separation of aluminum and beryllium is not satisfactory, probably because of interference by  $F^-$  ion. This procedure appears to give a more reliable aluminum-beryllium separation and also is much simpler.

The sample is fumed to dryness with  $H_2SO_4$  and  $HClO_4$  and ignited at  $550^\circ C$  for 30 min. Precipitations of hydroxides with  $NH_4OH$  are followed by  $La(OH)_3$  scavenges with  $NaOH$ ; beryllium, because of its amphoteric character, remains in solution in the  $NaOH$  scavenges. Then two precipitations of  $Be(OH)_2$  by  $NH_4OH$  are carried out, and the hydroxide is dissolved in  $0.25M H_2C_2O_4-0.1M HCl$ . The solution is passed through an AG MP-1 anion-exchange resin column and the beryllium-containing effluent is treated with  $NH_4OH$ . Any aluminum present is removed here. The  $Be(OH)_2$  precipitate is dissolved in conc  $HCl$  and another anion resin column step is performed; any uranium, tellurium, and zirconium in the solution remain on the column. Beryllium in the effluent is precipitated as the hydroxide with  $NH_4OH$ . The hydroxide is ignited to  $BeO$  and the  $477.6\text{-keV}$  alpha of beryllium is counted on a  $Ge(Li)$  counter. The chemical yield is 65 to 85%.

### 2. Reagents

Beryllium carrier: 10 mg beryllium/ml. Made by dissolving 99.88% pure metal in  $HCl$ .

Zirconium, lanthanum, yttrium, and neodymium carriers: 10 mg metal/ml, added as chlorides

Tellurium carrier: 10 mg tellurium/ml, added as  $Na_2TeO_4$  in dilute  $HCl$

$HClO_4$ : conc

$H_2SO_4$ : conc

$HCl$ :  $6M$ ; conc

$NaOH$ :  $10M$

$H_2C_2O_4-HCl$  solution:  $0.25M$  in  $H_2C_2O_4$  and  $0.1M$  in  $HCl$

$NH_4OH$ : conc

AG MP-1 anion-exchange resin, 50 to 100 mesh; packed in Econo-Column <sup>TM</sup>Polypropylene columns; source: Bio-Rad Laboratories, Richmond, California. Column dimensions:  $\sim 10$  cm long; reservoir volume:  $\sim 9$  ml; resin bed volume:  $\sim 2$  ml; bed dimensions:  $\sim 4$  cm by  $\sim 0.8$  cm.

Methyl red indicator: 0.1% in ethanol

### 3. Procedure

*Step 1.* To a 125-ml erlenmeyer flask, add 2 ml of beryllium carrier, the sample to be analyzed (25 to 50 ml), 1 drop each of zirconium, lanthanum, yttrium, neodymium, and tellurium carriers, and 2 ml each of conc  $H_2SO_4$  and  $HClO_4$ . Evaporate to dryness overnight on a hot plate (Note 1). Place the erlenmeyer flask in a furnace and heat at  $550^\circ C$  for 30 min. (The flask must be labeled by a metal marker; otherwise the identification number will burn off.) Let the flask cool and dissolve the residue in  $\sim 10$  ml of  $6M HCl$  at low heat on a hot plate.

*Step 2.* Transfer the solution to a 40-ml glass centrifuge tube and add enough conc  $NH_4OH$  to make the solution alkaline. Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in a slight excess of conc  $HCl$ , dilute the solution to  $\sim 20$  ml with  $H_2O$ , and make alkaline with  $10M NaOH$ . Add  $\sim 1$  ml of excess  $NaOH$  to ensure solution of beryllium. [ $Be(OH)_2$  is amphoteric.] Centrifuge the zirconium-lanthanum-yttrium-neodymium hydroxide precipitate, add 1 drop each of zirconium, lanthanum, yttrium, and neodymium carriers to the supernate, swirl gently, and centrifuge again. Transfer the supernate to a clean centrifuge tube and repeat twice the double hydroxide precipitation of zirconium, lanthanum, yttrium, and neodymium. Centrifuge and transfer the supernate to a clean centrifuge tube.

*Step 4.* Add 1 drop of methyl red indicator to the supernate, neutralize the solution with conc HCl, and add a few drops in excess. Precipitate hydroxides with conc  $\text{NH}_4\text{OH}$ . (If aluminum was originally present in the sample, it is still present.)

*Step 5.* Dissolve the precipitate in a minimum of conc HCl and reprecipitate hydroxides with conc  $\text{NH}_4\text{OH}$ . (Two precipitations are necessary to minimize the presence of  $\text{Na}^+$ .) Centrifuge and discard the supernate.

*Step 6.* Reduce the hydroxide precipitate to a very small volume by drying it in a steam bath. (The precipitate is voluminous and its  $\text{H}_2\text{O}$  content would change drastically the concentration of the  $\text{H}_2\text{C}_2\text{O}_4$ -HCl solution that is used to dissolve it.) Add 8 ml of the 0.25M  $\text{H}_2\text{C}_2\text{O}_4$ -0.1M HCl and use a stirring rod to help dissolve the precipitate. (The dissolving process is slow.) Prepare the AG MP-1 anion-exchange resin column and wash it with several ml of the  $\text{H}_2\text{C}_2\text{O}_4$ -HCl solution. Add the solution to the top of the resin column and allow it to drip through. Wash the column twice with 5-ml portions of  $\text{H}_2\text{C}_2\text{O}_4$ -HCl solution. Collect all effluents in a clean centrifuge tube. Any aluminum still in the sample remains on the column.

*Step 7.* To the combined effluents, add conc  $\text{NH}_4\text{OH}$  in slight excess to precipitate  $\text{Be}(\text{OH})_2$ . Centrifuge and discard the supernate.

*Step 8.* Prepare another anion-exchange column with AG MP-1 resin and wash the resin with conc HCl. Dissolve the  $\text{Be}(\text{OH})_2$  in 5 to 6 ml of conc HCl, pass the solution through the column, and collect the effluent in a clean centrifuge tube. (This step is used primarily to remove tellurium, which stays on the resin.) Wash the column twice with 2-ml portions of conc HCl and combine the three effluents.

*Step 9.* Dilute the combined effluents with an equal volume of  $\text{H}_2\text{O}$  and carefully neutralize the solution with conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{Be}(\text{OH})_2$  (Note 2). Centrifuge and discard the supernate.

Dissolve the precipitate in a minimum of conc HCl, dilute the solution to  $\sim 5$  ml with  $\text{H}_2\text{O}$ , add paper pulp, and precipitate  $\text{Be}(\text{OH})_2$  with conc  $\text{NH}_4\text{OH}$ . Filter and ignite to  $\text{BeO}$  at  $1000^\circ\text{C}$  in a furnace for 30 min.

## Notes

1. It is perfectly safe to fume to dryness a solution containing  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  if both acids are initially dilute. Do not add conc  $\text{H}_2\text{SO}_4$  to conc  $\text{HClO}_4$  and fume the solution. An explosion may occur.

2. This precipitate is checked on a Ge(Li) counter for contaminants, which, if present, are usually small amounts of lanthanum and cerium and sometimes arsenic. If there are only very small amounts of impurities, they are generally ignored because they do not interfere with the Ge(Li) counting of the 477.6-keV gammas of  $^7\text{Be}$ . If the  $\text{Be}(\text{OH})_2$  contains relatively large amounts of impurities, repeat the double NaOH scavenge as described in *Step 9*. Then carry out two double  $\text{NH}_4\text{OH}$  precipitations before igniting  $\text{Be}(\text{OH})_2$ . These precipitations are necessary to ensure that no sodium salts are present to distort the chemical yield.

(October 1989)



## MAGNESIUM

R. J. Prestwood and B. P. Bayhurst

### 1. Introduction

This procedure has been employed in a search for  $^{28}\text{Mg}$  in fission. After common decontamination steps, the magnesium is finally isolated as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . A sample containing  $3 \times 10^{14}$  fissions 3 d old gave a final precipitate with no detectable contaminants.

### 2. Reagents

Magnesium carrier: 10 mg magnesium/ml, added as a solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The carrier is standardized as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1M HCl

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Scandium carrier: 10 mg scandium/ml, added as  $\text{ScCl}_3$  in 1M HCl

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 1M HCl

Cadmium carrier: 10 mg cadmium/ml, added as  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Cobalt carrier: 10 mg cobalt/ml, added as  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Barium carrier: 1M  $\text{BaCl}_2$

Strontium carrier: 10 mg strontium/ml, added as  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{H}_4\text{TeO}_6$  in 0.3M HCl

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in 1M HCl

HCl: conc; 6M

$\text{H}_2\text{SO}_4$ : conc

$\text{NH}_4\text{OH}$ : conc; 0.1M

$\text{NaOH}$ : 10M

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : solid

$\text{NH}_4\text{Cl}$ : 3M

$(\text{NH}_4)_2\text{HPO}_4$ : 1.5M

$\text{H}_2\text{S}$ : gas

Ethanol: absolute

Dowex AG 50-X4, 100 to 200 mesh cation-exchange resin; slurry in  $\text{H}_2\text{O}$

Dowex AG 1-X8, 50 to 100 mesh anion-exchange resin; slurry in 6M HCl

### 3. Procedure

*Step 1.* Add the sample (Note) to 1 ml of magnesium carrier in a 40-ml conical centrifuge tube and precipitate  $\text{Mg}(\text{OH})_2$  by the dropwise addition of an excess of 10M NaOH. Centrifuge and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, add ~100 mg of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and warm on a steam bath for 3 to 5 min. Add 5 ml of 3M  $\text{NH}_4\text{Cl}$  and dilute to 20 ml with  $\text{H}_2\text{O}$ .

*Step 2.* Add 2 drops each of iron, lanthanum, scandium, and zirconium carriers and then an excess of conc  $\text{NH}_4\text{OH}$  dropwise. Centrifuge and transfer the supernate to a clean centrifuge tube; discard the precipitate.

*Step 3.* Add 2 drops each of iron and lanthanum carriers, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 4.* To the supernate add 10 drops of cadmium carrier, 2 drops of cobalt carrier, bubble in  $\text{H}_2\text{S}$  for ~2 min, centrifuge, and transfer the supernate to a clean centrifuge tube; discard the precipitate.

*Step 5.* Repeat the CdS-CoS precipitation. Centrifuge and filter the supernate into a clean centrifuge tube; discard the precipitate. Boil to remove  $\text{H}_2\text{S}$ .

*Step 6.* Add 2 drops of barium carrier, 10 drops of strontium carrier, a volume of absolute ethanol equal to the total volume of solution, and 4 drops of conc  $\text{H}_2\text{SO}_4$ . Let the solution stand for 10 min, then centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. To the supernate add 2 drops of barium carrier

and 10 drops of strontium carrier, let stand for 10 min, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 7.* To the supernate add an excess of 10M NaOH dropwise to precipitate  $\text{Mg}(\text{OH})_2$ . Centrifuge and discard the supernate.

*Step 8.* To the precipitate add 5 ml of conc HCl and 4 drops of tellurium(VI) carrier and boil the solution down to a volume of 1 ml. Dilute to 15 ml with  $\text{H}_2\text{O}$ , add 2 drops of palladium carrier, and bubble in  $\text{H}_2\text{S}$  for ~2 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 9.* Add 2 drops each of cadmium and palladium carriers and bubble in  $\text{H}_2\text{S}$  for ~2 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 10.* Repeat *Step 7*.

*Step 11.* To the precipitate add 3 ml of conc HCl and boil for 1 min. Dilute with  $\text{H}_2\text{O}$  to 20 ml, add 3 ml of 1.5M  $(\text{NH}_4)_2\text{HPO}_4$ , and then add an excess of conc  $\text{NH}_4\text{OH}$  dropwise to precipitate  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Centrifuge and discard the supernate. Wash the precipitate with  $\text{H}_2\text{O}$  containing a few drops of  $\text{NH}_4\text{OH}$  and discard the washings.

*Step 12.* Dissolve the precipitate in 1 to 2 drops of conc HCl and dilute to 10 ml with  $\text{H}_2\text{O}$ . Place the solution on a Dowex AG 50-X4, 100 to 200 mesh cation-exchange resin column (8-mm diam and 4-cm length), add two 5-ml portions of  $\text{H}_2\text{O}$  to the column, and discard the effluents.

*Step 13.* Place the cation-exchange column on top of a Dowex AG 1-X8, 50 to 100 mesh anion-exchange resin column (8-mm diam and 4-cm length) so that the effluent from the cation column can drip onto the anion column. To the cation column add two 5-ml portions of 6M HCl and permit the effluents to flow into the anion column.

Collect the effluent from the anion column in a clean centrifuge tube.

*Step 14.* Repeat *Steps 2* through *11*.

*Step 15.* Dissolve the precipitate in a few drops of conc HCl and dilute the solution to 20 ml with  $\text{H}_2\text{O}$ . Centrifuge and transfer the supernate to a clean centrifuge tube. To the supernate add 3 ml of 1.5M  $(\text{NH}_4)_2\text{HPO}_4$  and heat on a steam bath for 2 min. Add conc  $\text{NH}_4\text{OH}$  dropwise until  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  precipitates. Filter the precipitate onto a weighed filter paper, wash the precipitate with 0.1M  $\text{NH}_4\text{OH}$  and then with absolute ethanol. Dry in an oven at 110°C. Cool, weigh, and mount.

#### Note

If the original sample contains large amounts of salts, it should be treated in the following manner. Insoluble hydroxides are precipitated from a buffered  $\text{NH}_4^+-\text{NH}_4\text{OH}$  solution; most of the magnesium is left in the supernate and is recovered by precipitation with NaOH. The precipitate from the  $\text{NH}_4\text{OH}$  treatment is dissolved and reprecipitated until no detectable magnesium is found in the supernate after addition of NaOH. All  $\text{Mg}(\text{OH})_2$  precipitates are dissolved in conc HCl and combined. The solution is then treated with  $\text{NH}_2\text{OH} \cdot \text{HCl}$  as described in *Step 1* before *Step 2* is taken.

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# CALCIUM

W. H. Burgess

## 1. Introduction

Calcium is first separated from most of the fission products by appropriate  $\text{Fe}(\text{OH})_3$ , acid sulfide, and  $(\text{NH}_4)_2\text{S}$  scavenging steps, followed by separation of calcium, strontium, and barium as oxalates. The oxalates are then dissolved, and strontium and barium are removed quantitatively by precipitation of their nitrates from fuming  $\text{HNO}_3$ . The 40-h  $^{140}\text{La}$ , which has grown in from 12.5-d  $^{140}\text{Ba}$  during the interval between the  $\text{Fe}(\text{OH})_3$  scavenging step and the last separation of barium and strontium from calcium, is separated by means of  $\text{La}(\text{OH})_3$  scavenge. Calcium is finally precipitated as calcium oxalate monohydrate,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , and counted in this form. The chemical yield is ~30%.

## 2. Reagents

Calcium carrier: 10 mg calcium/ml, added as  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HCl}$

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in very dilute  $\text{HCl}$

Copper carrier: 10 mg copper/ml, added as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Nickel carrier: 10 mg nickel/ml, added as  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Cobalt carrier: 10 mg cobalt/ml, added as  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Strontium carrier: 10 mg strontium/ml, added as  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Barium carrier: 10 mg barium/ml, added as  $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : 6M

$\text{HNO}_3$ : conc; white fuming

$\text{NH}_4\text{OH}$ : conc

$(\text{NH}_4)_2\text{CO}_3$ : saturated aqueous solution

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ : 4% aqueous solution

$\text{NaBrO}_3$ : 1M

$\text{H}_2\text{S}$ : gas

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 59.0 of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ . Add 1 ml of  $\text{HNO}_3$ , and dilute to 1 l with  $\text{H}_2\text{O}$ .

Pipette a 2-ml aliquot of the above carrier solution into a 100-ml beaker, dilute to 50 ml, heat to boiling, precipitate  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by the addition of a slight excess of 4%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Filter into a weighed, sintered glass 15-ml Gooch crucible (fine porosity). Wash three times with 10-ml portions of hot  $\text{H}_2\text{O}$  and once with ethanol. Suck dry for several minutes. Dry to constant weight in an oven at no more than  $100^\circ\text{C}$ .

Four standardizations are performed. The results should agree within 0.5%.

## 4. Procedure

*Step 1.* To the sample in a 40-ml centrifuge tube, add sufficient  $\text{H}_2\text{O}$  to bring the volume to 15 to 20 ml, then add 2 ml of standard calcium carrier. If no appreciable quantity of uranium is present, proceed immediately to *Step 2*. If uranium is present, heat the solution to boiling and precipitate ammonium diuranate by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the precipitate, transferring the supernate to 40-ml centrifuge tube.

*Step 2.* Acidify the solution with conc  $\text{HNO}_3$ , add 6 drops of iron carrier, heat to boiling, and precipitate  $\text{Fe}(\text{OH})_3$  by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the precipitate, transferring the supernate to a 40-ml centrifuge tube.

*Step 3.* Repeat *Step 2* twice.

*Step 4.* Make the supernate, after the  $\text{Fe}(\text{OH})_3$  scavenging operation, 0.1M in HCl, and add 4 drops of palladium and 8 drops of copper carriers. Heat to boiling and pass in  $\text{H}_2\text{S}$  for 4 to 5 min. Filter and discard the precipitate, catching the filtrate in a 40-ml centrifuge tube.

*Step 5.* Add four drops each of nickel and cobalt carriers to the filtrate and heat to boiling. Add conc  $\text{NH}_4\text{OH}$  until the solution is alkaline to litmus, then add an additional 0.5 ml of  $\text{NH}_4\text{OH}$ . Pass in  $\text{H}_2\text{S}$  for 3 min, filter the ammonium sulfide scavenging precipitate and discard it, catching the filtrate in a 40-ml centrifuge tube.

*Step 6.* Add 3 ml of 4%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution to the filtrate from *Step 5*. Centrifuge, discard the supernate. Wash the precipitate with 30 ml of  $\text{H}_2\text{O}$ .

*Step 7.* Dissolve the precipitate in 5 ml of  $\text{H}_2\text{O}$  and 1 ml of conc  $\text{HNO}_3$ . Add 1 ml each of barium and strontium carriers. Precipitate  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$  by the addition of 30 ml of white fuming  $\text{HNO}_3$ . Cool in an ice bath for several minutes. Centrifuge, discard the precipitate, and transfer the supernate to a 125-ml erlenmeyer flask.

*Step 8.* Boil down the calcium-containing supernate to a volume of 1 to 2 ml. Add 5 ml of  $\text{H}_2\text{O}$ , 1 ml each of barium and strontium carriers, and 30 ml of fuming  $\text{HNO}_3$  to precipitate  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$ . Cool and transfer the mixture to a 40-ml centrifuge tube. Centrifuge, transfer the supernate to a 125-ml erlenmeyer flask, and discard the precipitate.

*Step 9.* Repeat *Step 8*.

*Step 10.* Boil down the supernate to 2 to 3 ml and add 30 ml of  $\text{H}_2\text{O}$ . Transfer to a 40-ml centrifuge tube and make ammoniacal with conc  $\text{NH}_4\text{OH}$ . Add 2 ml of 4%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution to ensure complete precipitation of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Centrifuge and discard the supernate.

*Step 11.* Dissolve the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in 2 ml of conc  $\text{HNO}_3$  and 2 ml of 1M  $\text{NaBrO}_3$  (Note 1). Boil down to ~1 ml. Add 30 ml of  $\text{H}_2\text{O}$ , make strongly ammoniacal, and add 4 ml of saturated  $(\text{NH}_4)_2\text{CO}_3$  solution. Centrifuge the  $\text{CaCO}_3$  and discard the supernate.

*Step 12.* Dissolve the  $\text{CaCO}_3$  in 1 to 2 ml of conc  $\text{HNO}_3$ . Dilute to 30 ml, and add 1 ml of lanthanum carrier. Precipitate  $\text{La}(\text{OH})_3$  by the addition of conc  $\text{NH}_4\text{OH}$ . Centrifuge, transfer the supernate to a 40-ml centrifuge tube, and discard the precipitate.

*Step 13.* Heat the supernate to boiling and precipitate  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by the dropwise addition of 3 ml of 4%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Filter the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  onto a weighed filter paper. Wash three times with 10-ml portions of hot  $\text{H}_2\text{O}$  and then with ethanol. Suck dry. Dry in oven at 100°C for 5 min. Weigh, mount, and count (Note 2).

## Notes

1.  $\text{NaBrO}_3$  is used to destroy oxalate and thus avoid precipitation of lanthanum oxalate when the lanthanum carrier is added (*Step 12*).

2. No special precautions need be taken in counting. If short-lived isotopes are present, the decay curve must be resolved. If 150-d  $^{45}\text{Ca}$  is to be counted, the chemistry employed for separation of calcium is carried out after the decay of the short-lived isotopes.

(October 1989)

## STRONTIUM-90

B. P. Bayhurst

### 1. Introduction

In the determination of  $^{90}\text{Sr}$ , the element is first separated as the nitrate. This is an excellent decontamination step: the major impurity is barium, which is removed by a series of  $\text{BaCrO}_4$  precipitations. The strontium is then converted to the carbonate; the chemical yield at this stage is  $\sim 75\%$ . Yttrium-90 is permitted to grow into equilibrium with the  $^{90}\text{Sr}$ . Yttrium carrier is added and separated with the  $^{90}\text{Y}$  from the strontium by precipitation as hydroxide. Finally, yttrium is precipitated as oxalate and ignited to oxide, in which form it is counted. The chemical yield of yttrium carrier is  $\sim 85\%$ .

### 2. Reagents

Strontium carrier: 10 mg strontium/ml, added as  $\text{Sr}(\text{NO}_3)_2$  in dilute  $\text{HNO}_3$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HCl}$

Yttrium carrier: 10 mg yttrium/ml (for preparation and standardization see YTTTRIUM II procedure)

Barium carrier: 10 mg barium/ml, added as  $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : 1M; conc

$\text{HNO}_3$ : fuming; conc

$\text{HC}_2\text{H}_3\text{O}_2$ : glacial

$\text{NH}_4\text{OH}$ : conc

$\text{Na}_2\text{CO}_3$ : saturated aqueous solution

$\text{Na}_2\text{CrO}_4$ : 10% aqueous solution

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ : saturated aqueous solution

$\text{KClO}_3$ : solid

Ethanol: 95%

### 3. Preparation and Standardization of Carrier

Dissolve 241.5 g of  $\text{Sr}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$ , add 10 ml of conc  $\text{HNO}_3$ , and dilute to 1 l with  $\text{H}_2\text{O}$ . Into a 40-ml centrifuge tube, pipette 5.0 ml of the

carrier solution and add 15 ml of saturated  $\text{Na}_2\text{CO}_3$  solution. Stir and allow to stand for at least 15 min. Filter the  $\text{SrCO}_3$  precipitate through a weighed 15-ml sintered glass crucible of fine porosity. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$  and again with 5 ml of 95% ethanol. Dry in oven at  $110^\circ\text{C}$ .

Four standardizations are carried out, and results agree within  $\sim 0.5\%$ .

### 4. Procedure

*Step 1.* Pipette 2.0 ml of standard strontium carrier into a 40-ml conical centrifuge tube. Add an aliquot of sample and adjust the volume to  $\sim 5$  ml with  $\text{H}_2\text{O}$ . Add 30 ml of cold, fuming  $\text{HNO}_3$  (Note 1) and permit the mixture to stand in an ice bath for  $\sim 10$  min. Centrifuge and discard the supernate.

*Step 2.* Dissolve the  $\text{Sr}(\text{NO}_3)_2$  precipitate in 10 ml of  $\text{H}_2\text{O}$  and add 5 drops of iron carrier. Make the solution alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$  and then add 10 drops in excess. Stir, centrifuge, decant the supernate into a clean 40-ml centrifuge tube, and discard the precipitate.

*Step 3.* Add 2 ml of glacial  $\text{HC}_2\text{H}_3\text{O}_2$  to bring the pH of the solution to 3.5 to 4.0. Then add 2 ml of barium carrier and 2 ml of 10%  $\text{Na}_2\text{CrO}_4$  solution and digest for 10 to 15 min on a steam bath with occasional stirring. Centrifuge, decant the supernate into a clean 40-ml centrifuge tube, and discard the precipitate.

*Step 4.* Add 5 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and digest on a steam bath for 5 to 10 min. Centrifuge and discard the supernate. Wash the precipitate by adding 2 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 20 ml of  $\text{H}_2\text{O}$  and stirring. Centrifuge and discard the wash.

*Step 5.* Add 2 ml of conc  $\text{HNO}_3$  and 5 ml of  $\text{H}_2\text{O}$ , stir, and then add 30 ml of fuming  $\text{HNO}_3$ . Allow to stand in an ice bath for  $\sim 10$  min. Centrifuge and discard the supernate.

*Step 6.* Repeat *Steps 2* through *4*.

*Step 7.* To the precipitate of  $\text{SrC}_2\text{O}_4$  add 2 ml of conc  $\text{HNO}_3$  and  $\sim 200$  mg of  $\text{KClO}_3$ . Carefully bring the solution to a boil and then boil vigorously for  $\sim 2$  min.

*Step 8.* Adjust the volume to  $\sim 15$  ml with  $\text{H}_2\text{O}$  and add 5 drops of iron carrier. Make the solution alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$  and then add 10 drops in excess. Stir, centrifuge, and decant the supernate into a clean 40-ml centrifuge tube, discarding the precipitate.

*Step 9.* Repeat *Step 3*, except filter the  $\text{BaCrO}_4$  precipitate through a 2-in.  $60^\circ$  funnel. Collect the filtrate in a clean 40-ml centrifuge tube.

*Step 10.* To the filtrate add conc  $\text{NH}_4\text{OH}$  until the solution is barely alkaline. Then add 5 ml of saturated  $\text{Na}_2\text{CO}_3$  solution to precipitate  $\text{SrCO}_3$ . Centrifuge and discard the supernate. Wash the precipitate with a mixture of 10 ml of  $\text{H}_2\text{O}$  and 2 ml of saturated  $\text{Na}_2\text{CO}_3$ . Centrifuge and discard the wash. Slurry the precipitate and filter onto a weighed filter circle. Wash the precipitate with 5 ml of  $\text{H}_2\text{O}$  and 5 ml of 95% ethanol, dry in an oven at  $110^\circ\text{C}$ , and weigh (Note 2). Transfer the precipitate into a clean 40-ml centrifuge tube and permit  $^{90}\text{Y}$  to grow into equilibrium with the  $^{90}\text{Sr}$ . (This process requires  $\sim 18$  d. Note 3.)

*Step 11.* After equilibrium has been attained, wash down the sides of the tube with 10 to 15 ml of 1M  $\text{HCl}$ . Add 2 ml of standard yttrium carrier and stir. Slide the filter circle up the side of the tube with the stirring rod and, while holding the paper, wash with 1M  $\text{HCl}$  and remove it.

*Step 12.* Add conc  $\text{NH}_4\text{OH}$  dropwise until  $\text{Y}(\text{OH})_3$  precipitates and then add 5 ml in excess. Centrifuge and save the supernate until the results of analysis for yttrium have been checked. Record the time (Note 4).

*Step 13.* Dissolve the  $\text{Y}(\text{OH})_3$  in a minimum of conc  $\text{HCl}$  and add 15 ml of  $\text{H}_2\text{O}$ . Add 20 mg of strontium holdback carrier and precipitate  $\text{Y}(\text{OH})_3$  with excess conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 14.* Repeat *Step 13*.

*Step 15.* Wash the precipitate with  $\text{H}_2\text{O}$ , dissolve in a minimum of conc  $\text{HCl}$ , and add 15 ml of  $\text{H}_2\text{O}$ . Again precipitate  $\text{Y}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ , but this time in the absence of strontium carrier.

*Step 16.* Wash the precipitate and dissolve as in *Step 15*.

*Step 17.* Add 5 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and a small amount of  $\text{HCl}$ , if necessary, to precipitate  $\text{Y}_2(\text{C}_2\text{O}_4)_3$ . Digest on a steam bath for 5 to 10 min.

*Step 18.* Filter the  $\text{Y}_2(\text{C}_2\text{O}_4)_3$  precipitate onto a weighed filter circle. Wash the precipitate with  $\text{H}_2\text{O}$  and place in a porcelain crucible. Ignite at  $900^\circ\text{C}$  for 30 min. Grind the  $\text{Y}_2\text{O}_3$  into a powder with a stirring rod and add a few drops of ethanol. Continue grinding until the precipitate is smooth and transfer with 95% ethanol onto a weighed filter circle. Wash the precipitate with ethanol, dry in an oven at  $110^\circ\text{C}$ , cool, weigh, and mount.

## Notes

1. Using refrigerated fuming  $\text{HNO}_3$  reduces the time required for cooling in an ice bath.
2. The  $\text{SrCO}_3$  formed in this step may be mounted and counted for  $^{89}\text{Sr}$ .
3. The 18-d waiting period may be shortened if a growth correction is made for the interval between the centrifugation operations in *Step 8* and *Step 12*.

4. The time at which  $^{90}\text{Y}$  is separated from  $^{90}\text{Sr}$  is recorded as  $t_0$  and all yttrium counts are corrected to this time.

(October 1989)

# THE SEPARATION OF STRONTIUM FROM YTTRIUM

R. J. Prestwood

## 1. Introduction

It is sometimes necessary to separate a strontium isotope that has grown in from a neutron-deficient yttrium parent. In many instances, the yttrium parent is also associated with large quantities of fission-product yttrium, for example,  $^{91}\text{Y}$ . The procedure for the analysis assumes that the yttrium has been separated from all other elements.

## 2. Reagents

Strontium carrier: 50 mg  $\text{SrCO}_3/2$  ml; standardized

Yttrium carrier: 10 mg yttrium/ml, added as  $\text{Y}_2\text{O}_3$  in dilute HCl

HCl: conc

$\text{HNO}_3$ : fuming; conc

$\text{NH}_4\text{OH}$ : conc

$(\text{NH}_4)_2\text{CO}_3$ : 10% aqueous solution

Methyl red indicator solution

Ethanol: absolute

## 3. Preparation and Standardization of Carrier

Preparation and standardization of the strontium carrier were done as described in the STRONTIUM-90 procedure, but with two modifications: the carrier solution contained 35.85 g of  $\text{Sr}(\text{NO}_3)_2/\ell$ , and  $(\text{NH}_4)_2\text{CO}_3$  rather than  $\text{Na}_2\text{CO}_3$  was employed to precipitate  $\text{SrCO}_3$ .

## 4. Procedure

*Step 1.* Following the procedure for the decontamination of yttrium (see the YTTRIUM procedures), weigh the  $\text{Y}_2\text{O}_3$  from ignition in a crucible and transfer to a 40-ml glass centrifuge tube. Weigh the crucible again to obtain the chemical yield in the original yttrium separation.

Add 1 ml of conc HCl and heat gently to effect solution of the  $\text{Y}_2\text{O}_3$ . Add 2.0 ml of strontium carrier, and permit the solution to stand long enough for the desired amount of growth of the strontium isotope to be separated (for example, the growth time suitable for  $^{87}\text{Sr}$  is  $\sim 16$  h). The time of the last  $\text{Y}(\text{OH})_3$  precipitation before ignition to the oxide marks the start of the strontium growth. The volume of solution should be  $\sim 15$  ml.

*Step 2.* To the solution add 3 drops of methyl red solution; add conc  $\text{NH}_4\text{OH}$  until the solution is just neutral. Then add 3 drops of the base in excess. Swirl and place on a steam bath for 2 min. Centrifuge, pour the supernate into a clean centrifuge tube, and record the time to mark the start of decay of the strontium isotope. Dissolve the  $\text{Y}(\text{OH})_3$  precipitate in a minimum of conc HCl, dilute with  $\text{H}_2\text{O}$  to 10 ml, add 3 drops of methyl red solution and an excess of 3 drops of conc  $\text{NH}_4\text{OH}$ . Centrifuge and add the supernate to the one from the first precipitation of  $\text{Y}(\text{OH})_3$ . The total volume should now be  $\sim 25$  ml.

*Step 3.* Add conc HCl until the solution is just acidic and then add 10 drops of yttrium carrier. Make alkaline with conc  $\text{NH}_4\text{OH}$  and add 3 drops in excess. Place on a steam bath for 2 min, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 4.* Repeat *Step 3* twice.

*Step 5.* To the supernate add 1 ml of conc  $\text{NH}_4\text{OH}$  and 5 ml of 10%  $(\text{NH}_4)_2\text{CO}_3$ . Place on a steam bath until  $\text{SrCO}_3$  precipitates. Centrifuge and discard the supernate.

*Step 6.* Dissolve the precipitate in 1 to 3 drops of conc  $\text{HNO}_3$  and 1 ml of  $\text{H}_2\text{O}$ . Add 30 ml of ice-cold fuming  $\text{HNO}_3$ .  $\text{Sr}(\text{NO}_3)_2$  precipitates immediately. Centrifuge and discard the supernate.

*Step 7.* Dissolve the  $\text{Sr}(\text{NO}_3)_2$  in 15 ml of  $\text{H}_2\text{O}$ , add 3 drops of methyl red solution, and repeat the  $\text{Y}(\text{OH})_3$  scavenge (*Step 3*) three times. (In the first



repetition of *Step 3*, it is not necessary to make the solution acidic with HCl.)

*Step 8.* Repeat *Step 5*.

*Step 9.* To the  $\text{SrCO}_3$  precipitate add  $\sim 5$  ml of  $\text{H}_2\text{O}$  and with the aid of a stirring rod suspend the solid. Filter onto a weighed filter circle. Wash the precipitate thoroughly with  $\text{H}_2\text{O}$  and then with absolute ethanol. Dry at  $110^\circ\text{C}$  for 5 min, weigh as  $\text{SrCO}_3$ , and mount.

(October 1989)

# BARIUM

W. G. Warren

## 1. Introduction

Barium may be separated from fission-product material by the specific cold precipitation as  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  by means of a conc HCl-ethyl ether mixture. The procedure for the determination of barium as outlined below consists of the isolation of  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  followed by conversion to the chromate,  $\text{BaCrO}_4$ . Three precipitations of the chloride are carried out; the first and second are followed by  $\text{Fe}(\text{OH})_3$  scavenging steps. The final precipitation of barium as the chromate is preceded by a  $\text{La}(\text{OH})_3$  scavenging step to remove lanthanum and other fission products that were not removed by  $\text{Fe}(\text{OH})_3$  scavenging and form insoluble hydroxides. The chemical yield is  $\sim 70\%$ .

## 2. Reagents

Barium carrier: 10 mg barium/ml,  $\text{Ba}(\text{NO}_3)_2$  solution; standardized  
Iron carrier: 10 mg iron/ml, added as aqueous  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   
Lanthanum carrier: 10 mg lanthanum/ml, added as aqueous  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$   
HCl-ethyl ether mixture: five parts (by volume) of conc HCl to one part of ethyl ether  
 $\text{NH}_4\text{OH}$ : 1M; 6M  
HCl: 6M  
 $\text{HC}_2\text{H}_3\text{O}_2$ : 6M  
 $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ : 3M  
 $\text{Na}_2\text{CrO}_4$ : 1.5M  
Phenolphthalein indicator solution  
Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 19.0 g of  $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$  and dilute to 1 l. Pipette 5.0 ml of carrier solution into a 250-ml beaker and dilute to  $\sim 100$  ml. Add 10 ml each of 6M  $\text{H}_2\text{C}_3\text{O}_2$  and 3M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . Place on a hot plate and bring to a boil. Add 5 ml

of 1.5M  $\text{Na}_2\text{CrO}_4$  dropwise with stirring, boil for 1 min with stirring, cool to room temperature, and filter the  $\text{Ba}_2\text{CrO}_4$  into a sintered glass crucible of fine porosity that has been washed with  $\text{H}_2\text{O}$  and ethanol, dried at  $110^\circ\text{C}$  for 15 min, and weighed. Wash the precipitate three times with 5-ml portions of  $\text{H}_2\text{O}$  and three times with 5-ml portions of ethanol. Dry at  $110^\circ\text{C}$ , cool, and weigh.

Four standardizations of the carrier solution are performed. The spread in results is  $\sim 0.5\%$ .

## 4. Procedure

*Step 1.* To the sample in a 40-ml centrifuge tube, add 2 ml of standardized barium carrier (combined volume not to exceed 5 ml). Evaporate to reduce volume, if necessary. Place the tube in an ice bath and add 30 ml of cold HCl-ether reagent (Note 1). Stir for 1 min or until a precipitate of  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  is formed. Centrifuge and discard the supernate (Note 2).

*Step 2.* Dissolve the precipitate in 4 ml of  $\text{H}_2\text{O}$  and add 1 drop of phenolphthalein solution and 3 drops of iron carrier. Neutralize with 6M  $\text{NH}_4\text{OH}$  and add 12 drops in excess. Centrifuge and pour the supernate into a clean centrifuge tube.

*Step 3.* Add 30 ml of HCl-ether mixture to the supernate and proceed as in Steps 1 and 2, but do not add additional barium carrier.

*Step 4.* Repeat the precipitation of  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  with HCl-ether reagent. Dissolve the precipitate in 10 ml of  $\text{H}_2\text{O}$ , and add 1 drop of phenolphthalein solution and 10 drops of lanthanum carrier. Neutralize with 6M  $\text{NH}_4\text{OH}$  and add 10 drops in excess. Bring the mixture to a boil, centrifuge, and pour the supernate into a clean centrifuge tube.

*Step 5.* Neutralize the supernate with 6M HCl, and then add 10 ml of the 6M  $\text{HC}_2\text{H}_3\text{O}_2$ -3M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution. Heat to boiling and dropwise add 2 ml of 1.5M  $\text{Na}_2\text{CrO}_4$ . Boil for 1 min with constant stirring, centrifuge, and discard

the supernate. Wash the precipitate by stirring with 20 ml of H<sub>2</sub>O, centrifuge, and discard the supernate. Slurry the precipitate with 20 ml of H<sub>2</sub>O and filter the BaCrO<sub>4</sub> on a previously washed, dried, and weighed filter paper. Wash the precipitate three times with 5-ml portions of H<sub>2</sub>O and three times with 5-ml portions of ethanol. Dry at 110°C, cool, weigh, and mount (Note 3).

### Notes

1. For a maximum yield of BaCl<sub>2</sub>•H<sub>2</sub>O, the solution must be cooled to ~5°C.

2. If sulfuric acid, hydrofluoric acid, or oxalate ion is present in the sample, or if the volume of sample plus carrier exceeds 5 ml, the following preliminary treatment is carried out before BaCl<sub>2</sub>•H<sub>2</sub>O is precipitated. To the mixture of sample and carrier in a 40-ml centrifuge tube add 2 to 4 drops of conc H<sub>2</sub>SO<sub>4</sub> to precipitate BaSO<sub>4</sub>. Wash the precipitate by stirring with 10 ml of H<sub>2</sub>O, centrifuge, and discard the supernate. Add 5 ml of saturated K<sub>2</sub>CO<sub>3</sub> solution and boil for 2 min, adding H<sub>2</sub>O if necessary. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H<sub>2</sub>O as above. Add 1 ml of conc HCl, heat to boiling, and then add 1 ml of 6M HCl, keeping the solution hot. Add 3 ml of H<sub>2</sub>O and cool in an ice bath. Proceed with the precipitation of BaCl<sub>2</sub>•H<sub>2</sub>O.

3. The BaCrO<sub>4</sub> precipitates are set aside for 134 h before counting is begun. This permits <sup>140</sup>Ba and <sup>140</sup>La daughter activities to come to equilibrium. If results are desired earlier, a computer program allows early consecutive counts and takes into account the growth and different absorption corrections for <sup>140</sup>Ba and <sup>140</sup>La.

(October 1989)

# SEPARATION OF GALLIUM FROM FISSION AND SPALLATION PRODUCTS

R. J. Prestwood

## 1. Introduction

This procedure was developed to study the gallium isotopes produced by the interaction of  $\pi^+$  ions of high energy and  $^{238}\text{U}$ . The main steps of the analysis are the extraction of gallium into isopropyl ether from an aqueous solution  $8M$  in  $\text{HCl}$ ,  $\text{PdS}$  scavenges from dilute acid solutions, and a final precipitation of gallium as the 8-quinolate (8-hydroxyquinolate). The chemical yield is  $\sim 80\%$ .

## 2. Reagents

Gallium carrier: added as  $\text{GaCl}_3$  in  $0.1M$   $\text{HCl}$ ;  $\sim 5$  mg  $\text{Ga}^{3+}/\text{ml}$ ; the carrier was standardized by precipitation of the metal as the 8-quinolate;  $1$  ml of carrier gave  $36$  mg of the quinolate.

Palladium carrier:  $10$  mg/ml, added as  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in  $1M$   $\text{HCl}$

$\text{HClO}_4$ : conc

$\text{HCl}$ : conc;  $8M$ ;  $0.2M$

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{S}$ : gas

$\text{NH}_4\text{Cl}$ : solid

$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$  (ammonium tartrate): solid

8-quinolinol (8-hydroxyquinoline) reagent:  $5\%$  solution in  $2M$   $\text{HC}_2\text{H}_3\text{O}_2$

Isopropyl ether

Methyl red indicator solution:  $0.1\%$  solution in ethanol

## 3. Procedure

*Step 1.* To the sample ( $3M$  in  $\text{HCl}$ ) in a  $60$ -ml separatory funnel, add sufficient conc  $\text{HCl}$  to make the acid concentration  $8M$ . Extract the solution with  $10$  ml of isopropyl ether and drain the aqueous (lower) layer into a clean separatory funnel. Extract this layer again with  $10$  ml of isopropyl ether, discard the aqueous layer, and combine the ether layer with the previous one.

*Step 2.* Wash the ether solution twice with  $10$ -ml portions of  $8M$   $\text{HCl}$  and discard the washes. Remove the gallium from the ether layer by extraction with two  $10$ -ml portions of distilled  $\text{H}_2\text{O}$  and drain the  $\text{H}_2\text{O}$  layers into a clean  $40$ -ml centrifuge tube. Discard the ether layer.

*Step 3.* Add  $\sim 2$  g of  $\text{NH}_4\text{Cl}$  and 2 drops of methyl red indicator solution, and neutralize the solution with conc  $\text{NH}_4\text{OH}$ , adding 1 drop in excess. Centrifuge the  $\text{Ga}(\text{OH})_3$  precipitate and discard the supernate. Wash the precipitate with  $10$  ml of  $\text{H}_2\text{O}$  and discard the wash.

*Step 4.* Dissolve the precipitate in  $10$  ml of  $0.2M$   $\text{HCl}$ . Add 2 drops of palladium carrier, place the solution on a steam bath, and bubble in  $\text{H}_2\text{S}$  until the  $\text{PdS}$  precipitate coagulates. Filter through a filter paper and collect the filtrate in a clean centrifuge tube. Wash the precipitate with a small amount of  $0.2M$   $\text{HCl}$ , add 2 drops of palladium carrier, and repeat the  $\text{PdS}$  scavenge and filtration.

*Step 5.* Boil the filtrate to remove excess  $\text{H}_2\text{S}$ . Add 2 drops of methyl red indicator solution and neutralize with conc  $\text{NH}_4\text{OH}$ , adding 1 drop in excess. Centrifuge the  $\text{Ga}(\text{OH})_3$  precipitate and discard the supernate.

*Step 6.* Add  $1$  ml of conc  $\text{HClO}_4$  to the precipitate and heat to fumes over a burner. (The fuming process removes any ruthenium present as the volatile  $\text{RuO}_4$ .) Cool the solution and add  $10$  ml of  $\text{H}_2\text{O}$  and  $\sim 1$  g of  $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ . Heat to boiling and add  $3$  ml of 8-quinolinol reagent. Stir the mixture vigorously while heating until the precipitate coagulates. Let stand for a few minutes and then filter the gallium 8-quinolate onto a previously washed, dried, and weighed filter circle. Wash the precipitate thoroughly with  $5$ -ml portions of  $\text{H}_2\text{O}$  and permit it to dry under suction. Finally, dry the precipitate in an oven at  $110^\circ\text{C}$  for  $10$  min and mount for counting.

(October 1989)

# INDIUM

G. A. Cowan

## 1. Introduction

To determine indium in the presence of fission products, it is first separated rapidly from cadmium so that a separation time from its parent activity is accurately known. The separation is accomplished by precipitation of  $\text{In}(\text{OH})_3$  by means of  $\text{NH}_4\text{OH}$ ; cadmium remains in solution as an ammonia complex. The hydroxide is then dissolved and acid-insoluble sulfides are precipitated from a buffered solution (pH 3-4) in the presence of sulfosalicylic acid. Indium is leached from the mixture of sulfides with hot 1M HCl and is then precipitated as the hydroxide and converted to the bromide by means of 4.5M HBr. The bromide is extracted into ethyl ether and indium is finally precipitated and weighed as the 8-quinolinol (8-hydroxyquinoline) derivative. The chemical yield is ~50%.

## 2. Reagents

Indium carrier: 10 mg indium/ml, added as  $\text{InCl}_3$  in 1.5M HCl; standardized

Antimony carrier: 10 mg antimony/ml, added as  $\text{SbCl}_3$  in 1M HCl

Cadmium carrier: 10 mg cadmium/ml, added as  $\text{CdCl}_2$  in 1M HCl

HCl: 1M; 1.5M

HBr: 4.5M

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{S}$ : gas

Buffer solution: (1M  $\text{HC}_2\text{H}_3\text{O}_2$ -2M  $\text{NaC}_2\text{H}_3\text{O}_2$ )

Sulfosalicylic acid: 5% in  $\text{H}_2\text{O}$

8-quinolinol (8-hydroxyquinoline) reagent: 5% in 2M  $\text{HC}_2\text{H}_3\text{O}_2$

Ethyl ether: saturated with 4.5M HBr

## 3. Preparation and Standardization of Carrier

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

Pipette 2.00 ml of the above solution into a 100-ml beaker, and add 20 ml of  $\text{H}_2\text{O}$ , 5 ml of  $\text{HC}_2\text{H}_3\text{O}_2$ - $\text{NaC}_2\text{H}_3\text{O}_2$  buffer solution, and 2 ml of 8-hydroxyquinoline solution. Permit the precipitate to settle and add 8-hydroxyquinoline solution dropwise to the supernate until no further precipitation occurs. Filter the precipitate on a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate thoroughly with  $\text{H}_2\text{O}$  and dry at 110°C for 30 min. Cool and weigh as  $\text{In}(\text{C}_9\text{H}_6\text{NO})_3$  (20.99% indium).

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

## 4. Procedure

*Step 1.* To 5-20 ml of sample in a 40-ml conical centrifuge tube, add 2.0 ml of indium carrier, 2 drops of cadmium holdback carrier, and an excess of conc  $\text{NH}_4\text{OH}$ . Centrifuge the precipitate and discard the supernate.

*Step 2.* Dissolve the precipitate in 20 ml of 1M HCl and repeat *Step 1* twice.

*Step 3.* Dissolve the precipitate in 10 ml of 1M HCl and add 2 ml of 5% sulfosalicylic acid, 5 ml of  $\text{HC}_2\text{H}_3\text{O}_2$ - $\text{NaC}_2\text{H}_3\text{O}_2$  buffer solution, and 1 drop of antimony carrier. Saturate the solution with  $\text{H}_2\text{S}$ , keeping the solution cold. Centrifuge and discard the supernate.

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

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

*Step 6.* Dilute the solution to 10 ml with  $\text{H}_2\text{O}$  and repeat *Steps 3* through *5* three times.

*Step 7.* To the solution containing  $\text{InCl}_3$  in  $1M$   $\text{HCl}$ , add an excess of conc  $\text{NH}_4\text{OH}$  and centrifuge. Discard the supernate.

*Step 8.* Dissolve the precipitate in  $25\text{ ml}$  of  $4.5M$   $\text{HBr}$ , transfer the solution to a  $125\text{-ml}$  separatory funnel, and extract  $\text{InBr}_3$  into  $50\text{ ml}$  of ethyl ether that is saturated with  $4.5M$   $\text{HBr}$ . Discard the aqueous layer and wash the ether layer twice with  $10\text{-ml}$  portions of  $4.5M$   $\text{HBr}$ .

*Step 9.* Draw off the ether into a  $250\text{-ml}$  erlenmeyer flask. Evaporate the ether on a steam bath and take the residue up in  $20\text{ ml}$  of  $1M$   $\text{HCl}$ . Add  $5\text{ ml}$  of buffer solution and  $2\text{ ml}$  of 8-hydroxyquinoline reagent. Test for completeness of precipitation by the addition of another drop of reagent to the clear supernate. Filter on a weighed filter circle. Wash the precipitate thoroughly with water and dry at  $110^\circ\text{C}$  for  $30\text{ min}$ . Cool, weigh, and mount. Count immediately in a proportional counter (Note).

#### Note

This procedure has been used for the determination of  $4.5\text{-h}$   $^{115}\text{In}$ , daughter product of  $58\text{-h}$   $^{115}\text{Cd}$ .

(October 1989)

## THALLIUM

R. J. Prestwood

### 1. Introduction

To determine radiothallium in the presence of fission products, tellurium and the more noble metals are removed by reduction to the elemental state by means of  $\text{SO}_2$  and  $\text{N}_2\text{H}_4$  in  $\text{HCl}$  medium. This is followed by a series of  $\text{TlI}$  and  $\text{La}(\text{OH})_3$  precipitations. The  $\text{TlI}$  precipitation serves as an excellent decontaminating step, effectively removing thallium from a large number of activities, including cadmium, chromium, cobalt, nickel, and alkaline earths. Thallium(I) is finally converted to the chromate, in which form it is counted. The chemical yield is  $\sim 80\%$ .

### 2. Reagents

Thallium carrier: 10 mg thallium/ml added as  $\text{TlCl}_3$  in dilute  $\text{HCl}$ ; standardized

Tellurium carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in dilute  $\text{HCl}$

Lanthanum carrier: 10 mg lanthanum/ml, added as aqueous  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

$\text{HCl}$ : 3M

$\text{HNO}_3$ : 6M

$\text{NH}_4\text{OH}$ : conc

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ : solid

$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ : 10% in  $\text{H}_2\text{O}$

$\text{KHSO}_3$ : solid

$\text{SO}_2$ : saturated aqueous solution

$\text{NaI}$ : solid

Methanol: absolute

### 3. Preparation and Standardization of Carrier

Dissolve 11.17 g of  $\text{Tl}_2\text{O}_3$  in dilute  $\text{HCl}$  and dilute the solution to a volume of 1 l with the acid.

Pipette exactly 5 ml of the carrier solution into a 125-ml erlenmeyer flask and add 50 mg of solid  $\text{KHSO}_3$ . Boil off excess  $\text{SO}_2$  and make the solution

alkaline with conc  $\text{NH}_4\text{OH}$ . Add 5 ml of 10%  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  solution to precipitate  $\text{Tl}_2\text{CrO}_4$ . Bring to a boil, permit the precipitate to stand for  $\sim 12$  h, and filter onto a weighed 30-ml sintered glass crucible of fine porosity. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$  and then with 10 ml of 95% ethanol. Dry at  $110^\circ\text{C}$  for 30 min. Cool and weigh.

Seven standardizations gave results that agreed within 0.5%.

### 4. Procedure

*Step 1.* To the sample in a 125-ml erlenmeyer flask, add 2 ml of thallium carrier and 1 ml of tellurium carrier. Evaporate barely to dryness over an open flame. Add 5 ml of conc  $\text{HCl}$  and again evaporate to dryness. Repeat evaporation once again with 5 ml of  $\text{HCl}$ . Add 20 ml of 3M  $\text{HCl}$  and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , and heat to boiling. Add 1 ml of  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and continue to boil, making three to four successive additions of  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . Particular care must be taken to ensure complete precipitation of tellurium metal. When the tellurium has been completely precipitated, the supernate is water-white with no suggestion of a bluish tint. Filter into a 125-ml erlenmeyer flask through a 2-in.  $60^\circ$  funnel using No. 40 Whatman filter paper. Wash the original flask and the precipitate with dilute  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . Discard the precipitate.

*Step 2.* Add enough  $\text{H}_2\text{O}$  to make the total volume  $\sim 75$  ml and then add  $\sim 2$  g of solid  $\text{NaI}$ . Centrifuge in two batches in a 40-ml conical centrifuge tube, discarding the supernate after each centrifugation.

*Step 3.* To the precipitate add 4 drops of lanthanum carrier and 1 ml of 6M  $\text{HNO}_3$ . Heat over open flame until all  $\text{I}_2$  color has disappeared. Dilute with  $\text{H}_2\text{O}$  to 20 ml, heat over flame until the solution is rather warm, add 2 to 3 drops of  $\text{SO}_2 \cdot \text{H}_2\text{O}$  to ensure complete reduction of thallium, and make alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Add 1 ml of  $\text{NH}_4\text{OH}$  in excess.

Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate of  $\text{La}(\text{OH})_3$ .

*Step 4.* To the supernate add ~1 g of NaI, centrifuge the precipitated TII, and discard the supernate. To the precipitate add 1 ml of 6M  $\text{HNO}_3$  and heat over open flame until  $\text{I}_2$  color has disappeared. Transfer to a 125-ml erlenmeyer flask, add 1 ml of tellurium carrier, and repeat *Step 1*.

*Step 5.* Repeat *Steps 2* and *3*.

*Step 6.* To the supernate add ~1 g of NaI, centrifuge, and discard the supernate.

*Step 7.* Repeat *Step 3*.

*Step 8.* To the supernate add 5 ml of 10%  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  solution. Allow to stand 5 to 10 min to permit the  $\text{Tl}_2\text{CrO}_4$  precipitate to coagulate. Filter on a weighed filter circle. Wash the precipitate with 5 ml of  $\text{H}_2\text{O}$ , and then with two 5-ml portions of absolute methanol. Dry at  $110^\circ\text{C}$  for 10 min. Cool, weigh, mount, and count.

(October 1989)



# SEPARATION OF RADIOACTIVE SPECIES OF THALLIUM, ARSENIC, AND SCANDIUM

INC-11 Radiochemistry Group

## 1. Introduction

In the separation of radioactive thallium, arsenic, and scandium, thallium is first removed as the iodide, after reduction to the +1 state. Arsenic is then precipitated as the sulfide from HCl medium. Scandium is left in solution.

## 2. Reagents

Thallium carrier: 10 mg thallium/ml, added as  $\text{TlCl}_3$  in dilute HCl; standardized (see THALLIUM procedure)

Arsenic carrier: 10 mg arsenic/ml, added as  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ; standardized (see ARSENIC procedure)

Scandium carrier: 10 mg scandium/ml, added as  $\text{ScCl}_3$  in dilute HCl; standardized; (see SCANDIUM I procedure)

Tellurium carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_4$  in  $\text{H}_2\text{O}$

$\text{HNO}_3$ : 6M

$\text{HClO}_4$ : conc

HCl: conc; 3M

$\text{NH}_4\text{OH}$ : conc

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ : solid

$\text{SO}_2$ : saturated aqueous solution

NaI: solid

## 3. Procedure

*Step 1.* To an aliquot of the sample in a 40-ml centrifuge tube, add 20 mg each of thallium, arsenic, and scandium carriers and dilute the solution to ~30 ml with  $\text{H}_2\text{O}$ . Add a few drops of saturated aqueous  $\text{SO}_2$  solution and then ~2 g of solid NaI. Stir well and centrifuge. Transfer the supernate to a 125-ml erlenmeyer flask.

*Step 2.* Add 1 ml of 6M  $\text{HNO}_3$  to the TII precipitate and heat over an open flame until all  $\text{I}_2$

color has disappeared. Add 1 ml each of tellurium carrier and conc  $\text{HClO}_4$  and evaporate to heavy fumes over an open flame. Add 5 ml of conc HCl and again evaporate to heavy fumes. Add 15 ml of 3M HCl and ~0.5 g of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  and heat to boiling. Add 1 ml of saturated aqueous  $\text{SO}_2$  and continue to boil while making three or four successive additions of  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . When the tellurium has been completely precipitated (the supernate is essentially water-white), filter into a 125-ml erlenmeyer flask through a 2-in. 60° funnel. Wash the centrifuge tube and the precipitate with dilute  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and discard the precipitate. To determine thallium in the filtrate, start with *Step 2* of the THALLIUM procedure.

*Step 3.* Evaporate the solution containing the arsenic and scandium to ~20 ml and transfer to a clean centrifuge tube. Add 5 to 10 ml of conc HCl and pass in  $\text{H}_2\text{S}$  until precipitation of  $\text{As}_2\text{S}_3$  is complete. Centrifuge and transfer the supernate to a clean centrifuge tube. For analysis of arsenic in the precipitate, start with *Step 2* of the ARSENIC procedure.

*Step 4.* Boil the supernate to expel  $\text{H}_2\text{S}$  and excess HCl. Precipitate  $\text{Sc}(\text{OH})_3$  by making the solution alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate. To determine scandium, start with *Step 2* of the SCANDIUM II procedure.

(October 1989)

# GERMANIUM

R. J. Prestwood

## 1. Introduction

In the separation of radiogermanium from other fission products, acid sulfide,  $\text{LaF}_3$ , and  $\text{BaSO}_4$  scavengings are performed in the presence of the  $\text{F}^-$  ion, which keeps germanium in solution as the  $\text{GeF}_6^{2-}$  ion. The fluoro complex is then decomposed and germanium distilled as the tetrachloride in a specially designed multiple still. Germanium is finally precipitated and mounted as the sulfide  $\text{GeS}_2$ . The chemical yield is 80 to 90%.

## 2. Reagents

Germanium(IV) carrier: 10.00 mg germanium/ml  
(see Preparation of Carrier)

Arsenic carrier: 10 mg arsenic/ml, added as  
 $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Barium carrier: 10 mg barium/ml, added as  
 $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$

Lanthanum carrier: 10 mg lanthanum/ml, added  
as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Copper carrier: 10 mg copper/ml, added as  
 $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as  
 $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

HCl: 4.5 to 5.5M; conc

HI: 47% aqueous solution

$\text{H}_2\text{SO}_4$ : conc

HF: conc

$\text{H}_3\text{BO}_3$ : saturated solution

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{S}$ : gas

$\text{CH}_3\text{OH}$ : anhydrous

## 3. Preparation of Carrier

Fuse 14.4092 g of reagent grade  $\text{GeO}_2$  with 30.0 g of  $\text{Na}_2\text{CO}_3$ . Dissolve the melt in  $\text{H}_2\text{O}$  and dilute to 1 l. Permit to stand for 24 h and filter. The solution contains 10.00 mg germanium/ml and is used as a primary standard.

## 4. Procedure

*Step 1.* To the sample in a 125-ml erlenmeyer flask add the following: 2 ml of standard germanium carrier, 1 ml of arsenic carrier, 1 ml of barium carrier, 1 ml of copper carrier, 1 ml of lanthanum carrier, 2 ml of 47% HI solution, and 1 ml of conc HF. Make the solution neutral by the addition of conc  $\text{NH}_4\text{OH}$ , add 10 to 20 drops of conc  $\text{H}_2\text{SO}_4$ , place on a steam bath, and saturate with  $\text{H}_2\text{S}$  for a few min.

*Step 2.* Filter into a clean 125-ml erlenmeyer flask through a 2-in. 60° funnel. Wash the precipitate with a small quantity of  $\text{H}_2\text{O}$ . Discard the precipitate.

*Step 3.* To the filtrate add 10 drops of lanthanum carrier and 1 ml of copper carrier and saturate with  $\text{H}_2\text{S}$  on a steam bath. Filter as in *Step 2* and wash the precipitate.

*Step 4.* To the filtrate add 1 ml of copper carrier and saturate with  $\text{H}_2\text{S}$  in the cold. Filter as in *Step 2* and wash the precipitate.

*Step 5.* Repeat *Step 4*.

*Step 6.* To the filtrate add 10 ml of conc HCl and 10 ml of saturated  $\text{H}_3\text{BO}_3$ ; saturate with  $\text{H}_2\text{S}$ . Transfer to 40-ml conical centrifuge tube, centrifuge the  $\text{GeS}_2$  precipitate, and discard the supernate (Note 1).

*Step 7.* Dissolve the  $\text{GeS}_2$  in 1 ml of conc  $\text{NH}_4\text{OH}$  and dilute to 15 to 20 ml with  $\text{H}_2\text{O}$ . Add 4 drops of zirconium carrier, centrifuge, and discard the precipitate. Make the supernate 3M with HCl, saturate with  $\text{H}_2\text{S}$ , centrifuge, and discard the supernate.

*Step 8.* Slurry the  $\text{GeS}_2$  with 4.5 to 5.5M HCl (Note 2) and transfer the solution to the special still

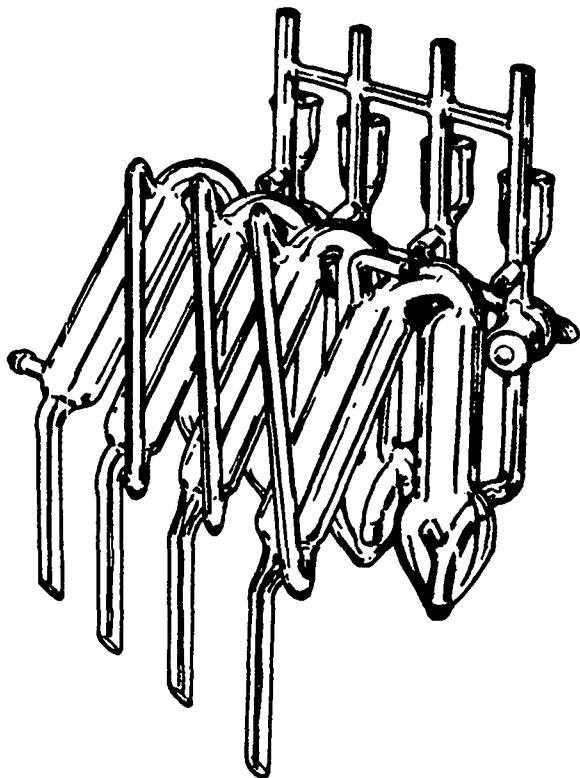


Fig. 1. Special distilling flask.

(Fig. 1). The total volume of acid used should be about 15 ml.

*Step 9.* Distill the  $\text{GeCl}_4$  on an oil bath at  $120^\circ\text{C}$  into a 50-ml beaker containing 5 ml of 4.5 to 5.5M HCl that has been saturated at room temperature with  $\text{H}_2\text{S}$  and kept in an ice bath (Note 3).  $\text{GeCl}_4$  begins to distill after 15 to 20 min, and then the distillation must be maintained for 10 to 15 min more to ensure completion. Almost 100% yield is obtained.

*Step 10.* Transfer the distillate to another special still and repeat the distillation.

*Step 11.* Saturate the receiver with  $\text{H}_2\text{S}$  and filter the precipitate onto a weighed filter circle. Wash the precipitate with anhydrous  $\text{CH}_3\text{OH}$  and dry in an oven at 110 to  $120^\circ\text{C}$  for 10 min. Cool, weigh as  $\text{GeS}_2$ , and mount.

## Notes

1. A water-clear supernate is not ordinarily obtained upon centrifugation of the  $\text{GeS}_2$  unless the mixture is permitted to stand for several hours. Because it is not practical to wait so long and because the losses are insignificant, do not hesitate to discard a slightly turbid supernate from a  $\text{GeS}_2$  precipitation.

2. The concentration of HCl must not exceed that of the constant boiling mixture, or  $\text{GeCl}_4$  will escape during the distillation (unless the delivery tube is below the surface of the receiving liquid). If the HCl concentration in the still is less than that required for the constant boiling mixture, only  $\text{H}_2\text{O}$  and no  $\text{GeCl}_4$  is distilled. As soon as the composition of the still reaches that of the constant boiling mixture, all the  $\text{GeCl}_4$  distills rapidly. At higher HCl concentrations, the  $\text{GeCl}_4$  is immediately swept out with HCl gas.

3. The  $\text{H}_2\text{S}$  is present in the receiver to show (by the formation of white  $\text{GeS}_2$ ) when  $\text{GeCl}_4$  begins to distill.

(October 1989)

# SEPARATION OF GERMANIUM AND ARSENIC FROM A FISSION-PRODUCT SOLUTION

R. J. Prestwood

*Step 2.* To the filtrate containing the germanium, add 5 to 6 ml of saturated  $\text{H}_3\text{BO}_3$  and saturate with  $\text{H}_2\text{S}$ . Centrifuge the  $\text{GeS}_2$  precipitate and discard the supernate. Then carry out *Steps 7* through *11* of the GERMANIUM procedure.

(October 1989)

## 1. Introduction

Arsenic(III) is separated from germanium(IV) by precipitation as the sulfide in a HCl medium containing the  $\text{F}^-$  ion; the latter strongly complexes germanium(IV) as  $\text{GeF}_6^{2-}$  and prevents its precipitation. Before the sulfide precipitation, arsenic(V) is reduced to the tripositive state by means of iodide ion.

## 2. Reagents

Arsenic(V) carrier: see ARSENIC procedure  
Germanium(IV) carrier: see GERMANIUM procedure  
HCl: 6M  
HF: conc  
 $\text{H}_3\text{BO}_3$ : saturated solution  
 $\text{H}_2\text{S}$ : gas  
NaI: solid  
Aerosol: 0.1% in  $\text{H}_2\text{O}$

## 3. Procedure

*Step 1.* To a solution of the sample in a 40-ml conical centrifuge tube, add 2.0 ml each of arsenic(V) and germanium(IV) carriers. Make the solution 3 to 5M in HCl and the volume to 10 to 15 ml. (Nitrate ion should be absent or present only in small amount.) Add 50 to 100 mg of NaI and warm the solution gently. Add 10 drops of conc HF and saturate the solution with  $\text{H}_2\text{S}$  until the  $\text{As}_2\text{S}_3$  precipitate has coagulated (time required is 3 to 5 min). Centrifuge and pour the supernate through filter paper in a 2-in. 60° funnel into a clean centrifuge tube. The  $\text{As}_2\text{S}_3$  precipitate is then treated as described, beginning with *Step 2* of the ARSENIC procedure.

## TIN I

D. C. Hoffman, F. O. Lawrence,  
and W. R. Daniels

### 1. Introduction

This procedure for separating tin from fission products is performed  $\sim 2$  d after irradiation; this interval is necessary to allow 2-h  $^{127}\text{Sn}$  to decay to 93-h  $^{127}\text{Sb}$ . When performed after the 2-d waiting period, the procedure gives excellent decontamination from fission products.

The sample is first treated with  $\text{Br}_2\text{-H}_2\text{O}$  to convert all the tin to the +4 condition and to promote complete exchange between fission-product tin and tin(IV) carrier. The oxidation is followed by precipitation of  $\text{SnS}_2$  from acid solution, and then the tin is dissolved and adsorbed on an anion-exchange resin column from 0.9M HCl solution. Molybdenum, tellurium, and antimony pass through the column. The tin is eluted from the column with 1.8M  $\text{HClO}_4$  and is again precipitated as the sulfide. The sulfide is dissolved, the tin is complexed by means of HF, and two acid sulfide scavenges are performed. Following destruction of  $\text{F}^-$  ion with  $\text{H}_3\text{BO}_3$ , the tin is again precipitated as the sulfide, dissolved, adsorbed on an anion-exchange column, and eluted. After a final  $\text{SnS}_2$  precipitation, the tin is dissolved and reduced to the metal by  $\text{CrCl}_2$ . It is weighed and counted in this form. The chemical yield is  $\sim 70\%$ .

### 2. Reagents

Tin carrier: 10 mg tin/ml, added as tin metal dissolved in 3M HCl; standardized  
Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 3M HCl  
Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_4$  in 3M HCl  
Molybdenum carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 6M HCl  
Antimony carrier: 10 mg antimony/ml, added as  $\text{SbCl}_3$  in 6M HCl

Lanthanum carrier: 10 mg lanthanum/ml, added as aqueous  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$

HCl: 0.9M; conc

HF: conc

$\text{HClO}_4$ : 1.8M

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{H}_2\text{S}$ : gas

$\text{Br}_2\text{-H}_2\text{O}$ : saturated solution

$\text{CrCl}_2$  solution:  $\sim 1.6\text{M}$ ; cold

Anion-exchange resin: AG 1-X4, 100 to 200 mesh (treated with 0.9M HCl)

Aerosol: 0.1% in  $\text{H}_2\text{O}$

Ethanol: absolute

Rubber cement: 6% in benzene

### 3. Preparation and Standardization of Carrier

Accurately weigh  $\sim 2.5$  g of tin metal and dissolve it quantitatively in  $\sim 25$  ml of 6M HCl, using heat and  $\text{Br}_2\text{-H}_2\text{O}$  as necessary to complete the dissolution. Dilute to exactly 250 ml, making the solution  $\sim 3\text{M}$  in HCl. The concentration of the carrier solution can then be calculated, but it also may be confirmed by precipitation of the tin by the following method. Dilute 1 ml of tin carrier to 15 ml with  $\text{H}_2\text{O}$ . Add 10 ml of a saturated aqueous solution of phenylarsonic acid, and heat at  $110^\circ\text{C}$  for 10 min. Cool to room temperature, allow to stand for 15 min, centrifuge, and discard the supernate. Wash with 5 ml of absolute ethanol, centrifuge, and discard the supernate. Add 5 ml of ethanol and filter through a weighed filter circle. Dry for 10 min at  $110^\circ\text{C}$ , cool, and weigh. Multiply by 0.2288 to obtain the weight of tin metal in the precipitate.

### 4. Procedure

*Step 1.* To 2.0 ml of the tin carrier solution in a 40-ml glass centrifuge tube, add the sample and 0.5 ml of  $\text{Br}_2\text{-H}_2\text{O}$ . Heat until the  $\text{Br}_2$  is gone; dilute with  $\text{H}_2\text{O}$  until the solution is 1M in HCl. Place in an ice bath and saturate with  $\text{H}_2\text{S}$ . Centrifuge, discard the supernate, wash the precipitate with 0.9M HCl, and discard the washings.

*Step 2.* Dissolve the precipitate in 1 ml of conc HCl with heat and boil for 3 min to remove H<sub>2</sub>S. If the volume is less than 1 ml, make up to this volume with conc HCl. Add 1 drop each of the following carriers: tellurium(VI), tellurium(IV), antimony, and molybdenum. Then add 0.5 ml of Br<sub>2</sub>-H<sub>2</sub>O and heat until the Br<sub>2</sub> is gone.

*Step 3.* Dilute the sample to 12 ml with H<sub>2</sub>O. (The solution is now ~1M in HCl.) Pour the solution onto a column of AG 1-X4, 100 to 200 mesh, anion-exchange resin, 5 cm by 9.5 mm, that has been treated with 10 ml of 0.9M HCl. After the solution has passed through the resin column, wash the column with four 20-ml portions of 0.9M HCl. Discard the effluent, including the washings.

*Step 4.* Elute the tin with 25 ml of 1.8M HClO<sub>4</sub> and collect the eluate in a 40-ml centrifuge tube. Add 4 drops of molybdenum carrier and saturate with H<sub>2</sub>S. Add 4 drops of aerosol and centrifuge. Discard the supernate, wash the precipitate with 0.9M HCl, and discard the washings.

*Step 5.* Dissolve the precipitate in 2 ml of conc HCl (any MoS<sub>3</sub> present will not dissolve) and boil for 3 min to remove H<sub>2</sub>S. Add 1 drop each of the following carriers: tellurium(VI), tellurium(IV), and antimony. Add 0.5 ml each of Br<sub>2</sub>-H<sub>2</sub>O and conc HF. Dilute the sample to 6 ml with H<sub>2</sub>O and boil. Saturate the *hot* solution with H<sub>2</sub>S, adding 2 drops of lanthanum carrier at the completion of saturation. Add 3 to 4 drops of aerosol and centrifuge.

*Step 6.* Transfer the supernate to a clean 40-ml centrifuge tube by means of a transfer pipette and add 1 drop each of tellurium(VI), tellurium(IV), and molybdenum carriers. Also add 0.5 ml of Br<sub>2</sub>-H<sub>2</sub>O and boil. Again saturate the *hot* solution with H<sub>2</sub>S, adding 2 drops of lanthanum carrier at the completion of saturation. Add 3 to 4 drops of aerosol, centrifuge, and transfer the supernate to a clean 40-ml centrifuge tube as above.

*Step 7.* Adjust the volume of the supernate to 15 ml by the addition of H<sub>2</sub>O. Add 10 ml of saturated H<sub>3</sub>BO<sub>3</sub> solution and cool in an ice bath. Bubble in H<sub>2</sub>S. Centrifuge, discard the supernate, and wash the precipitate with 0.9M HCl.

*Step 8.* Dissolve the precipitate in 1 ml of conc HCl and boil for 3 min to expel H<sub>2</sub>S. Add 1 drop each of tellurium(VI), tellurium(IV), and antimony carriers and 0.5 ml of Br<sub>2</sub>-H<sub>2</sub>O. Heat until all the Br<sub>2</sub> has been expelled. If a precipitate (MoS<sub>3</sub>) is still present, centrifuge, and pipette the supernate into a clean centrifuge tube.

*Step 9.* Repeat *Steps 3* and *4*.

*Step 10.* Dissolve the precipitate in 2 ml of conc HCl with heat and boil the solution for 3 min to remove H<sub>2</sub>S. Dilute the solution to ~8 ml with H<sub>2</sub>O, cool, and add an equal volume of *cold* CrCl<sub>2</sub> solution. To avoid coagulation of the tin, *filter immediately* onto a previously washed, dried, and weighed filter circle. Wash the precipitate first with 0.9M HCl, then with H<sub>2</sub>O, and finally with absolute ethanol.

*Step 11.* Dry the precipitate in an oven at 110°C for 5 to 10 min. Cool and weigh. Secure the precipitate with 3 drops of 6% rubber cement in benzene. When the precipitate is again dry, mount and count (Note).

#### Note

Analysis for either or both 26.85-h <sup>121</sup>Sn and 9.625-d <sup>125</sup>Sn can be performed. Small amounts of 129.0-d <sup>123</sup>Sn and 2.8-y <sup>125</sup>Sb (daughter of <sup>125</sup>Sn) can also be observed at later times. (The half-life values quoted here are those reported by Lawrence *et al.*) If <sup>121</sup>Sn is to be determined, a least squares analysis of the data is performed with the half-lives fixed. If only <sup>125</sup>Sn is to be determined, beta-counting is begun ~12 d after bombardment, when the contribution of <sup>121</sup>Sn is small, and a correction is applied for the small amount of <sup>123</sup>Sn in the sample. A least squares analysis of the

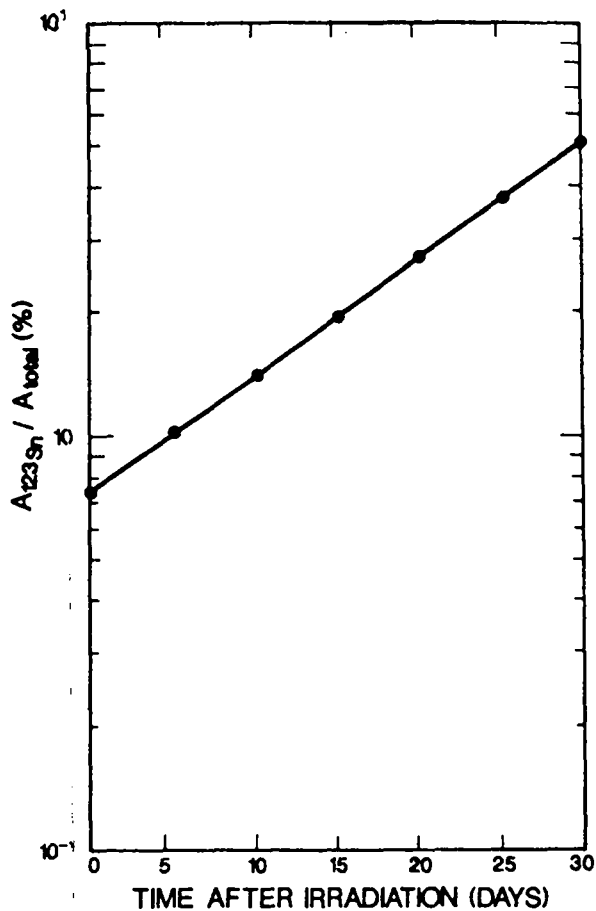


Fig. 1. Contribution of  $^{123}\text{Sn}$  to total beta count.

decay data for several samples showed that the contribution of  $^{123}\text{Sn}$  was only  $\sim 0.7\%$  of the total tin activity at  $t_0$ . (The samples were counted on gas flow, beta-proportional counters that have 2-in. diam,  $4.9\text{-mg/cm}^2$  aluminum windows. The proportion of  $^{123}\text{Sn}$  activity may, of course, be different for different counting conditions.) For ease of calculation, a graph showing the contribution of  $^{123}\text{Sn}$  to the total beta count of the sample at various times after irradiation was constructed from the data (see Fig. 1) for tin separation from thermal-fission products of  $^{235}\text{U}$ .

#### Reference

F. O. Lawrence, W. R. Daniels, and D. C. Hoffman, *J. Inorg. Nucl. Chem.* **28**, 2477 (1966).

(October 1989)

## TIN II

B. R. Erdal

### 1. Introduction

This rapid, relatively simple procedure for the separation of tin from fission products is taken from an article by B. R. Erdal and A. C. Wahl. The primary decontamination process makes use of a cyclic solvent extraction system consisting of three steps: (1) extraction of tin(II) from an aqueous  $\text{H}_2\text{SO}_4$ -KI solution into 4-methyl-2-pentanone (hexone); (2) oxidation of the tin to the IV state; and (3) back-extraction of tin(IV) into aqueous  $\text{H}_2\text{SO}_4$ -KI. Following two cycles of the process, an  $\text{Sb}_2\text{S}_3$  scavenge is performed; after  $\text{SnS}_2$  precipitation, the tin is reduced to the elemental state, in which form it is counted.

The procedure requires  $\sim 15$  min per sample and gives chemical yields of 40 to 60% with a decontamination factor of at least  $10^5$  for all  $^{235}\text{U}$  thermal-neutron fission products.

### 2. Reagents

Tin carrier: 10 mg tin/ml, standard solution prepared by dissolving pure tin metal in conc HCl and making a solution 2M in the acid by the addition of oxygen-free  $\text{H}_2\text{O}$

Antimony carrier: 4 mg antimony/ml, added as  $\text{SbCl}_3$  in 12M HCl

HCl: conc

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_2\text{OH}\cdot\text{HCl}$ : 1M aqueous solution

$\text{NaBrO}_3$ : 1M aqueous solution

$\text{H}_2\text{SO}_4$ -NaCl solution: 0.6M in  $\text{H}_2\text{SO}_4$  and 0.4M in NaCl

KI: 1.2M aqueous solution

KI- $\text{I}_2$  solution: 1.2M KI-4 mg  $\text{I}_2$ /ml

$\text{CrCl}_2$ :  $\sim 1.6$ M aqueous solution

$[(\text{CH}_3)_4\text{N}]\text{Cl}$ : 4M aqueous solution

4-methyl-2-pentanone (hexone)

Ethanol: 95%

$\text{H}_2\text{S}$ : gas

$\text{N}_2$ : oxygen-free

### 3. Procedure

*Step 1.* To 2.0 ml of standard tin carrier in a 40-ml glass centrifuge tube, add the sample, 4 drops of 1M  $\text{NaBrO}_3$ , and then an excess of 1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . Dilute to 40 ml with  $\text{H}_2\text{O}$  (the solution should be  $< 1$ M in HCl) and saturate with  $\text{H}_2\text{S}$ . Heat to digest the  $\text{SnS}_2$  and when the precipitate has coagulated, centrifuge, and discard the supernate.

*Step 2.* Dissolve the  $\text{SnS}_2$  in  $\sim 0.6$  ml of conc HCl and add 1 ml of 4M  $[(\text{CH}_3)_4\text{N}]\text{Cl}$  and 17 ml of 95% ethanol to precipitate  $[(\text{CH}_3)_4\text{N}]_2\text{SnCl}_6$ . Digest on a steam bath for 1 min, centrifuge, and discard the supernate.

*Step 3.* Dissolve the precipitate in 10 ml of 0.6M  $\text{H}_2\text{SO}_4$ -0.4M NaCl and add the solution to 10 ml of 1.2M KI solution that has been flushed with oxygen-free  $\text{N}_2$  in the upper extraction vessel of the extraction apparatus (Fig. 1). Continuing the  $\text{N}_2$  flow, start the stirrer, add 2 ml of  $\sim 1.6$ M  $\text{CrCl}_2$  solution, and then immediately add 2 ml of hexone (Note). Stir for 15 s, stop the nitrogen flow and the stirrer, and discard the aqueous (lower) phase.

*Step 4.* To the hexone phase, add 10 ml of 0.6M  $\text{H}_2\text{SO}_4$ -0.4M NaCl solution and 10 ml of KI- $\text{I}_2$  solution. Stir for 60 to 90 s with nitrogen flowing and then stop the nitrogen flow and the stirrer. [Tin(II) is oxidized to Sn(IV) by the  $\text{I}_2$  and is extracted into the aqueous phase.]

*Step 5.* Run the aqueous phase into the lower extraction vessel, add 3 ml of  $\sim 1.6$ M  $\text{CrCl}_2$  solution, and then immediately add 20 ml of hexone. Stir for 15 s, stop the stirrer, and discard the aqueous phase.

*Step 6.* Repeat Step 4.

*Step 7.* Run the aqueous phase into a clean 40-ml glass centrifuge tube containing 10 ml of antimony carrier. Cool the solution by swirling it



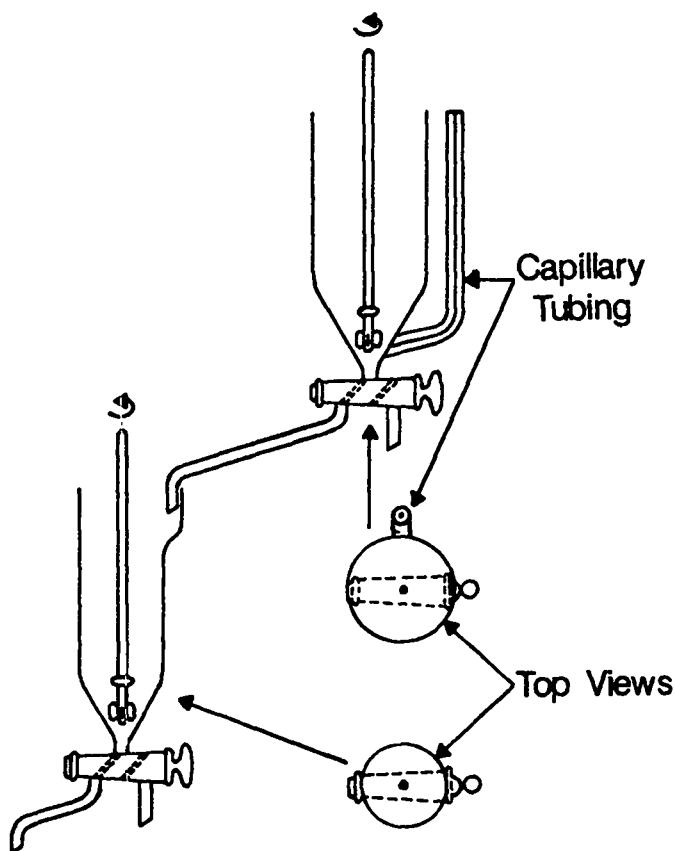


Fig. 1. Extraction vessels.

in a dry ice-isopropanol bath for 45 s, saturate with a very rapid stream of  $\text{H}_2\text{S}$  for 30 s, and centrifuge for 45 s. Filter through a Millipore HA,  $0.45\text{-}\mu\text{m}$  pore filter paper with absorbent pad, and collect the filtrate in a clean centrifuge tube. Discard the precipitate.

*Step 8.* Add  $\sim 8$  ml of conc  $\text{NH}_4\text{OH}$  to the filtrate, saturate with  $\text{H}_2\text{S}$ , and digest on a steam bath until the precipitate coagulates. Centrifuge and discard the supernate.

*Step 9.* Dissolve the  $\text{SnS}_2$  in 2 ml of hot conc  $\text{HCl}$ , add 40 ml of  $\text{H}_2\text{O}$  previously saturated with  $\text{H}_2\text{S}$ , and digest on a steam bath until the precipitate coagulates. Centrifuge and discard the supernate.

*Step 10.* Repeat *Step 2*.

*Step 11.* Dissolve the  $[(\text{CH}_3)_4\text{N}]_2\text{SnCl}_6$  precipitate in 2 ml of hot conc  $\text{HCl}$ , dilute to

40 ml with  $\text{H}_2\text{O}$ , and saturate with  $\text{H}_2\text{S}$ . Digest the precipitate on a steam bath, centrifuge, and discard the supernate.

*Step 12.* Dissolve the  $\text{SnS}_2$  in 0.5 ml of hot conc  $\text{HCl}$ , add 8 ml of  $\text{H}_2\text{O}$ , and then add 3 ml of  $\sim 1.6M$   $\text{CrCl}_2$  to precipitate elemental tin. Filter through a weighed,  $10\text{-}\mu\text{m}$ -pore polypropylene filter paper, wash the precipitate with 95% ethanol, and air dry under suction for  $\sim 1.5$  min. Weigh and mount.

#### Note

Unless the hexone is added immediately to extract tin(II), the yield drops substantially because elemental tin begins to form and precipitate.

#### Reference

B. R. Erdal and A. C. Wahl, *J. Inorg. Nucl. Chem.* **30**, 1985 (1968).

October 1989

# LEAD

J. S. Gilmore

## 1. Introduction

In the determination of radiolead, four decontamination cycles are carried out; each consists of the precipitation of (1)  $\text{Pb}(\text{NO}_3)_2$ , (2)  $\text{PbCl}_2$ , (3)  $\text{Fe}(\text{OH})_3$ , and (4)  $\text{PbS}$ . Lead is finally precipitated and mounted as the chromate. The chemical yield is 60 to 70%.

## 2. Reagents

Lead carrier: 20 mg lead/ml, added as  $\text{Pb}(\text{NO}_3)_2$  in 0.01M  $\text{HNO}_3$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1M  $\text{HCl}$

$\text{HCl}$ : conc

$\text{HNO}_3$ : conc; fuming (sp gr 1.5)

$\text{HC}_2\text{H}_3\text{O}_2$ : 6M

$\text{NH}_4\text{OH}$ : 1M; conc

$\text{NaOH}$ : 12M

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ : 6M

$\text{Na}_2\text{CrO}_4$ : 1.5M

$\text{NH}_4\text{Cl}$ : solid

$\text{H}_2\text{S}$ : gas

Ethanol: 95%

Bromophenol blue indicator solution

## 3. Preparation and Standardization of Carrier

Weigh out 32.0 g of  $\text{Pb}(\text{NO}_3)_2$  and make up to 1 l in  $\text{H}_2\text{O}$ . Pipette 5.0 ml of the solution into a 250-ml beaker, add 3 ml of 6M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  and 2 ml of 6M  $\text{HC}_2\text{H}_3\text{O}_2$ , and dilute to 30 ml with  $\text{H}_2\text{O}$ . Heat to boiling and add 5 ml of 1.5M  $\text{Na}_2\text{CrO}_4$  dropwise. Digest on a steam bath for 30 min and filter onto a weighed 15-ml sintered glass crucible. Wash the precipitate with  $\text{H}_2\text{O}$  until the washings have no dichromate color, and then wash with 95% ethanol. Dry in an oven at 115°C for 30 min. Cool and weigh as  $\text{PbCrO}_4$ .

Four standardizations gave results agreeing within 0.2%.

## 4. Procedure

*Step 1.* Pipette 2.0 ml of lead carrier into a 40-ml glass centrifuge tube, add an aliquot of sample and 1 ml of conc  $\text{HNO}_3$ , and evaporate nearly to dryness.

*Step 2.* Dissolve the residue in a minimum amount of  $\text{H}_2\text{O}$ , add 30 ml of fuming  $\text{HNO}_3$  (sp gr 1.5), and cool in an ice bath. Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in 1 ml of  $\text{H}_2\text{O}$ . Add 1 ml of conc  $\text{HNO}_3$ , 25 ml of 95% ethanol, and 4 drops of conc  $\text{HCl}$ . Chill in an ice bath. Centrifuge and discard the supernate.

*Step 4.* Dissolve the precipitate in 20 ml of  $\text{H}_2\text{O}$ , add ~2 g of solid  $\text{NH}_4\text{Cl}$ , 4 drops of iron carrier, and heat to boiling. Add 2 drops of bromophenol blue indicator solution and neutralize to an alkaline endpoint with 1M  $\text{NH}_4\text{OH}$ . Centrifuge while hot and transfer the supernate to a clean centrifuge tube; discard the precipitate.

*Step 5.* Saturate the supernate with  $\text{H}_2\text{S}$ . Centrifuge and discard the supernate.

*Step 6.* Dissolve the precipitate in 2 ml of conc  $\text{HCl}$  and evaporate to dryness. Add 1 ml of conc  $\text{HNO}_3$  and evaporate nearly to dryness.

*Step 7.* Repeat Steps 2 and 3.

*Step 8.* Add 20 ml of  $\text{H}_2\text{O}$  and 4 drops of iron carrier to the precipitate and heat to boiling. Add 12M  $\text{NaOH}$  dropwise until the  $\text{Pb}(\text{OH})_2$  precipitate dissolves, leaving only the  $\text{Fe}(\text{OH})_3$  precipitate. Then add 5 drops of 12M  $\text{NaOH}$  in excess, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 9.* Repeat Steps 5 and 6.

*Step 10.* Repeat Steps 2, 3, 4, 5, and 6.

*Step 11.* Repeat *Steps 2, 3, 8,* and *5.*

*Step 12.* Dissolve the precipitate in 2 ml of conc HCl and evaporate nearly to dryness. Add 2 ml of 6M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 3 ml of 6M NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, dilute to 20 ml with H<sub>2</sub>O, heat to boiling, and add 3 ml of 1.5M Na<sub>2</sub>CrO<sub>4</sub> while the solution is at the boiling point. Filter onto a weighed filter circle. Wash the PbCrO<sub>4</sub> precipitate with H<sub>2</sub>O and then with 95% ethanol. Dry the precipitate in an oven for 10 min at 115°C. Cool, weigh, and mount for counting.

(October 1989)

# PHOSPHORUS

N. A. Bonner and H. A. Potratz

## 1. Introduction

The principal decontamination steps in the determination of radiophosphorus in the presence of fission-product material involve precipitations of the element as  $Zr_3(PO_4)_4$  and  $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O(?)$ . Arsenic is removed by precipitation of the pentasulfide. Lanthanum fluoride scavenging is included. Phosphorus is finally precipitated as  $MgNH_4PO_4 \cdot 6H_2O$ , in which form it is counted. The chemical yield is 70 to 80%. A sample containing  $1.5 \times 10^{15}$  fissions was decontaminated to  $<3$  counts/min measured 2 d after bombardment. A small amount of short-lived contamination (probably 80-min  $^{78}As$ ) remains if the sample is counted  $\sim 8$  h after the end of bombardment.

## 2. Reagents

Phosphorus carrier: 5 mg phosphorus/ml, added as  $(NH_4)_2HPO_4$  in  $H_2O$ ; standardized

Zirconium carrier: 10 mg zirconium/ml, added as  $ZrO(NO_3)_2 \cdot 2H_2O$  in 1M  $HNO_3$

Arsenic carrier: 10 mg arsenic/ml, added as  $Na_2HASO_4 \cdot 7H_2O$  in  $H_2O$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $La(NO_3)_3 \cdot 6H_2O$  in  $H_2O$

HCl: 3M; conc

$HNO_3$ : 6M; conc

HF: conc

Citric acid: 500 g/l of aqueous solution

$NH_4OH$ : 1:20; conc

$H_2O_2$ : 30% (Superoxol)

$H_2S$ : gas

Ammonium molybdate reagent: 200 g  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ , 800 ml  $H_2O$ , and 160 ml conc  $NH_4OH$

"Magnesia" mixture: 50 g  $MgCl_2 \cdot 6H_2O$ , 100 g  $NH_4Cl$ , 3 to 5 drops conc HCl, and 500 ml  $H_2O$

Aerosol solution: 0.1% in  $H_2O$

Ethanol: 50%; 95%

## 3. Precipitation and Standardization of Carrier

Make up 1 l of an aqueous solution containing 21.3 g of  $(NH_4)_2HPO_4$ .

Pipette exactly 5 ml of the above carrier solution into a 100-ml beaker and add 20 ml of "magnesia" mixture. Make the solution slightly alkaline by the dropwise addition of conc  $NH_4OH$  and permit to stand for 5 min with occasional stirring. Then add 10 ml of conc  $NH_4OH$  and allow the mixture to stand for 4 h, again stirring occasionally. Filter the precipitate onto a weighed 15-ml coarse sintered glass crucible. Wash the precipitate with 1:20  $NH_4OH$ , 50% ethanol, and finally 95% ethanol. Pull air through the filter for  $\sim 10$  min and then allow the precipitate to stand in the balance case for  $\sim 30$  min. Weigh as  $MgNH_4PO_4 \cdot 6H_2O$ .

Four standardizations gave results agreeing within 0.5%.

## 4. Procedure

*Step 1.* To the sample in a 40-ml plastic centrifuge tube (Note 1), add 20 ml of 6M  $HNO_3$  and 1.0 ml of  $(NH_4)_2HPO_4$  carrier solution. Heat the solution on a steam bath and add 2 ml of zirconium carrier to precipitate  $Zr_3(PO_4)_4$ . Continue heating for 3 to 5 min. Centrifuge and discard the supernate. Wash the precipitate with  $H_2O$  and discard the washings.

*Step 2.* Dissolve the precipitate in 0.1 ml of conc HF and add 5 ml of  $H_2O$ , 10 ml of 6M  $HNO_3$ , 5 drops of 0.1% aerosol solution, and 5 ml of ammonium molybdate reagent. Heat the mixture on a steam bath for 2 to 5 min. Centrifuge and discard the supernate. Wash the ammonium phosphomolybdate precipitate with 10 ml of  $H_2O$  containing a few drops of aerosol (Note 2).

*Step 3.* Dissolve the precipitate in 0.5 ml of conc  $NH_4OH$ , add 10 ml of  $H_2O$  and 4 drops of 30%

H<sub>2</sub>O<sub>2</sub> (Superoxol), and stir thoroughly. Add 10 ml of conc HCl and 2 ml of zirconium carrier (Note 3), and heat on a steam bath for 5 min. Centrifuge and discard the supernate. Wash the precipitate with H<sub>2</sub>O and discard the washings.

*Step 4.* Dissolve the precipitate in 0.2 ml of conc HF and add 10 ml of 3M HCl, 0.5 ml of arsenic carrier, and a few drops of aerosol solution. Heat on a steam bath for 15 min while bubbling H<sub>2</sub>S through the solution. Centrifuge and transfer the supernate to a clean 40-ml plastic centrifuge tube. Wash the precipitate with 1 to 2 ml of H<sub>2</sub>O containing a few drops of aerosol solution. While the precipitate is being washed, pass H<sub>2</sub>S through the original supernate that is being heated on a steam bath. Combine the supernate from the washing with the original supernate. Discard the As<sub>2</sub>S<sub>5</sub> precipitate.

*Step 5.* Add 2 ml of lanthanum carrier to the solution from *Step 4*. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the LaF<sub>3</sub> precipitate.

*Step 6.* To the supernate, add 4 ml of conc HNO<sub>3</sub> and 5 ml of ammonium molybdate reagent. Heat on a steam bath for 2 to 5 min, centrifuge, and discard the supernate. Wash the precipitate with 10 ml of H<sub>2</sub>O that contains a few drops of aerosol and discard the washings.

*Step 7.* Repeat *Steps 3* through *6* twice.

*Step 8.* Dissolve the ammonium phosphomolybdate precipitate in 1 ml of conc NH<sub>4</sub>OH and add 2 ml of citric acid solution (0.5 g/ml). Add 10 ml of "magnesia" mixture and conc NH<sub>4</sub>OH (dropwise) until the solution is barely alkaline, then add 10 drops more. Swirl the solution for ~1 min and if a precipitate does not begin to form, add 5 more drops of conc NH<sub>4</sub>OH. After precipitation begins, swirl the mixture for at least 1 min and then add 4 ml of conc NH<sub>4</sub>OH. Allow the mixture to stand, with occasional stirring, for at least 10 min. Filter through a 15-ml fine sintered

glass funnel and wash the precipitate with a small amount of 1:20 NH<sub>4</sub>OH. Dissolve the precipitate in a few drops of conc HCl and a few ml of H<sub>2</sub>O. Collect the filtrate in a 100-ml beaker.

*Step 9.* Add 10 ml of "magnesia" mixture and just enough conc NH<sub>4</sub>OH to neutralize the HCl in the mixture. (One drop of NH<sub>4</sub>OH in excess should cause the precipitate of MgNH<sub>4</sub>PO<sub>4</sub>•6H<sub>2</sub>O to start forming.) Swirl for ~1 min and then add 3 ml of conc NH<sub>4</sub>OH. Allow the mixture to stand for at least 10 min. Filter onto a weighed filter circle. Wash the precipitate with small portions of 1:20 NH<sub>4</sub>OH, 50% ethanol, and 95% ethanol. Pull air through the filter for 5 min, allow the precipitate to stand in the balance case for ~30 min, weigh, mount, and count (Note 4).

## Notes

1. If large amounts of SO<sub>4</sub><sup>2-</sup> ion are present in the sample, the precipitation of zirconium phosphate is not complete.

2. If the ammonium phosphomolybdate precipitate shows a tendency to peptize, dilute NH<sub>4</sub>NO<sub>3</sub> solution should be used for the wash.

3. The reagents should be added in the indicated order. If HCl is added before dilution with H<sub>2</sub>O, ammonium phosphomolybdate reprecipitates.

4. The 14.1-d <sup>32</sup>P is the isotope determined; it has a 1.71-MeV beta and no gamma.

(October 1989)

## ARSENIC

R. J. Prestwood and B. J. Dropesky

### 1. Introduction

In the separation of radioarsenic from fission products, the sulfide is first precipitated in acid medium. The chief contaminants of this precipitate are germanium, tellurium, molybdenum, and cadmium. Fuming the sulfide with a mixture of  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{HClO}_4$  removes germanium, which volatilizes as the tetrachloride; arsenic is oxidized to  $\text{H}_3\text{AsO}_4$ . The arsenic is then converted to the triiodide by treatment with  $\text{HI}$  and extracted into benzene; tellurium, molybdenum, and cadmium remain in the aqueous phase. The extraction is an excellent decontamination step. After washing, the benzene solution is treated with dilute  $\text{H}_2\text{SO}_4$ , and arsenic is extracted into the aqueous phase. After appropriate repetition of the extraction process, the arsenic is precipitated as the sulfide. The latter is dissolved and arsenic is finally reduced by  $\text{CrCl}_2$  to the free element, in which form it is weighed and counted. The chemical yield is  $\sim 90\%$ .

### 2. Reagents

Arsenic carrier: 10 mg arsenic/ml, added as  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ; standardized  
 $\text{HCl}$ : 3M; 6M; conc  
 $\text{HNO}_3$ : conc  
 $\text{H}_2\text{SO}_4$ : 1M  
 $\text{HClO}_4$ : conc  
 $\text{HI}$ : 47%  
 $\text{NaI}$ : solid  
 $\text{CrCl}_2$ :  $\sim 1.6M$  solution  
 $\text{H}_2\text{S}$ : gas  
Aerosol: 0.1% aqueous solution  
Benzene  
Ethanol: absolute

### 3. Preparation and Standardization of Carrier

Prepare an aqueous solution containing 56.6 g of  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}/\ell$ . Pipette exactly 5 ml of the carrier solution into a 40-ml glass centrifuge tube, add 10 ml of 6M  $\text{HCl}$ , and heat. To the hot solution add 10 to 15 ml of  $\text{CrCl}_2$  solution and stir vigorously for 2 min while maintaining the solution near its boiling point. Filter the elemental arsenic precipitate into a weighed 30-ml sintered glass crucible of medium porosity. Wash the precipitate three times with 5-ml portions of  $\text{H}_2\text{O}$  and once with 5 ml of absolute ethanol. Dry at  $110^\circ\text{C}$  for 15 min. Cool and weigh.

Four standardizations are carried out.

### 4. Procedure

*Step 1.* Pipette the sample into a 40-ml glass centrifuge tube that contains exactly 2 ml of standard arsenic carrier. Add 10 ml of conc  $\text{HCl}$  and  $\sim 20$  mg of solid  $\text{NaI}$ . Pass  $\text{H}_2\text{S}$  into the solution, which is maintained at room temperature. Centrifuge the sulfide precipitate and discard the supernate.

*Step 2.* To the  $\text{As}_2\text{S}_3$  precipitate add 0.5 ml each of conc  $\text{HNO}_3$  and  $\text{HCl}$  and 1 ml of conc  $\text{HClO}_4$ . Heat the solution gently and then to fumes of  $\text{HClO}_4$  over a burner, and continue heating until all free sulfur has been oxidized. Permit the solution to cool.

*Step 3.* Transfer the dissolved arsenic (now in the +5 state) with 10 ml of 3M  $\text{HCl}$  into a 125-ml separatory funnel. Add 5 ml of 47%  $\text{HI}$  and 30 ml of  $\text{C}_6\text{H}_6$ . Shake the mixture thoroughly and then permit it to stand for 1 min (Note 1). Drain the aqueous phase and discard.

*Step 4.* Wash the  $\text{C}_6\text{H}_6$  phase containing  $\text{AsI}_3$  with 5 ml of 3M  $\text{HCl}$  and 2 ml of 47%  $\text{HI}$ . Drain and discard the wash solution.

*Step 5.* Add 10 ml of 1M H<sub>2</sub>SO<sub>4</sub> to the C<sub>6</sub>H<sub>6</sub> phase and shake for 1 min. Permit the mixture to stand for 1 to 2 min, drain the aqueous phase into a clean 125-ml separatory funnel, and discard the C<sub>6</sub>H<sub>6</sub> layer.

*Step 6.* To the aqueous phase add 10 ml of 6M HCl, 8 ml of 47% HI, and 30 ml of C<sub>6</sub>H<sub>6</sub>. Shake the mixture thoroughly and drain and discard the aqueous phase.

*Step 7.* Repeat Steps 4, 5, and 6 and then Step 4 again.

*Step 8.* Add 15 ml of 1M H<sub>2</sub>SO<sub>4</sub> to the C<sub>6</sub>H<sub>6</sub> solution and shake for 1 min. Let the mixture stand for 1 to 2 min and then drain the aqueous phase into a clean 40-ml centrifuge tube.

*Step 9.* Add 10 ml of conc HCl and saturate the solution with H<sub>2</sub>S. Centrifuge the As<sub>2</sub>S<sub>3</sub> precipitate and discard the supernate.

*Step 10.* Repeat Step 2.

*Step 11.* Add 10 ml of 6M HCl and heat to boiling. Add 5 ml of CrCl<sub>2</sub> solution and stir continuously for 1 min, while keeping the solution hot. Again add 5 ml of CrCl<sub>2</sub> and stir continuously for 1 min. Wash down the walls of the tube with a few drops of aerosol solution.

*Step 12.* Filter the elementary arsenic onto a weighed filter circle. Wash the precipitate with several 5-ml portions of H<sub>2</sub>O and then with absolute ethanol. Dry at 110°C for 10 min, cool, weigh, and mount (Note 2).

#### Notes

1. Because of the toxicity of benzene vapor, it is advisable to perform extractions with this solvent in a fume hood.

2. Beta-counting of the 38.7-h <sup>77</sup>As formed in fission is begun immediately. If a half-life of <38.7 h

is obtained, it is likely that some normal arsenic was present and the (n,γ) reaction on it gave <sup>76</sup>As (26.5 h). The thermal neutron capture cross section for arsenic is quite high and <sup>76</sup>As is a prevalent contaminant.

(October 1989)

ADDITIONS TO ARSENIC PROCEDURE:  
FOR USE WITH  
UNDERGROUND NUCLEAR DEBRIS

I. Binder

1. The Dissolving Process

*Step 1.* Place the ground sample in a Parr acid digestion bomb and add a weighed amount of  $As_4O_6$  carrier (~30 mg). For each gram of sample add 2.5 ml of 90% fuming  $HNO_3$  and 5 ml of conc HF. (The total volume of mixture should not exceed 66% that of the bomb.) Seal the bomb and heat overnight at ~125°C. Allow the bomb to cool and then open it.

*Step 2.* Transfer the contents of the bomb to a Teflon beaker. Wash out the bomb successively with 15 ml of 90% fuming  $HNO_3$ , 15 ml of conc HF, and 10 ml of 70%  $HClO_4$ ; transfer the washes to the Teflon beaker. (Additional  $HNO_3$  and HF may be necessary for debris samples larger than several grams.)

*Step 3.* Heat the beaker on a hot plate until  $HClO_4$  fumes are evolved and the volume of solution is reduced to ~5 ml. Cool and transfer the contents of the beaker to a 50-ml plastic centrifuge tube. Wash the beaker with 5 ml of  $H_2O$  and add the wash to the centrifuge tube. Centrifuge and transfer the supernate to another plastic tube. Centrifuge and transfer the supernate to a 40-ml glass centrifuge tube. Wash any solid remaining in the plastic tube with 10 ml of conc HCl, centrifuge, and combine the wash with the supernate in the glass tube.

2. Procedure

Add 20 mg of solid NaI as in *Step 1* of the ARSENIC procedure and complete that procedure (Note).

Note

It is advisable to use toluene rather than benzene for extractions of  $AsI_3$ . Toluene is believed to be much less toxic than benzene.

(October 1989)



# SEPARATION OF ARSENIC, GERMANIUM, AND GALLIUM

R. J. Prestwood

## 1. Introduction

In the separation of radioactive arsenic, germanium, and gallium, arsenic(III) is first removed as the sulfide in the presence of  $F^-$  ion that serves to complex and keep germanium in solution. The fluoro complex is then destroyed and germanium is separated as the sulfide. Gallium is finally precipitated by means of 8-quinolinol (8-hydroxyquinoline).

## 2. Reagents

Gallium carrier: added as  $GaCl_3$  in 1M HCl;  
~5 mg gallium/ml. (One milliliter of carrier solution is equivalent to ~36 mg of gallium 8-quinolinate)

Germanium carrier: 10 mg germanium/ml. See GERMANIUM procedure for preparation.

Arsenic carrier: 10 mg arsenic/ml added as  $Na_3AsO_4 \cdot 12H_2O$  in  $H_2O$

$HNO_3$ : conc

$HClO_4$ : conc

HCl: 4M; 3M

HF: conc

$H_3BO_3$ : saturated aqueous solution

$H_2C_4H_4O_6$  (tartaric acid): saturated aqueous solution

$HC_2H_3O_2$ : 2M

$H_2S$ : gas

$NH_4OH$ : conc

NaI: solid

8-quinolinol (8-hydroxyquinoline) solution: 5% in 2M  $HC_2H_3O_2$

Phenolphthalein indicator solution

Methanol: absolute

## 3. Procedure

*Step 1.* To an aliquot of the sample (Note 1) in a 125-ml erlenmeyer flask, add 5 mg of gallium carrier and 20 mg each of germanium and arsenic carriers. Add 2 ml of conc  $HNO_3$  and 1 to 2 ml of conc  $HClO_4$  and evaporate to copious  $HClO_4$  fumes (Note 2).

*Step 2.* Adjust the volume of solution to ~15 ml with 4M HCl. Add 10 drops of conc HF and ~100 mg of solid NaI and bubble in  $H_2S$  for several min, warming if necessary to coagulate the  $As_2S_3$  precipitate. Transfer to a 40-ml centrifuge tube, centrifuge, and filter through a 2-in. 60° funnel into a clean 125-ml erlenmeyer flask. Wash the precipitate with a small amount of  $H_2O$ ; collect the washings in the clean erlenmeyer flask. To determine arsenic in the sulfide precipitate, proceed with Steps 11 and 12 of the ARSENIC procedure.

*Step 3.* To the solution in the erlenmeyer flask, add 5 ml of saturated  $H_3BO_3$  and bubble in  $H_2S$  until  $GeS_2$  has been completely precipitated. (If the precipitate is not pure white, all the arsenic has not been removed.) Filter onto a weighed filter circle and transfer the filtrate to a clean 125-ml erlenmeyer flask. The  $GeS_2$  precipitate is washed with a small amount of  $H_2O$  and then with absolute methanol. The precipitate is dried in an oven at 110°C, cooled, weighed as  $GeS_2$ , mounted, and counted.

*Step 4.* To the filtrate containing the gallium, add 1 drop of phenolphthalein indicator, just neutralize with  $NH_4OH$ , and then add 10 drops of saturated aqueous tartaric acid. Heat to boiling and add dropwise ~1.5 ml of 5% 8-quinolinol in 2M  $HC_2H_3O_2$ . Transfer to a clean 40-ml centrifuge tube, centrifuge, and discard the supernate. Dissolve the precipitate in ~3M HCl by heating. Centrifuge and transfer the supernate to a clean centrifuge tube (Note 3). Neutralize and precipitate the 8-quinolinate as above.

Filter while hot onto a weighed filter circle. Wash the precipitate with H<sub>2</sub>O and then with ether. Dry in oven at 110°C, cool, weigh as the 8-quinolate, mount, and count.

#### Notes

1. This procedure was developed primarily for (n,p) and (n, $\alpha$ ) reactions on arsenic. Therefore, only germanium and gallium carriers were added. However, the procedure is generally applicable for these three elements.

2. With this treatment, GeO<sub>2</sub> precipitates. However, the germanium is brought back into solution in *Step 2*.

3. This centrifugation is performed merely to clean up the solution if it is necessary.

(October 1989)

## ANTIMONY I

D. C. Hoffman and J. W. Barnes

### 1. Introduction

In this procedure for the determination of antimony in fission-product solutions, the antimony is first converted to the +5 state. Decontamination from the bulk of the molybdenum activity present is then effected by  $\text{MoS}_3$  precipitation in the presence of  $\text{F}^-$  ion, which strongly complexes antimony(V), thus keeping it in solution. After reduction of antimony to the tripositive state, separation from tin is effected by precipitation of  $\text{Sb}_2\text{S}_3$  in the presence of tin carrier and  $\text{F}^-$  ion; the latter keeps the tin in solution as a fluoro complex. Tellurium, which precipitates along with antimony, is removed by precipitation with  $\text{H}_2\text{S}$  from conc HCl solution; the antimony remains in solution. The antimony is then absorbed on a Dowex 1-X10 anion-exchange column from 0.9M HCl solution. The last traces of molybdenum are removed with a wash by the acid. The antimony is eluted from the column by means of a 20% ammoniacal tartrate solution and is again precipitated as a sulfide. The sulfide is dissolved in conc HCl and then converted to the metal by reduction with  $\text{CrCl}_2$ . In this form it is weighed and counted. The chemical yield is ~50%.

### 2. Reagents

Antimony carrier: 10 mg antimony/ml, added as  $\text{SbCl}_3$  in 6M HCl; standardized

Molybdenum carrier: 10 mg molybdenum/ml, added as  $\text{Na}_2\text{MoO}_4$  in  $\text{H}_2\text{O}$

Tin carrier: 10 mg tin/ml, added as  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 6M HCl

Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 12M HCl

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{H}_4\text{TeO}_6$  in 3M HCl

HCl: conc; 6M; 1M; 0.9M

HI: conc

HF: conc

$\text{H}_2\text{SO}_4$ : conc

$\text{H}_2\text{S}$ : gas

$\text{Br}_2\text{-H}_2\text{O}$ : saturated solution

$\text{NH}_4\text{OH}$ : conc

$\text{CrCl}_2$ : ~1.6M aqueous solution

$\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ : 20% aqueous solution

Aerosol solution: 1% in  $\text{H}_2\text{O}$

Methanol: absolute

Dowex 1-X10 anion-exchange resin, 100 to 200 mesh

### 3. Preparation and Standardization of Carrier

Dissolve 18.7 g of  $\text{SbCl}_3$  in 6M HCl and make the solution up to a volume of 1 l with the acid.

Pipette 5 ml of the above carrier solution into a weighed filter beaker. (This beaker has a 15-ml sintered glass crucible of fine-porosity sealed into the side near the top so that the operations that follow—reduction, filtration, drying, and weighing—may all be carried out in this one vessel.) Add 5 to 10 ml of  $\text{CrCl}_2$  solution. After conversion to antimony metal is complete, filter and wash the precipitate with small portions of  $\text{H}_2\text{O}$  and absolute methanol. Dry the filter beaker containing the antimony at 100°C for 1 h. Cool and weigh.

### 4. Procedure

*Step 1.* To a 40-ml glass centrifuge tube add 2 ml of antimony carrier, a few drops of molybdenum carrier, the sample, and 2 ml of  $\text{Br}_2\text{-H}_2\text{O}$ . Boil off the  $\text{Br}_2$  and make the solution ~1.5M in HCl. Add 1 ml each of conc HF and conc  $\text{H}_2\text{SO}_4$  per 25 ml of solution. Bring to a boil, saturate with  $\text{H}_2\text{S}$  to precipitate  $\text{MoS}_3$ , add some filter paper pulp, centrifuge, and pour the supernate through a filter into a 90-ml centrifuge tube. Wash the filter with 2 to 3 ml of 1M HCl and permit the washings to drain into the same centrifuge tube.

*Step 2.* To the solution add 1 ml of tin carrier, 2 drops of molybdenum carrier, 2 ml of conc HI, boil for ~2 min, and add 5 ml of  $\text{H}_2\text{O}$ . Saturate with  $\text{H}_2\text{S}$  to precipitate  $\text{Sb}_2\text{S}_3$ , add a few drops of aerosol solution, and centrifuge. Discard the

supernate, wash the precipitate with 1M HCl, and discard the washings.

*Step 3.* Dissolve the precipitate in 4 ml of conc HCl, boil off H<sub>2</sub>S, and remove any undissolved MoS<sub>3</sub> precipitate by filtering the solution into a clean 40-ml centrifuge tube. To the filtrate add 4 drops of tin carrier, 4 drops of tellurium(IV) carrier, 2 drops of tellurium(VI) carrier, and 1 ml each of conc HI and conc HF. Boil for ~2 min (until the original vigorous reaction subsides). Dilute to 25 ml with 1M HCl, add a few drops of aerosol solution, and saturate with H<sub>2</sub>S to precipitate Sb<sub>2</sub>S<sub>3</sub>. Centrifuge and wash the precipitate as in *Step 2*.

*Step 4.* Repeat *Step 3*, but use no tin or tellurium carrier.

*Step 5.* Dissolve the precipitate in 4 ml of conc HCl, boil off the H<sub>2</sub>S, add 2 ml of tellurium(IV) carrier, and boil for 1 to 2 min. Add 2 ml more of conc HCl, bring to a boil, saturate with H<sub>2</sub>S, and filter on a 15-ml medium fritted glass funnel into a 40-ml centrifuge tube. Wash the original tube with 2 ml of conc HCl and filter into the original filtrate. Discard the precipitate. Boil the combined filtrate, add 2 ml of tellurium(IV) carrier, boil for 1 to 2 min, saturate with H<sub>2</sub>S, filter into a 40-ml centrifuge tube, and discard the precipitate.

*Step 6.* Boil off the H<sub>2</sub>S, evaporate the solution to about half of its original volume (it will now be ~6M in HCl), and dilute with H<sub>2</sub>O to make the solution 0.9M in HCl. Add 6 ml of H<sub>2</sub>O for every 1 ml of solution. Measure volumes accurately and do the dilution carefully. The 0.9M value is critical because the distribution coefficient for molybdenum rises steeply both above and below 0.9M HCl concentration (Note 1).

*Step 7.* Prepare a Dowex 1-X10 anion-exchange resin (100 to 200 mesh) column (1.1 cm by 5.5 cm) with a glass wool plug both above and below the resin bed. Prewash the column with ~10 ml of 0.9M HCl. Place the solution from *Step 6* on the

column and permit it to flow through. Discard the effluent. Wash the column with 250 ml of 0.9M HCl, discarding the washings. Elute the antimony with 20 ml of 20% NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> that has been made alkaline with 12 drops (~1 ml) of conc NH<sub>4</sub>OH. Collect the eluate in a 40-ml centrifuge tube.

*Step 8.* Add conc HCl (~2 ml) until a precipitate just forms. Dissolve the precipitate by adding conc HCl dropwise, and then add 2 ml of the acid in excess. Saturate with H<sub>2</sub>S, centrifuge, and discard the supernate.

*Step 9.* Dissolve the precipitate in 5 to 10 ml of conc HCl and boil off the H<sub>2</sub>S. Make the solution 3 to 5M in HCl and filter through a 60-ml sintered glass crucible of fine porosity into a 40-ml centrifuge tube.

*Step 10.* Add sufficient CrCl<sub>2</sub> solution to precipitate antimony completely as the metal. Start filtering through a weighed filter circle within 1 min or less. Wash the metal with 5-ml portions of H<sub>2</sub>O and absolute methanol. Dry at 100°C for 15 min. Cool, weigh, and mount (Note 2).

## Notes

1. As an alternative to *Step 6*, after the H<sub>2</sub>S is boiled off, the solution may be evaporated nearly to dryness on a steam bath; however, the material must not be left on the steam bath dry or at elevated temperatures because the antimony may volatilize. Add a few drops of H<sub>2</sub>O until a white precipitate forms, dilute to 10 ml with 0.9M HCl, and proceed with *Step 7*.

2. The antimony is ordinarily not counted until 4 d after the column step (*Step 7*), to allow 9.3-h <sup>127</sup>Te to grow into equilibrium with 93-h <sup>127</sup>Sb.

(October 1989)

## ANTIMONY II

B. R. Erdal

### 1. Introduction

This rapid procedure for the separation of antimony from fission products is based on an article by A. E. Greendale and D. L. Love. The main decontamination process is the formation of stibine,  $\text{SbH}_3$ , and the collection of this volatile compound in a  $\text{Br}_2$ -HCl solution. A  $\text{TeS}_2$  scavenger is then performed and the antimony is reduced to the elemental state for counting and chemical yield purposes.

The procedure requires  $\sim 15$  min per sample and gives chemical yields of 40 to 60%. Decontamination factors of at least  $10^5$  are obtained from  $^{235}\text{U}$  thermal-neutron fission products.

### 2. Reagents

Antimony carrier: 10 mg antimony/ml, added as  $\text{SbCl}_3$  in 6M HCl. The solution is standardized by precipitation of antimony metal with  $\sim 1.6M$   $\text{CrCl}_2$  (ANTIMONY I procedure)

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{H}_4\text{TeO}_6$  in 6M HCl

HCl: conc; 6M

$\text{Br}_2$

$\text{NH}_4\text{OH}$ : conc

Drierite ( $\text{CaSO}_4$ )

$\text{N}_2$ : gas

$\text{H}_2\text{S}$ : gas

Zinc: dust

$\text{NH}_2\text{OH}\cdot\text{HCl}$ : solid

Ethanol: absolute

$\text{CrCl}_2$ :  $\sim 1.6M$  aqueous solution

### 3. Procedure

*Step 1.* Assemble the separation apparatus as shown in Fig. 1. Fill the U-tube with Drierite ( $\text{CaSO}_4$ ) and cover each side with glass wool. Place 10 ml of 6M HCl and 10 drops of  $\text{Br}_2$  in each of the traps. Add 20 g of zinc dust to the round-bottomed

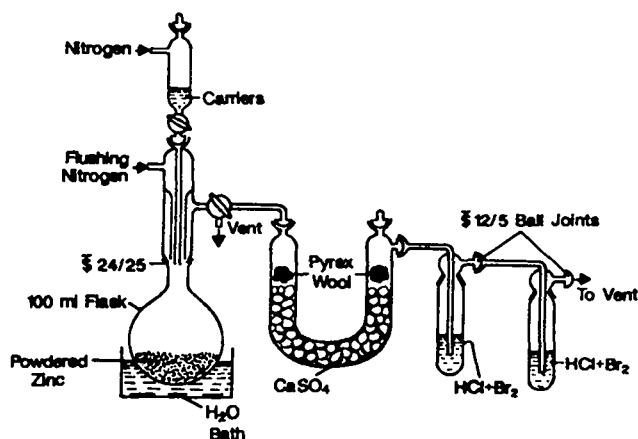


Fig. 1. Separation apparatus.

flask and bring the water bath to a boil. Flush the entire system well with  $\text{N}_2$ .

*Step 2.* Pipette 3.0 ml of standard antimony carrier into the reservoir of the apparatus, add the sample, and make the solution up to a volume of  $\sim 5$  ml with 6M HCl. Drop the solution onto the zinc in one batch, collect the gas ( $\text{SbH}_3$  and  $\text{H}_2$ ) for 10 to 15 s, and then open the vent.

*Step 3.* Transfer the  $\text{Br}_2$ -HCl solutions (Note) to a 40-ml glass centrifuge tube, add 10 mg of Te(VI) carrier, heat in a steam bath for a few min, add 100 mg of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , and saturate with  $\text{H}_2\text{S}$ . Digest in a steam bath until the precipitate has coagulated, and filter through a glass frit of medium porosity into a clean centrifuge tube. Discard the precipitate.

*Step 4.* Add ~4 ml of conc  $\text{NH}_4\text{OH}$  (the resulting solution should be ~2M in HCl), saturate with  $\text{H}_2\text{S}$ , and digest in a steam bath for a few minutes. Filter the  $\text{Sb}_2\text{S}_3$  precipitate onto a glass frit of medium porosity. Wash the  $\text{Sb}_2\text{S}_3$  with  $\text{H}_2\text{O}$ , discontinue suction, and discard the filtrate. Dissolve the  $\text{Sb}_2\text{S}_3$  in 10 ml of conc HCl, start suction, and collect the filtrate in a clean centrifuge tube.

*Step 5.* Heat the filtrate in a steam bath to expel  $\text{H}_2\text{S}$ , add 10 ml of absolute ethanol, mix, and then add 5 ml of ~1.6M  $\text{CrCl}_2$ . Swirl for 15 s and filter the metal precipitate onto a weighed Gelman VF-6 filter paper (0.45- $\mu\text{m}$  pore). Wash the precipitate with a 50/50 mixture of 6M HCl and ethanol, then with  $\text{H}_2\text{O}$ , and finally with ethanol alone. Dry under suction for a few minutes, weigh, and mount.

#### Note

The first  $\text{Br}_2$ -HCl trap generally contains ~90% of the antimony.

#### Reference

A. E. Greendale and D. L. Love, *Anal. Chem.* **35**, 632 (1963).

(October 1989)

## ANTIMONY-127

E. A. Bryant

### 1. Introduction

This simplified procedure permits a relatively rapid analysis for  $^{127}\text{Sb}$ . It was developed primarily for samples containing large amounts of zirconium, niobium, uranium, and HF and  $\text{HClO}_4$ . The simplification of the chemistry results from using a Ge(Li) detector to measure  $^{127}\text{Sb}$  and  $^{125}\text{Sb}$  (spike) gamma rays in an imperfectly purified sample. Major interference in the measurements is caused by the  $^{132}\text{I}$  daughter of  $^{132}\text{Te}$ .

The chemical separation consists of a series of  $\text{Sb}_2\text{S}_3$  and  $\text{TeI}_2$  (by-product) precipitations. Exchange with antimony(V) carrier is effected in the presence of aqueous  $\text{Br}_2$  at elevated temperatures. Recovery is measured by means of the  $^{125}\text{Sb}$  tracer-carrier; yields are high.

### 2. Reagents

$^{125}\text{Sb}$  tracer-carrier: sufficient activity for measurement on the available detector + 10 mg antimony(V)/ml, added as  $\text{SbCl}_5$  in dilute HCl.

Molybdenum(VI) carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$

Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 12M HCl

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{H}_4\text{TeO}_6$  in 3M HCl

HCl: conc

HI: conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{H}_2\text{S}$ : gas

$\text{Br}_2\text{-H}_2\text{O}$ : saturated solution

### 3. Procedure

*Step 1.* Pipette 1 ml of  $^{125}\text{Sb}$  tracer-carrier solution into a 40-ml glass centrifuge tube. Add 10 ml of saturated  $\text{H}_3\text{BO}_3$  and 1 ml of  $\text{Br}_2\text{-H}_2\text{O}$ , then pipette the sample into the tube. Stir the solution and place the tube on a steam bath for a minimum of 2 h, but < 4 h. (Prolonged standing results in precipitation of  $\text{Nb}_2\text{O}_5$ , which carries down antimony.)

*Step 2.* Dilute by a factor of 2 with  $\text{H}_2\text{O}$  and saturate with  $\text{H}_2\text{S}$ . (If an orange precipitate of  $\text{Sb}_2\text{S}_3$  does not form, it will be necessary to dilute the solution further and to use more  $\text{H}_3\text{BO}_3$  to remove  $\text{F}^-$  ion still in solution.) Warm the mixture and set it aside for 20 min. Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in 5 ml of conc HCl and boil for 30 s. Add 2 drops each of tellurium(IV) and molybdenum(VI) carriers and boil for 20 s. Dilute to 20 ml with  $\text{H}_2\text{O}$  and saturate with  $\text{H}_2\text{S}$ . Warm, set aside for 20 min, centrifuge, and discard supernate.

*Step 4.* Add 5 ml of conc HCl to the precipitate, warm, and stir. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate of  $\text{MoS}_3$  and  $\text{TeS}_2$ . Boil the supernate for 30 s.

*Step 5.* Add 5 ml of  $\text{H}_2\text{O}$  and 2 ml of conc HI and boil for 30 s. Add 2 drops of tellurium(IV) carrier, boil, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the  $\text{TeI}_2$  precipitate. Add 2 drops of tellurium(VI) carrier and bring the solution to a boil. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the  $\text{TeI}_2$  precipitate.

*Step 6.* Dilute to 20 ml with  $\text{H}_2\text{O}$ , saturate with  $\text{H}_2\text{S}$ , and warm gently. Centrifuge and discard the supernate. Dissolve the precipitate in 3 ml of conc HCl and centrifuge; discard any insoluble residue.

*Step 7.* Pour the solution into a convenient container for counting. Take a preliminary measurement of the activity to determine whether there has been adequate decontamination. The number of counts in the 228-keV  $^{132}\text{Te}$  full-energy peak should be no > 50 times larger than the counts in the 473-keV  $^{127}\text{Sb}$  full-energy peak. If this ratio is exceeded, repeat *Steps 5* and *6*. When adequate decontamination has been attained, measure the  $^{125}\text{Sb}$  activity by means of its 176-, 428-, 464-, and 635-keV gamma rays and that of  $^{127}\text{Sb}$  by means of its 473-, 685-, and 783-keV gamma rays.

(October 1989)



# BISMUTH I

R. J. Prestwood

## 1. Introduction

In the separation of radiobismuth from other activities, essential steps consist of (a) precipitation of bismuth as  $\text{BiOCl}$ , (b) extraction of  $\text{BiI}_3$  into hexone, (c)  $\text{AgCl}$  scavenging, and (d) precipitation of  $\text{Bi}_2\text{S}_3$  from  $1.5M$   $\text{HCl}$ . The bismuth is finally weighed and mounted as the oxochloride. The chemical yield is  $\sim 65\%$ .

## 2. Reagents

Bismuth carrier: 10 mg bismuth/ml, added as

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in  $1M$   $\text{HCl}$ ; standardized

Rhodium carrier: 10 mg rhodium/ml, added as

$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$  in  $0.01M$   $\text{HCl}$

Ruthenium carrier: 10 mg ruthenium/ml, added

as  $\text{RuCl}_3$  in  $0.01M$   $\text{HCl}$

Silver carrier: 10 mg silver/ml, added as  $\text{AgNO}_3$

in  $\text{H}_2\text{O}$

Tellurium(IV) carrier: 10 mg tellurium/ml, added

as  $\text{Na}_2\text{TeO}_3$  in dilute  $\text{HCl}$

$\text{HCl}$ : conc;  $1M$ ;  $3M$ ;  $6M$ ;

$\text{HClO}_4$ : conc

$\text{NH}_4\text{OH}$ : conc

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ : solid

$\text{NaI}$ : solid

$\text{NaNO}_2$ : solid

$\text{H}_2\text{S}$ : gas

$\text{SO}_2$ : saturated aqueous solution

Hexone (4-methyl-2-pentanone)

Methanol: anhydrous

## 3. Preparation and Standardization of Carrier

Dissolve 23.21 g of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in  $1M$   $\text{HCl}$ , make up to 1 l with the acid, and filter. Pipette 10 ml of the solution into a 250-ml erlenmeyer flask, add 200 ml of boiling  $\text{H}_2\text{O}$ , and digest overnight on a steam bath. Filter into a weighed 15-ml sintered glass crucible of medium porosity. Wash the  $\text{BiOCl}$  precipitate with  $\text{H}_2\text{O}$  and then

with methanol. Dry at  $110^\circ\text{C}$  for 15 min, cool, and weigh.

Four standardizations gave a total spread of 0.2% (Note 1).

## 4. Procedure

*Step 1.* To 2 ml of bismuth and 1 ml of tellurium(IV) carriers in a 125-ml erlenmeyer flask, add an aliquot of the sample. Place on a hot plate and evaporate to dryness. Add 5 ml of conc  $\text{HCl}$  and again evaporate to dryness. (Evaporation is necessary to ensure tellurium exchange and also to remove  $\text{NO}_3^-$ , which inhibits reduction of tellurium to metal.) Add 15 ml of  $3M$   $\text{HCl}$  and  $\sim 100$  mg of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ . Heat to boiling on a hot plate and add saturated aqueous  $\text{SO}_2$  periodically while the solution is boiling until all the tellurium is precipitated as metal and the solution has no blue tinge. (This may take as long as 10 min if  $\text{SO}_2\text{-H}_2\text{O}$  is added at  $\sim 2$ -min intervals.) Filter and collect the filtrate in a 40-ml conical centrifuge tube. Rinse the erlenmeyer flask with hot  $3M$   $\text{HCl}$  containing  $\text{SO}_2\text{-H}_2\text{O}$  and pass the solution through the filter into the centrifuge tube.

*Step 2.* To the filtrate add conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{Bi}(\text{OH})_3$ . Centrifuge and discard the supernate (Note 2).

*Step 3.* To the precipitate add 10 drops of  $6M$   $\text{HCl}$  and 5 drops of rhodium carrier; stir to dissolve. Wash the sides of the centrifuge tube with 2 to 4 ml of  $\text{H}_2\text{O}$  and heat on a steam bath. (The solution at this point should be clear.) Add 30 ml of boiling  $\text{H}_2\text{O}$  and digest for 5 min. Centrifuge the  $\text{BiOCl}$  precipitate and discard the supernate.

*Step 4.* To the precipitate add 2 ml of conc  $\text{HClO}_4$  and 5 drops of ruthenium carrier, and with vigorous stirring heat to fumes. Fume until all the  $\text{RuO}_4$  has been volatilized and then allow the solution to cool.

*Step 5.* Add 10 drops of silver carrier, dilute to 20 ml with H<sub>2</sub>O, and then add 2 ml of 6M HCl with vigorous stirring. Centrifuge and transfer the supernate to a clean centrifuge tube containing 5 ml of conc NH<sub>4</sub>OH. Centrifuge and discard the supernate.

*Step 6.* Add 5 ml of 6M HCl to the Bi(OH)<sub>3</sub> precipitate and transfer the solution to a 60-ml separatory funnel. Wash the centrifuge tube with 10 ml of 6M HCl and add the washings to the separatory funnel. Add 15 ml of hexone and shake vigorously. Drain the H<sub>2</sub>O layer into a clean separatory funnel. Add 10 ml of hexone and 1 to 2 g of solid NaI, shake, and discard the H<sub>2</sub>O layer. Add 10 ml of 6M HCl (containing ~1 g of NaI) to the hexone layer. Shake and discard the H<sub>2</sub>O layer. To the hexone phase add 10 ml of 6M HCl and ~0.5 g of solid NaNO<sub>2</sub> and swirl. Place the stopper in the separatory funnel and shake vigorously. (At this point the aqueous layer is essentially colorless and the hexone phase may be slightly yellow.) Drain the H<sub>2</sub>O layer into a clean 40-ml centrifuge tube containing 5 ml of conc NH<sub>4</sub>OH. Centrifuge and discard the supernate.

*Step 7.* To the Bi(OH)<sub>3</sub> precipitate add 10 ml of 3M HCl and 10 ml of H<sub>2</sub>O. Place on a steam bath and saturate with H<sub>2</sub>S for at least 2 min. Centrifuge and discard the supernate. Dissolve the Bi<sub>2</sub>S<sub>3</sub> precipitate by boiling in 5 ml of 6M HCl.

*Step 8.* Precipitate Bi(OH)<sub>3</sub> as in *Step 2*.

*Step 9.* Repeat *Steps 3, 4, and 5*.

*Step 10.* Transfer the Bi(OH)<sub>3</sub> precipitate with 15 ml of 6M HCl to a 60-ml separatory funnel. Add 10 ml of hexone and 1 to 2 g of solid NaI, shake, and discard the H<sub>2</sub>O layer. Add 10 ml of 6M HCl containing ~1 g of NaI to the hexone layer. Shake and discard the H<sub>2</sub>O layer. To the hexone phase add 10 ml of 6M HCl and ~0.5 g of solid NaNO<sub>2</sub> and swirl. Place the stopper in the separatory funnel and shake vigorously. Drain the H<sub>2</sub>O layer into a clean 40-ml centrifuge tube

containing 5 ml of conc NH<sub>4</sub>OH. Centrifuge and discard the supernate.

*Step 11.* Repeat *Step 7*.

*Step 12.* Repeat *Step 2* and then *3*, the latter in the absence of rhodium holdback carrier.

*Step 13.* Filter the BiOCl onto a weighed filter circle. Wash the precipitate with H<sub>2</sub>O and then with methanol. Dry at 110°C for 5 min, cool for 20 min, weigh, and mount for counting.

## Notes

1. The weight of Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O employed in the standardization corresponded (by calculation) to 10.0 mg of bismuth/ml, whereas the actual standardization as BiOCl showed 10.1 mg bismuth/ml.

2. If large quantities of lead activities are present in the sample at this stage of the procedure, they may be removed by using the following extremely effective process. To the Bi(OH)<sub>3</sub> precipitate add 5 drops of lead carrier and 2 ml of 12M NaOH; boil with vigorous stirring. Add 20 ml of H<sub>2</sub>O and continue boiling for 3 to 5 min. Centrifuge and discard the supernate, which contains the lead as plumbite.

(October 1989)

## BISMUTH II

A. J. Gancarz

### 1. Introduction

This procedure has been used to separate 1 to 20  $\mu\text{g}$  of bismuth from up to 25 g of underground nuclear debris. The separation process prepares  $^{205}\text{Bi}$ ,  $^{206}\text{Bi}$ ,  $^{207}\text{Bi}$ (?), and  $^{210}\text{Bi}$  for radiochemical determination and  $^{207}\text{Bi}$  and  $^{208}\text{Bi}$  for mass spectrometric analysis. The procedure is carrier-free.

The major steps include (1) extraction of bismuth into tri-*n*-octylamine from a medium that is 0.1M in each  $\text{H}_2\text{SO}_4$  and KBr, (2) back-extraction with 0.5M  $\text{HClO}_4$ , (3) adsorption of the element on a cation-exchange resin column, (4) elution from the resin by means of 1M HCl, (5) adsorption as a chloro complex on an anion-exchange resin column, and (6) elution with 2M HF. After a portion of the eluate is taken for radiochemical analysis, the remainder is prepared for mass spectrometric analysis by converting the bismuth to the nitrate and electroplating the metal onto a rhenium cathode.

### 2. Reagents

$\text{H}_2\text{SO}_4$ : 0.1M; conc

HCl: 0.01M; 0.15M; 1.5M; 7M; conc

$\text{HClO}_4$ : 0.5M

$\text{HNO}_3$ : 0.1M, 4M

HF: 2M

KBr: solid

$\text{H}_2\text{SO}_4$ -KBr solution: 0.1M in each

Tri-*n*-octylamine reagent: 0.005M in cyclohexane  
Dowex AG 1-X8 anion-exchange resin: 100 to 200 mesh; stored in 4M HCl

Dowex AG 50W-X8 cation-exchange resin: 100 to 200 mesh; stored in 1M HCl

### 3. Procedure

*Step 1.* Mix 200 ml of tri-*n*-octylamine solution with 200 ml of the 0.1M  $\text{H}_2\text{SO}_4$ -0.1M KBr solution in a separatory funnel. Shake the mixture for 2 min, permit the phases to separate, and discard the aqueous (lower) phase.

*Step 2.* Add conc  $\text{H}_2\text{SO}_4$  to a sample of  $\sim 5$  g of the debris in 3M HCl and fume to dryness. Dissolve the residue in 0.1M  $\text{H}_2\text{SO}_4$  and, by appropriate addition of solid KBr and 0.1M  $\text{H}_2\text{SO}_4$ , make up 1 l of sample solution that is 0.1M in each acid and salt. Warm the solution to  $\sim 35^\circ\text{C}$ .

*Step 3.* To the solution of sample, add 100 ml of the tri-*n*-octylamine reagent prepared in *Step 1* and shake the mixture for 5 min. Remove the aqueous phase and save the organic phase. Add another 100 ml of amine solution to the aqueous phase and shake the mixture for 5 min. Remove the aqueous layer and combine the amine phases. Wash the combined organic phases with 200 ml of 0.1M  $\text{H}_2\text{SO}_4$ -0.1M KBr solution and discard the washes.

*Step 4.* To the amine solution (now containing the bismuth), add 100 ml of 0.5M  $\text{HClO}_4$ , shake the mixture for 2 min, and remove the aqueous phase. Repeat the extraction with  $\text{HClO}_4$  twice more and combine the aqueous phases into which the bismuth has been extracted.

*Step 5.* Fill a Pyrex column (0.5-cm i.d., 15-cm length, and equipped with a bulb of 25-cm<sup>3</sup> capacity at the top and a sintered glass disk of medium porosity near the bottom) with 10 cm of Dowex AG 50W-X8, 100 to 200 mesh, cation-exchange resin. Condition the column first with 10 ml of 7M HCl and then with 10 ml of 0.5M  $\text{HClO}_4$ . Pass the combined aqueous phases from *Step 4* through the column. Wash the column with 5 ml of 0.01M HCl. (For tantalum-rich samples, wash with 10 or 15 ml of 0.01M HCl to remove that element.) Wash the tip of the column with  $\text{H}_2\text{O}$  and elute the bismuth with 10 ml of 1M HCl. Evaporate the eluate to dryness.

*Step 6.* Load a Teflon column (2.5-mm i.d., 15-cm length, and equipped with a Teflon hub and a Teflon wool plug) with 4 cm of Dowex AG 1-X8, 100 to 200 mesh, anion-exchange resin. Wash the column with 1 ml of conc HCl and then with one column volume of 1.5M HCl. Dissolve the residue from *Step 5* in 0.5 ml of 1.5M HCl; load onto the column; and wash with five column volumes of 0.15M HCl, eight column volumes of 7M HCl, and five column volumes of 4M HNO<sub>3</sub>. Wash the tip of the column with H<sub>2</sub>O.

*Step 7.* Elute the bismuth with 10 column volumes of 2M HF and remove an aliquot of eluate for radiochemical analysis.

*Step 8.* Evaporate the remaining eluate to near dryness, add HNO<sub>3</sub>, and evaporate to dryness. Dissolve the residue in 0.1M HNO<sub>3</sub> and add it to a plating cell that has a rhenium filament as the cathode and a platinum wire as the anode. Plate out the bismuth on the rhenium at a current of 2.8 A for 1 h. Any lead present is deposited as PbO<sub>2</sub> on the anode.

(October 1989)

## BISMUTH III

A. J. Gancarz, K. W. Thomas,  
and D. B. Curtis

### 1. Introduction

This carrier-free procedure is designed for the separation of bismuth from as much as 100 g of nuclear debris. The various bismuth isotopes are finally determined by Ge(Li) counting and mass spectrometry.

The following are the major steps in the analysis. Bismuth is extracted into a solution of tri-*n*-octylamine (TOA) in cyclohexane. It is then back-extracted into 0.5M HClO<sub>4</sub> and the bismuth is adsorbed on a cation-exchange resin column. (Beyond this point, all operations are carried out in a class 100 "clean" laboratory to eliminate contamination by lead. Lead isotopes that are isobaric with bismuth isotopes interfere with mass spectrometric determination of bismuth.) The bismuth is eluted from the cation-exchange resin with 0.5M HCl and, after appropriate treatment, is placed on an anion-exchange resin column. It is eluted from that column with 10M HNO<sub>3</sub> and Ge(Li) counted. An aliquot of the collected sample is placed on another anion-exchange column, from which the bismuth is eluted with 10M HNO<sub>3</sub>. Bismuth, as metal, is then electroplated on a rhenium filament and is used as the source for the mass spectrometer.

### 2. Reagents

#### A. For operations in ordinary laboratory

H<sub>2</sub>SO<sub>4</sub>: conc  
HCl: 7M  
HClO<sub>4</sub>: 0.5M  
H<sub>2</sub>SO<sub>4</sub>-KBr solution: 0.1M in each compound  
KBr: solid  
Tri-*n*-octylamine (TOA) reagent: 0.005M TOA in cyclohexane  
AG 50-X8 cation-exchange resin, 100 to 200 mesh.  
Dimensions of resin bed: 10 cm by 0.5 cm

B. For operations in clean laboratory (these reagents should be of the highest purity; for example, NBS purity).

HNO<sub>3</sub>: 10M; 4M  
HClO<sub>4</sub>: 0.5M  
HCl-HNO<sub>3</sub>: 0.1M in each acid  
HCl: 0.1M; 0.5M; 8M  
AG 1-X8 anion-exchange resin, 100 to 200 mesh.  
Resin bed volumes: 0.5 and 0.25 ml

### 3. Procedure

The sample solution should contain no more than several grams of dissolved nuclear debris per liter. The extractions are performed on 1-ℓ aliquots (Note).

*Step 1.* Make the sample solution 0.1M in H<sub>2</sub>SO<sub>4</sub> and 0.1M in KBr and bring it to 35°C in a water bath. Let it stand at this temperature until it is needed in *Step 3*.

*Step 2.* Mix 200 ml of TOA reagent with 200 ml of 0.1M H<sub>2</sub>SO<sub>4</sub>-0.1M KBr solution in a 500-ml separatory funnel. Shake the mixture for 2 min, let the phases separate, and discard the aqueous (lower) phase.

*Step 3.* Pour the sample solution into a 2-ℓ separatory funnel and add 100 ml of the previously equilibrated TOA reagent from *Step 2*. Shake the mixture for 5 min. (Vent the funnel very slowly and carefully before shaking.) Allow the phases to separate and save both of them.

*Step 4.* Transfer the aqueous phase back to the separatory funnel, add the remaining 100 ml of TOA reagent, and repeat the extraction. Discard the aqueous phase and combine the TOA phases in the separatory funnel.

*Step 5.* Add 200 ml of 0.1M H<sub>2</sub>SO<sub>4</sub>-0.1M KBr to the TOA phase and shake the mixture for 2 min. Allow the phases to separate and discard the aqueous phase.

*Step 6.* Add 100 ml of warm ( $\sim 30^{\circ}\text{C}$ ) 0.5M  $\text{HClO}_4$  and shake the mixture for 2 min. Allow the phases to separate and remove and save the aqueous phase.

*Step 7.* Repeat *Step 6* twice and combine the three aqueous phases.

*Step 8.* Prepare the AG 50-X8 cation-exchange resin column. Wash it with 10 ml of 7M HCl followed by 10 ml of 0.5M  $\text{HClO}_4$ .

*Step 9.* Load the combined aqueous phases (*Step 7*) on the column; set the flow rate at 3 to 4 ml/min. Discard the effluent and carry out all succeeding operations in a clean laboratory. Pass no  $>1500$  ml of solution through the column; use two columns if  $>1500$  ml must be processed.

*Step 10.* Wash the resin column(s) with ten 2-ml portions of 0.5M  $\text{HClO}_4$ .

*Step 11.* Elute the bismuth with 6 ml of 0.5M HCl. If two columns were used, combine the eluates.

*Step 12.* Prepare the AG 1-X8 anion-exchange resin column with the 0.5-ml resin bed and wash the column with  $\sim 5$  ml of 8M HCl and then with 1 ml of 0.5M HCl. This column selectively removes cadmium and lead from bismuth.

*Step 13.* Load the eluate from *Step 11* onto the column.

*Step 14.* Rinse the reservoir walls of the column with four 0.5-ml portions of 0.1M HCl and allow the acid to pass through the resin. Rinse the resin column with 3 ml of 0.1M HCl. Discard the rinses.

*Step 15.* Wash the column with 2.5 ml of 4M  $\text{HNO}_3$  and then with 0.5 ml of 10M  $\text{HNO}_3$ .

*Step 16.* Elute the bismuth with 5 ml of 10M  $\text{HNO}_3$  and collect the eluate in a counting vial.

*Step 17.* Count the sample on a Ge(Li) detector to determine  $^{205}\text{Bi}$ ,  $^{206}\text{Bi}$ , and  $^{207}\text{Bi}$ .

*Step 18.* Take an aliquot containing an estimated 1 to 2  $\mu\text{g}$  of bismuth from the counted sample and evaporate it to dryness.

*Step 19.* Prepare the AG 1-X8 anion-exchange resin with a 0.25-ml resin bed. (This column further removes lead.)

*Step 20.* Wash the column with 10 ml of 8M HCl and then with 1 ml of 0.1M HCl.

*Step 21.* Dissolve the residue from *Step 18* in 0.250 ml of 0.1M HCl and load the solution on the anion column. Rinse the residue container and the transfer pipette with 0.1M HCl and load the rinse on the anion column.

*Step 22.* Rinse the column reservoir walls with four 0.250-ml portions of 8M HCl and allow the acid to pass through the column. Rinse the column with 1.5 ml of 8M HCl.

*Step 23.* Rinse the resin column with 0.250 ml of 10M  $\text{HNO}_3$ .

*Step 24.* Elute bismuth with 2.5 ml of 10M  $\text{HNO}_3$ ; collect the eluate and evaporate it to dryness.

*Step 25.* Dissolve the residue in 0.10 ml of 0.1M HCl-0.1M  $\text{HNO}_3$ . Electroplate for 1 h at 2.8 V on a rhenium filament, the source for the mass spectrometer. (The rhenium filament is the cathode of the cell, and a platinum wire of NBS purity is the anode.)

*Step 26.* Perform mass spectrometry to determine the relative abundance of  $^{209}\text{Bi}$ ,  $^{208}\text{Bi}$ ,  $^{207}\text{Bi}$ , and  $^{206}\text{Bi}$ .

## Note

If  $>1$  l of sample is to be processed, the following adjustments to the extraction procedure may be made. (1) Follow the procedure through *Step 4*. Then go back to *Step 1* and process a second liter of sample. (2) Combine the TOA fractions from both 1-l aliquots of sample and wash them as in *Step 5*, except use 400 ml of wash solution. Then use 200-ml portions of 0.5M HClO<sub>4</sub> in *Steps 6* and *7*. (3) Continue processing 2-l aliquots of the sample solution as just described until finished. (4) Combine all the 0.5M HClO<sub>4</sub> fractions and proceed with the cation exchange, *Step 8*.

(October 1989)

# SEPARATION OF CARRIER-FREE BISMUTH FROM LEAD, IRON, AND URANIUM

R. J. Prestwood

## 1. Introduction

This procedure was designed to separate microgram (or less) quantities of bismuth from milligram amounts of lead, iron, and uranium in ore samples from the Oklo mine. After separation, the bismuth is determined quantitatively by atomic absorption. A measure of the  $^{209}\text{Bi}$  content of the ore is important because the isotope is the final decay product of  $^{237}\text{Np}$ .

The procedure was developed from information given by O. Samuelson. The bismuth, in solution in a minimum of conc HCl, is placed on an anion-exchange resin column. The column is then treated with the same acid to remove lead. Next, iron and uranium are eluted with  $0.5M$  HCl, and finally bismuth is removed with  $1M$   $\text{H}_2\text{SO}_4$ . This procedure was checked with carrier-free  $^{207}\text{Bi}$  and a chemical yield of 99% was obtained.

## 2. Reagents

HCl: conc;  $0.5M$

$\text{H}_2\text{SO}_4$ :  $1M$

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh. The glass column that holds the resin is made by fusing a 15-ml conical centrifuge tube to an 8-cm length of 1-cm tubing drawn to a tip. A glass wool plug is placed in the tip of the column, which is then filled with 1.75 to 2 in. of resin. Before it is used, wash the resin column with conc HCl.

## 3. Procedure

*Step 1.* Dissolve the ore sample and make up to  $3M$  in HCl so that there are 5 mg of ore/ml of solution. Evaporate 1 to 2 ml of sample solution nearly to dryness, take up in 1 ml of conc HCl, and, using 1 ml of the same acid, transfer the

solution onto the top of the Bio-Rad AG 1-X8 anion-exchange resin column.

*Step 2.* Add successively 2, 2, and 1 ml of conc HCl to the resin column. Lead comes off almost immediately and is essentially removed completely after 4 ml of acid have been added.

*Step 3.* Add three 2-ml portions of  $0.5M$  HCl to the column. This treatment removes the iron and uranium completely.

*Step 4.* Add seven successive 2-ml portions of  $1M$   $\text{H}_2\text{SO}_4$  to the column. Although the first three additions remove no bismuth, it is removed quantitatively by the last four portions of the acid. Collect the last 8 ml of the  $1M$   $\text{H}_2\text{SO}_4$  in a 10-ml volumetric flask and make up to exactly 10 ml with  $\text{H}_2\text{O}$ . Aliquots of this solution are used for the determination of bismuth by atomic absorption.

## Reference

O. Samuelson, *Ion Exchange Separations in Analytical Chemistry* (John Wiley & Sons, Inc., New York, 1963), pp. 407-408.

(October 1989)



## SULFATE

B. P. Bayhurst

### 1. Introduction

In this procedure for the separation of  $\text{SO}_4^{2-}$  ion from fission-product solutions, sulfate is finally precipitated as the barium salt after appropriate decontamination steps. With the use of the procedure, there was no detectable activity in the  $\text{BaSO}_4$  separated from a fission-product solution 6 d old and containing  $3 \times 10^{13}$  fissions. The chemical yield is  $\sim 75\%$ .

### 2. Reagents

$\text{SO}_4^{2-}$  carrier: equivalent to 10 mg  $\text{BaSO}_4/\text{ml}$ ;  
prepared by diluting 2.4 ml of conc  $\text{H}_2\text{SO}_4$  to  
1 l and standardized by conversion to  $\text{BaSO}_4$

Iron carrier: 10 mg iron/ml, added as  
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1M HCl

Zirconium carrier: 10 mg zirconium/ml, added as  
 $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

HCl: conc; 6M; 3M; 0.75M

$\text{NH}_4\text{OH}$ : 1M

NaOH: 0.5M

$\text{BaCl}_2$ : 1M

$\text{K}_2\text{CO}_3$ : 50% solution

Benzidine reagent: prepared by dissolving 5 g of  
benzidine hydrochloride in 40 ml of 1M HCl  
and diluting to 250 ml with 50% ethanol

Acetone

Dowex AG 1-8X, 50 to 100 mesh anion-exchange  
resin; slurry in  $\text{H}_2\text{O}$

### 3. Procedure

*Step 1.* Add the sample (in dilute acid medium) to 3 ml of  $\text{SO}_4^{2-}$  carrier in a 40-ml glass centrifuge tube. Then add 2 ml of 1M  $\text{BaCl}_2$ , centrifuge, and discard the supernate. Wash the  $\text{BaSO}_4$  precipitate with  $\text{H}_2\text{O}$  and discard the washings.

*Step 2.* With the aid of a minimum amount of  $\text{H}_2\text{O}$ , transfer the precipitate to a 125-ml erlenmeyer flask. Add 10 drops of 50%  $\text{K}_2\text{CO}_3$

solution and heat to dryness. Add 20 ml of  $\text{H}_2\text{O}$ , boil, and transfer the mixture to a clean centrifuge tube. Centrifuge and transfer the supernate containing the  $\text{SO}_4^{2-}$  ion to a clean centrifuge tube. (The  $\text{K}_2\text{CO}_3$  treatment should have converted the  $\text{BaSO}_4$  completely to  $\text{BaCO}_3$ . The precipitate should be treated with 6M HCl, and if it does not dissolve completely, the  $\text{K}_2\text{CO}_3$  treatment should be repeated on the remaining  $\text{BaSO}_4$ . The supernate from the second treatment is then combined with that from the first.)

*Step 3.* To the supernate (or combined supernates), carefully add 3M HCl dropwise until the pH of the solution is  $\sim 2.5$ . Add 5 ml of benzidine reagent, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of  $\text{H}_2\text{O}$  and 2 drops of conc HCl, centrifuge, and discard the supernate.

*Step 4.* Dissolve the benzidine sulfate in 5 ml of 0.5M NaOH, add 2 drops each of iron and zirconium carriers, heat, centrifuge, and transfer the supernate to a clean centrifuge tube.

*Step 5.* Repeat the hydroxide scavenging precipitations twice.

*Step 6.* To the supernate from the last precipitation, add 5 ml of acetone and transfer the solution onto a Dowex 1-X8, 50 to 100 mesh, anion-exchange resin column (8-mm diam and 4- to 5-cm length), which has been washed with  $\text{H}_2\text{O}$  and dilute NaOH. Wash the column first with 10 ml of a mixture of equal volumes of acetone and  $\text{H}_2\text{O}$  and then with 10 ml of a mixture of equal volumes of 1M  $\text{NH}_4\text{OH}$  and acetone. Discard both washes. To elute the  $\text{SO}_4^{2-}$  ion from the column, add first 5 ml of 6M HCl and then 10 ml of 0.75M HCl; collect the eluate in a clean centrifuge tube.

*Step 7.* Add 2 ml of 1M  $\text{BaCl}_2$ , precipitate  $\text{BaSO}_4$  as in *Step 1*, and then repeat *Steps 2* and *3*.

*Step 8.* Dissolve the benzidine sulfate precipitate in a mixture of 2 ml of conc HCl and 10 ml of H<sub>2</sub>O. (Warming speeds dissolution.) Add 2 ml of 1M BaCl<sub>2</sub>, centrifuge, and discard the supernate. Wash the precipitate with H<sub>2</sub>O that contains a few drops of BaCl<sub>2</sub> solution and HCl. Centrifuge and discard the wash. Slurry the precipitate in H<sub>2</sub>O and filter through a weighed Millipore (0.8- $\mu$ m) filter. Wash the precipitate with H<sub>2</sub>O and dry in an oven at 100°C. Cool, weigh, and mount.

(October 1989)

# TELLURIUM

E. A. Bryant

## 1. Introduction

This procedure, for the determination of tellurium in fission products, makes use of the difference in behavior between tellurium(IV) and tellurium(VI) in 6M HCl on an anion-exchange resin column. Tellurium in the +4 state is adsorbed on AG 1-X4 resin, eluted with 0.2M HCl, reduced to the metal, and then oxidized to the +6 state with NaBiO<sub>3</sub> in HNO<sub>3</sub>. The bismuthate is removed on an anion-exchange column, and the tellurium(VI) is made 6M in HCl and passed through another column. This last step effectively removes molybdenum(VI), which stays on the column. The tellurium is finally reduced to the elemental state, in which form it is weighed and counted. Chemical yields of ~75% are obtained.

## 2. Reagents

Tellurium carrier: 10 mg tellurium/ml; 10.7 g Na<sub>2</sub>TeO<sub>4</sub>•2H<sub>2</sub>O and 8.7 g Na<sub>2</sub>TeO<sub>3</sub> in 1 l of 4M HCl; standardized

HBr: conc

HCl: conc; 6M; 3M; 0.2M

HNO<sub>3</sub>: conc; 3M

SO<sub>2</sub>: gas

NaBiO<sub>3</sub>: solid

Dowex AG 1-X4 anion-exchange resin column;  
slurry in 6M HCl

Ethanol: absolute

## 3. Preparation and Standardization of Carrier

Pipette exactly 5 ml of carrier solution into a 125-ml erlenmeyer flask, add 3 ml of conc HBr, and boil nearly to dryness. Repeat the addition of HBr and again boil the solution nearly to dryness. Add 50 ml of 3M HCl, saturate the solution with SO<sub>2</sub>, and let it stand for ~20 min. Saturate again with SO<sub>2</sub> and filter the elemental tellurium onto a weighed, fritted filter funnel of fine porosity. Wash

the tellurium first with H<sub>2</sub>O and then with absolute ethanol. Dry in an oven at 110°C, cool, and weigh.

## 4. Procedure

*Step 1.* Add the sample to 3 ml of carrier in a 125-ml erlenmeyer flask. Add 3 ml of conc HBr and boil nearly to dryness. Repeat the HBr treatment twice more and then dissolve the residue in 5 ml of 6M HCl.

*Step 2.* Transfer the solution to the top of a 0.6- by 5-cm Dowex AG 1-X4 50 to 100 mesh anion-exchange resin column that has been washed with 6M HCl. When the solution reaches the resin, wash the erlenmeyer flask with 3 ml of 6M HCl and transfer the washings to the column. Discard the effluents.

*Step 3.* Wash the column with three 5-ml batches of 6M HCl and discard the effluents.

*Step 4.* Wash the column with two 5-ml portions of 0.2M HCl and collect the eluates in a clean 40-ml glass centrifuge tube.

*Step 5.* To the combined eluates add 2 ml of conc HCl and saturate the solution with SO<sub>2</sub>. Let stand for ~20 min, centrifuge, and discard the supernate. Wash the precipitate with 5 ml of H<sub>2</sub>O.

*Step 6.* To the precipitate add 3 drops of conc HNO<sub>3</sub>, warm with stirring, and then add 3 ml of 3M HNO<sub>3</sub>. Add ~50 mg of NaBiO<sub>3</sub>, stir for 1 min, and add another 50 mg of the salt. Set aside for 10 min.

*Step 7.* Transfer the solution to an anion-exchange resin column that was made up as already described but washed with H<sub>2</sub>O rather than with 6M HCl. Wash the centrifuge tube with 1 ml of 3M HNO<sub>3</sub> and add the washings to the column. Wash the column with 5 ml of 0.2M HCl and then with 5 ml of 6M HCl. Collect all effluents in a clean centrifuge tube.

*Step 8.* Add 8 ml of conc HCl to the combined effluents and pass the solution through another anion resin column that has been washed with 6M HCl. When the solution has passed through, wash the column with 5 ml of 6M HCl. Collect the effluents in a clean 125-ml erlenmeyer flask.

*Step 9.* Add 3 ml of conc HBr and boil to dryness. Repeat the HBr treatment twice.

*Step 10.* Dissolve the residue in a minimum of 3M HCl and transfer the solution to a clean centrifuge tube. Saturate with SO<sub>2</sub>, let stand for 10 min, centrifuge, and discard the supernate. Wash the precipitate with H<sub>2</sub>O and discard the washings. Slurry the precipitate in absolute ethanol, filter onto a weighed filter paper, dry at 110°C, cool, weigh, and mount.

(October 1989)

# CHLORINE

W. H. Burgus

## 1. Introduction

In the determination of chlorine in the presence of fission products, considerable decontamination is achieved by  $\text{Fe}(\text{OH})_3$  scavenging and by precipitation of  $\text{AgI}$  from ammoniacal medium. Precipitation of  $\text{AgCl}$  in the presence of the disodium salt of ethylenediamine tetraacetic acid (EDTA) is then performed, primarily to remove chlorine from alkaline earth metal ions but also to separate this element from many other activities. After additional decontamination,  $\text{AgCl}$  is formed and the chlorine is removed as  $\text{HCl}$  by treatment with conc  $\text{H}_2\text{SO}_4$ . Chlorine is finally precipitated as the mercury(I) compound, in which form it is counted. The chemical yield is  $\sim 75\%$ .

## 2. Reagents

$\text{Cl}^-$  ion carrier: 10 mg  $\text{Cl}^-/\text{ml}$ ;  $\text{NaCl}$  is used as a primary standard

$\text{I}^-$  ion carrier: 10 mg  $\text{I}^-/\text{ml}$ , added as  $\text{KI}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ $\text{ml}$ , added as  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

$\text{HNO}_3$ : conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HCHO}$ : 37% aqueous solution

$\text{NH}_4\text{OH}$ : conc

$\text{KOH}$ : 10M

$\text{AgNO}_3$ : 0.1M

$\text{Hg}_2(\text{NO}_3)_2$ : 0.1M solution in dilute  $\text{HNO}_3$

$\text{KNO}_2$ : solid

EDTA reagent: 8% aqueous solution of the disodium salt of ethylenediamine tetraacetic acid

$\text{CCl}_4$

Ethanol: absolute

## 3. Procedure

*Step 1.* To the solution containing radioactive chlorine and fission products in a 40-ml glass centrifuge tube, add 1.0 ml of standard  $\text{NaCl}$  carrier. Then add 4 to 6 drops of iron carrier and precipitate  $\text{Fe}(\text{OH})_3$  by the addition of a slight excess of conc  $\text{NH}_4\text{OH}$ . Centrifuge, transfer the supernate containing  $\text{Cl}^-$  ion to a clean centrifuge tube, and discard the precipitate (Note 1).

*Step 2.* To the supernate add 5 ml of conc  $\text{NH}_4\text{OH}$  and 4 drops of  $\text{KI}$  carrier solution. Precipitate  $\text{AgI}$  by the addition of a slight excess of 0.1M  $\text{AgNO}_3$  solution. Coagulate the precipitate by heating, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 3.* To the supernate again add 4 drops of  $\text{KI}$  carrier and remove a  $\text{AgI}$  by-product precipitate as in the previous step. This time, however, filter the supernate through filter paper in a 2-in.  $60^\circ$  funnel to ensure complete removal of  $\text{AgI}$ .

*Step 4.* To the filtrate add 5 ml of EDTA reagent and slowly acidify with conc  $\text{HNO}_3$  to precipitate  $\text{AgCl}$ . Boil to coagulate the precipitate, centrifuge, and wash the  $\text{AgCl}$  with 30 to 40 ml of  $\text{H}_2\text{O}$  containing 2 drops of conc  $\text{HNO}_3$ . Discard the supernate and washings.

*Step 5.* Dissolve the  $\text{AgCl}$  precipitate in 3 ml of conc  $\text{NH}_4\text{OH}$ , add 5 ml of EDTA reagent, dilute to 30 ml, and reprecipitate  $\text{AgCl}$  by the addition of conc  $\text{HNO}_3$ . Boil to coagulate the  $\text{AgCl}$  and wash as in the previous step.

*Step 6.* Dissolve the  $\text{AgCl}$  in 40 drops of conc  $\text{NH}_4\text{OH}$ ; add 15 ml of  $\text{H}_2\text{O}$ , 10 drops of 10M  $\text{KOH}$ , and 10 drops of 37%  $\text{HCHO}$ . Heat to boiling to coagulate the metallic silver precipitate. Add 4 drops of 0.1M  $\text{AgNO}_3$  and again remove a silver precipitate. Filter both silver precipitates together through filter paper in a 2-in.  $60^\circ$  funnel, and collect the filtrate in a 125-ml erlenmeyer flask.

*Step 7.* Acidify the filtrate with conc  $\text{HNO}_3$ , add an additional 2 ml of the acid, and heat to boiling (Note 2). Cool and add 4 drops of KI carrier solution. Transfer to a 125-ml separatory funnel, add 50 ml of  $\text{CCl}_4$ , and a few crystals of  $\text{KNO}_2$ . Extract  $\text{I}_2$  into the  $\text{CCl}_4$  layer and discard. Add three separate additional 10-ml portions of  $\text{CCl}_4$ , extract  $\text{I}_2$ , and discard the  $\text{CCl}_4$  layer after each extraction.

*Step 8.* To the remaining aqueous layer add 2 to 3 ml of conc  $\text{HNO}_3$ , transfer to a 40-ml glass centrifuge tube, and heat to boiling to remove excess  $\text{NO}_2^-$  ion. Add 4 drops of iron carrier and precipitate  $\text{Fe}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ . Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 9.* Again add 4 drops of iron carrier and remove a  $\text{Fe}(\text{OH})_3$  scavenger precipitate as in the previous step.

*Step 10.* To the  $\text{Cl}^-$ -containing supernate add 0.1M  $\text{AgNO}_3$  to precipitate  $\text{AgCl}$ . Centrifuge and wash the precipitate as in *Step 4*.

*Step 11.* Dissolve the  $\text{AgCl}$  precipitate in 2 ml of conc  $\text{NH}_4\text{OH}$ . Wash with several milliliters of  $\text{H}_2\text{O}$  into a special distilling flask (see GERMANIUM procedure). Bubble air through the solution to remove most of the  $\text{NH}_4\text{OH}$ . Cautiously add 6 ml of conc  $\text{H}_2\text{SO}_4$  (Note 3) and heat until all the  $\text{HCl}$  has distilled over into a 50-ml beaker containing 20 ml of  $\text{H}_2\text{O}$ .

*Step 12.* After adding 1 to 2 ml of conc  $\text{HNO}_3$ , precipitate  $\text{Hg}_2\text{Cl}_2$  from the solution of  $\text{HCl}$  distillate by the dropwise addition of 0.1M  $\text{Hg}_2(\text{NO}_3)_2$  solution. Wash the precipitate with  $\text{H}_2\text{O}$  after filtering on a weighed filter circle. Wash with absolute ethanol and dry in an oven for 20 min at  $110^\circ\text{C}$ . Cool, weigh, mount, and count (Note 4).

## Notes

1. If the radiochlorine is originally in a form other than  $\text{Cl}^-$  ion or  $\text{Cl}_2$ , care must be taken to reduce it to one of these forms before beginning the procedure. Otherwise the radiochlorine may be lost as a result of its failure to exchange with  $\text{Cl}^-$  carrier. The total volume in *Step 1* should not exceed 20 ml.

2. Boiling is necessary at this stage to remove most of the volatile  $\text{HCHO}$ .

3. Addition of conc  $\text{H}_2\text{SO}_4$  precipitates  $\text{Ag}_2\text{SO}_4$ . During distillation continue bubbling air through the solution.

4.  $\text{Hg}_2\text{Cl}_2$  is used as the compound mounted in preference to  $\text{AgCl}$  because it does not form agglomerates as  $\text{AgCl}$  does.  $\text{PbCl}_2$  is too soluble and therefore not suitable. For counting  $4 \times 10^5$ -y  $^{36}\text{Cl}$ , a self-absorption curve should be constructed and corrections applied for a 0.72-MeV  $\beta^-$ .

(October 1989)

## ZIRCONIUM-95 AND ZIRCONIUM-97

C. W. Stanley, G. P. Ford, and E. J. Lang

### 1. Introduction

In the procedure described below, exchange between carrier and  $^{95}\text{Zr}$  and  $^{97}\text{Zr}$  is effected by formation of the fluorozirconate complex  $[\text{ZrF}_6]^{2-}$ . Lanthanide and alkaline-earth activities are removed by  $\text{LaF}_3$  scavenging, and then zirconium is separated by three  $\text{Ba}[\text{ZrF}_6]$  precipitations. Zirconium is finally precipitated with mandelic acid from  $\text{HCl}$  medium and ignited to the oxide,  $\text{ZrO}_2$ , in which form it is weighed and counted. The chemical yield is  $\sim 75\%$ .

The procedure may be used either to assay for  $^{95}\text{Zr}$  or  $^{97}\text{Zr}$  separately or to determine them together. To assay for  $^{95}\text{Zr}$ , the chemistry is not begun until the 17-h  $^{97}\text{Zr}$  has decayed. After completion of the chemical procedure, the  $\text{ZrO}_2$  is counted on the top shelf of a beta-proportional counter before too much  $^{95}\text{Nb}$  has grown in. To analyze for  $^{97}\text{Zr}$ , the  $\text{ZrO}_2$  is counted through a 112-mg  $\text{Al}/\text{cm}^2$  absorber.

To determine both  $^{95}\text{Zr}$  and  $^{97}\text{Zr}$  in the sample, the  $\text{ZrO}_2$  is counted on the top shelf of the beta-proportional counter for sufficient time to resolve the decay curve, which has 17-h ( $^{97}\text{Zr}$ ), 35-d ( $^{95}\text{Nb}$ ), and 65-d ( $^{95}\text{Zr}$ ) components. The decay curve may be analyzed by least squares.

### 2. Reagents

Zirconium carrier: 10 mg zirconium/ml, added as

$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$ ; standardized

Lanthanum carrier: 10 mg lanthanum/ml, added

as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Niobium hold-back carrier: solution of  $\text{K}_3\text{Nb}_6\text{O}_{19}$

10 g per 100 ml of solution.

$\text{HCl}$ : 1M; 8M; conc

$\text{HNO}_3$ : 1M; conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HF}$ : conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : solid

$\text{Ba}(\text{NO}_3)_2$ : 50 mg barium/ml

Cupferron: 6% aqueous solution (freshly prepared and kept in refrigerator)

Mandelic acid: 16% aqueous solution

Aerosol: 1% aqueous solution

Ethanol: 95%

### 3. Preparation and Standardization of Carrier

Dissolve 30.0 g of  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  and add sufficient conc  $\text{HNO}_3$  to make the solution 1M in  $\text{HNO}_3$ . Filter and make the filtrate up to 1 l with 1M  $\text{HNO}_3$ .

Pipette 10.0 ml of the solution into a 100-ml beaker, make the solution 2M in  $\text{HCl}$ , and cool in an ice bath. Add a slight excess of 6% cupferron solution and filter. Wash the precipitate with 1M  $\text{HCl}$  containing a little cupferron. (Keep all solutions and the cupferron derivative of zirconium cold.) Transfer the precipitate to a weighed porcelain crucible and ignite for 1 h at 600 to 800°C. Cool and weigh as  $\text{ZrO}_2$ .

### 4. Procedure

*Step 1.* Place the sample in a 50-ml plastic centrifuge tube and add 4.0 ml of zirconium carrier. Adjust to 4 to 5M in  $\text{HNO}_3$  and to a volume of  $\sim 12$  ml (Note 1). Add solid  $\text{NH}_2\text{OH} \cdot \text{HCl}$  so that the solution is 2 to 3% in  $\text{NH}_2\text{OH}$  (Note 2). Add 3 drops of niobium carrier and make the solution 5M in  $\text{HF}$ . Heat for 10 min on a steam bath.

*Step 2.* Add 10 drops of lanthanum carrier and centrifuge for a short time. Add another 10 drops of lanthanum carrier and centrifuge thoroughly. Decant the supernate into another plastic tube and discard the precipitate.

*Step 3.* Repeat *Step 2* twice.

*Step 4.* After a total of six  $\text{LaF}_3$  scavengings, add 1 ml of  $\text{Ba}(\text{NO}_3)_2$  solution per 5 ml of the supernate. Let stand for 1 min and centrifuge. Discard the supernate.

*Step 5.* To the precipitate add 4 ml of saturated  $\text{H}_3\text{BO}_3$  (Note 3) and slurry. Add 2 ml of conc  $\text{HNO}_3$  and slurry again. Add 10 to 12 ml of  $\text{H}_2\text{O}$  and mix well. If the precipitate does not dissolve completely, centrifuge and decant the supernate into another plastic tube. (This step is made easier by heating the  $\text{H}_3\text{BO}_3$ , the  $\text{HNO}_3$ , and the  $\text{H}_2\text{O}$  on a steam bath before they are used.)

*Step 6.* Precipitate  $\text{Ba}[\text{ZrF}_6]$  by the addition of 2 ml of  $\text{Ba}(\text{NO}_3)_2$  solution and 2 ml of conc HF. Centrifuge and dissolve as in *Step 5*.

*Step 7.* Precipitate  $\text{Ba}[\text{ZrF}_6]$  as in *Step 6*, and dissolve the precipitate in 4 ml of saturated  $\text{H}_3\text{BO}_3$ , 4 ml of conc HCl, and 10 ml of  $\text{H}_2\text{O}$ . Add 3 drops of conc  $\text{H}_2\text{SO}_4$  diluted with 5 ml of  $\text{H}_2\text{O}$  and let stand for 15 min. Add 1 to 2 drops of aerosol solution and centrifuge. Transfer the supernate to a 40-ml glass centrifuge tube and discard the  $\text{BaSO}_4$  precipitate.

*Step 8.* To the supernate add conc  $\text{NH}_4\text{OH}$  until the solution is alkaline. Centrifuge down the  $\text{Zr}(\text{OH})_4$  and discard the supernate. Dissolve the precipitate in 2 ml of conc HCl, 4 ml of saturated  $\text{H}_3\text{BO}_3$ , and 10 ml of  $\text{H}_2\text{O}$ . Centrifuge and, if a precipitate forms, transfer the supernate to a 40-ml centrifuge tube; discard the precipitate. Reprecipitate  $\text{Zr}(\text{OH})_4$  with conc  $\text{NH}_4\text{OH}$ . Centrifuge and dissolve the precipitate in 15 ml of 8M HCl. Heat to boiling, add 10 ml of 16% mandelic acid, and again bring to a boil. Wait 2 to 3 min, centrifuge, and discard the supernate. Dissolve the zirconium mandelate in 20 ml of  $\text{H}_2\text{O}$  and 8 drops of conc  $\text{NH}_4\text{OH}$ . (The dissolution of the precipitate takes 2 to 3 min and may be hastened by the addition of another 1 to 2 drops of  $\text{NH}_4\text{OH}$ .) Add 3 ml of conc HCl, heat to boiling, and add 10 ml of 16% mandelic acid. Again bring to a boil, wait 2 to 3 min, centrifuge, and discard the supernate.

*Step 9.* Slurry the precipitate with 10 ml of ethanol and filter onto a filter circle. Transfer the paper and precipitate to a porcelain crucible and ignite for 1 h at  $800^\circ\text{C}$ . Powder the  $\text{ZrO}_2$  with the fire-polished end of a stirring rod. Add 2 drops of ethanol, slurry, and grind again. Add 10 ml of ethanol, stir, and filter onto a washed, dried, and weighed filter circle. Wash the  $\text{ZrO}_2$  with 5 ml of ethanol. Dry at  $110^\circ\text{C}$  for 10 to 15 min, cool, weigh, mount, and count.

## Notes

1. When this volume of solution is used, the chemical yield is good because the loss of zirconium with the  $\text{LaF}_3$  scavengings is small.

2.  $\text{NH}_2\text{OH}$  reduces neptunium(VI) and plutonium(VI) so that they will be carried on the  $\text{LaF}_3$  and thus not interfere in the zirconium separation.  $\text{NH}_2\text{OH}$  may decompose on the addition of HF, which causes the solution to effervesce.

3.  $\text{H}_3\text{BO}_3$  removes  $\text{F}^-$  ion by conversion to  $\text{BF}_4^-$ , and thus aids in the dissolution of  $\text{Ba}[\text{ZrF}_6]$  by  $\text{HNO}_3$ .

(October 1989)



## ZIRCONIUM

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and W. A. Sedlacek

### 1. Introduction

This procedure originally was devised for the determination of zirconium in large (up to 300-g) amounts of dissolved nuclear debris. The various steps in the analysis are given below in Sec. 4.A. Zirconium is first extracted from a solution 6M in HCl into HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. It is then back-extracted into aqueous solution as a fluorocomplex and, following other decontamination steps, the zirconium is finally precipitated as the hydroxide. This material can either be ignited to ZrO<sub>2</sub> or milked for daughter products. The chemical yield is ~65%.

Section 4.B contains a version of the procedure that is quite satisfactory for samples that do not contain large amounts of metal ion impurities. The chemical yield is over 80%.

### 2. Reagents

Zirconium carrier: ~20 mg ZrO<sub>2</sub>/ml, added as ZrOCl<sub>2</sub>•8H<sub>2</sub>O in H<sub>2</sub>O; standardized

Lanthanum carrier: 10 mg lanthanum/ml, added as La(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O in H<sub>2</sub>O

Yttrium carrier: 10 mg yttrium/ml, prepared by dissolving Y<sub>2</sub>O<sub>3</sub> in dilute HCl

Scandium carrier: 10 mg scandium/ml, added as ScCl<sub>3</sub> in 1M HCl

HNO<sub>3</sub>: conc

HCl: conc; 6M

H<sub>2</sub>SO<sub>4</sub>: conc

HNO<sub>3</sub>-HF solution: 4M in HNO<sub>3</sub> and 2.5M in HF

NH<sub>4</sub>OH: conc

NH<sub>4</sub>HF<sub>2</sub> solution: 4M in NH<sub>4</sub>HF<sub>2</sub> and 1M in HF

NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>: 1.5M aqueous solution

HDEHP solution: 0.5M solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane

BaCl<sub>2</sub>: 1M aqueous solution

Methyl red indicator solution

Ethanol: absolute

### 3. Preparation and Standardization of Carrier

Dissolve 52.31 g of ZrOCl<sub>2</sub>•8H<sub>2</sub>O in H<sub>2</sub>O and dilute to 1 ℓ with 0.1M HCl. Pipette 5.0 ml of the carrier solution into an ignited and weighed porcelain crucible and carefully evaporate to dryness on a hot plate. Ignite at 900°C for 30 min. Cool and weigh as ZrO<sub>2</sub>.

### 4. Procedure

#### A. For Large Amounts of Dissolved Debris

*Step 1.* For 25 g or more of debris, no zirconium carrier is added. (The natural zirconium content of the debris usually is appreciable—~100 to 200 ppm. If the chemical yield of zirconium is needed, other similar samples are analyzed quantitatively for the element.) Transfer the sample in 6M HCl to an extraction vessel of appropriate size and add 50 ml of 0.5M HDEHP solution in *n*-heptane. (If the sample volume is too large for a single extraction, batch-extract with repeated use of the same HDEHP solution.) Extract by vigorous stirring or shaking for ~5 min. Allow the layers to separate, and discard the aqueous (lower) layer. Wash the heptane layer three times with 100-ml portions of 6M HCl and discard the washes.

*Step 2.* Transfer the heptane layer to a 4-oz. plastic bottle fitted with a tight cap and add 20 ml of a solution that is 4M in HNO<sub>3</sub> and 2.5M in HF. Add 2 drops of methyl red indicator solution to help distinguish the aqueous from the organic layer. Place on a mechanical shaker and shake for 5 to 10 min. The zirconium is now in the aqueous layer as a fluorocomplex. Use a syringe attached to a plastic pipette to transfer the aqueous layer to a 40-ml plastic centrifuge tube and discard the heptane layer.

*Step 3.* To the aqueous layer, add 4 drops of lanthanum carrier, centrifuge, and transfer the supernate to a clean plastic centrifuge tube. Repeat

the  $\text{LaF}_3$  scavenge four times; after each scavenge transfer the supernate to a clean plastic tube.

*Step 4.* Place the sample on a steam bath, add 1 ml of 1M  $\text{BaCl}_2$ , and heat for a few minutes. Centrifuge and discard the supernate. To the  $\text{Ba}[\text{ZrF}_6]$  precipitate, add 1 to 2 ml of conc  $\text{H}_2\text{SO}_4$ , stir, and place on a steam bath for a few minutes. Dilute to 20 ml with  $\text{H}_2\text{O}$  and allow to stand until  $\text{BaSO}_4$  precipitates. Centrifuge, transfer the supernate to a 40-ml glass centrifuge tube and discard the precipitate.

*Step 5.* To the supernate, add 2 drops of methyl red indicator solution; neutralize with conc  $\text{NH}_4\text{OH}$  and add 4 to 5 drops in excess. Place on a steam bath for 2 min, centrifuge, and discard the supernate.

*Step 6.* Dissolve the  $\text{Zr}(\text{OH})_4$  precipitate in 10 drops of conc  $\text{HCl}$  and dilute to 20 ml with  $\text{H}_2\text{O}$ . (At this point there may be a small amount of  $\text{BaSO}_4$  present; remove it by centrifugation after the  $\text{Zr}(\text{OH})_4$  has dissolved completely.) To the solution containing the zirconium, add an excess of conc  $\text{NH}_4\text{OH}$ , centrifuge, and discard the supernate. The  $\text{Zr}(\text{OH})_4$  precipitate may be used for milking experiments or may be converted to  $\text{ZrO}_2$  for counting as described below.

*Step 7.* Dissolve the  $\text{Zr}(\text{OH})_4$  in conc  $\text{HCl}$ , add 5 ml of filter paper pulp slurry, make ammoniacal with conc  $\text{NH}_4\text{OH}$ , and filter onto a 9-cm filter paper. Transfer to a porcelain crucible and ignite at  $900^\circ\text{C}$  for 5 to 10 min. With a polished stirring rod or the ultrasonic technique, powder the  $\text{ZrO}_2$  and, using absolute ethanol, transfer to a weighed filter circle. Dry at  $110^\circ\text{C}$ , weigh as  $\text{ZrO}_2$ , and count.

## B. For Samples Containing Small Amounts of Metal Ion Impurities

*Step 1.* To the dissolved sample in an erlenmeyer flask of suitable size, add 2.0 ml of zirconium carrier and make the solution  $\sim 4M$  in either  $\text{HNO}_3$  or  $\text{HCl}$ . For each 50 ml of sample

solution add 2 ml of 1.5M  $\text{NH}_4\text{H}_2\text{PO}_4$  solution. Heat until the  $\text{Zr}_3(\text{PO}_4)_4$  coagulates, centrifuge portions of the solution in a 40-ml plastic tube, and discard the supernate. (This is an excellent decontamination step, especially for the removal of macro-quantities of iron, aluminum, barium, calcium, and magnesium.)

*Step 2.* Add 4 ml of  $\text{NH}_4\text{HF}_2$  to dissolve the  $\text{Zr}_3(\text{PO}_4)_4$ . Add 2 drops each of lanthanum and yttrium carriers, stir vigorously, dilute to 15 ml with  $\text{H}_2\text{O}$ , and neutralize to a methyl red end point with conc  $\text{NH}_4\text{OH}$ . Centrifuge and transfer the supernate to a clean plastic centrifuge tube. Discard the  $\text{LaF}_3\text{-YF}_3$  precipitate.

*Step 3.* Add 2 drops each of lanthanum and yttrium carriers, transfer the supernate to a clean plastic tube, and discard the precipitate.

*Step 4.* Add 1 ml of scandium carrier, 6 to 8 ml of conc  $\text{HCl}$ , and heat on a steam bath until  $\text{ScF}_3$  coagulates. Centrifuge, transfer the supernate to a clean plastic tube, and discard the precipitate.

*Step 5.* Add 1.5 ml of 1M  $\text{BaCl}_2$ , place on a steam bath until  $\text{Ba}[\text{ZrF}_6]$  coagulates, centrifuge, and discard the supernate.

*Step 6.* Add 2 ml of conc  $\text{H}_2\text{SO}_4$  to the  $\text{Ba}[\text{ZrF}_6]$  precipitate, stir, and place on a steam bath for a few minutes. Dilute to 20 ml with  $\text{H}_2\text{O}$  and let stand until  $\text{BaSO}_4$  precipitates. Centrifuge, transfer the supernate to a clean plastic tube, and discard the precipitate.

*Step 7.* Add 2 drops each of lanthanum and yttrium carriers and an excess of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 8.* Repeat *Step 2* (but use no lanthanum and yttrium carriers) and *Steps 3* through *5*.

*Step 9.* Repeat *Step 6*, but transfer the supernate to a clean 40-ml glass centrifuge

tube. Add conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{Zr}(\text{OH})_4$ , centrifuge, and discard the supernate.

*Step 10.* Dissolve the  $\text{Zr}(\text{OH})_4$  in conc  $\text{HCl}$ , centrifuge out any  $\text{BaSO}_4$ , and reprecipitate  $\text{Zr}(\text{OH})_4$  with conc  $\text{NH}_4\text{OH}$ . The  $\text{Zr}(\text{OH})_4$  may be milked for other experiments or may be converted to  $\text{ZrO}_2$  and counted as described in Sec. 4.A, *Step 7*.

(October 1989)

# SEPARATION OF ZIRCONIUM FROM NUCLEAR DEBRIS

K. W. Thomas and H. L. Smith

## 1. Introduction

This procedure describes the separation of zirconium from nuclear debris samples in the presence and the absence of tantalum carrier. In the former case, zirconium and tantalum carriers are added to a solution of sample and  $^{205}\text{Ta}$  is precipitated as the oxide by heating with conc  $\text{HNO}_3$ . The oxide is discarded. Aluminum, calcium, and magnesium are removed from solution by appropriate treatment with  $\text{NH}_4\text{OH}$  and  $\text{NaOH}$ . The lanthanide elements are then removed by  $\text{LaF}_3$  scavenges and the zirconium is precipitated as  $\text{Ba}[\text{ZrF}_6]$ . The latter step gives some decontamination from niobium. The zirconium is converted to the chloride and is passed through an anion-exchange resin column; niobium is adsorbed on the column. Finally, zirconium is precipitated as the mandelate (additional decontamination from niobium) and is ignited to the oxide. The chemical yield is ~60%.

For the separation of zirconium in the absence of tantalum, the procedure begins with  $\text{LaF}_3$  scavenges and proceeds as described above. The chemical yield is ~75%.

The procedures may be interrupted without harm at the times indicated below.

(a) After tantalum removal in Sec. 3.A.

(b) After adding  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , niobium hold-back carrier, and HF, but before the  $\text{LaF}_3$  scavenge. Interruption at this point permits good exchange for any niobium that grows in (for example, overnight).

(c) After  $\text{LaF}_3$  scavenges.

(d) Once  $\text{Ba}[\text{ZrF}_6]$  precipitations are started, it is best to complete the procedure to obtain

the best zirconium/niobium separation. However, the procedure may be interrupted after the final precipitation of  $\text{Ba}[\text{ZrF}_6]$  has been effected. (The  $\text{Ba}[\text{ZrF}_6]$  precipitates appear to age rapidly and are sometimes difficult to dissolve if they are permitted to stand for several hours.)

## 2. Reagents

Standardized zirconium carrier: 10 mg zirconium/ml, added either as  $\text{ZrO}(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$  or  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  in 1M  $\text{HCl}$  (for standardization see ZIRCONIUM-95 AND ZIRCONIUM-97 procedure)

Tantalum carrier: Prepared by dissolving pure tantalum metal in a solution of equal volumes of HF and  $\text{HNO}_3$ . The final solution is made up so that it contains the equivalent of ~10 to 12 mg of  $\text{Ta}_2\text{O}_5/\text{ml}$  in 0.5M HF/0.5M  $\text{HNO}_3$

Niobium carrier: 10 g of  $\text{K}_8\text{Nb}_6\text{O}_{19}$  in 100 ml of aqueous solution

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Barium carrier: 50 mg barium/ml, added as  $\text{BaCl}_2$  in  $\text{H}_2\text{O}$

HF: conc

$\text{HClO}_4$ : conc

$\text{HNO}_3$ : conc

$\text{HCl}$ : 6M; conc

$\text{HCl-HF}$  solution: 9M in  $\text{HCl}$  and 0.004M in HF

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{H}_2\text{SO}_4$ : conc

$\text{NaOH}$ : 10M

$\text{NH}_4\text{OH}$ : conc

Mandelic acid solutions: 15 g of the racemic acid in 100 ml of  $\text{H}_2\text{O}$ ; 2 g of acid in 100 ml of 1M  $\text{HCl}$ .

$\text{NH}_2\text{OH}\cdot\text{HCl}$ : solid

Ethanol

Dowex AG 1-8X anion-exchange resin, 50 to 100 mesh. Column dimensions: 7-cm length by 0.8-cm i.d.

### 3. Procedure

#### A. In the Presence of Tantalum Carrier

*Step 1.* To a solution of the sample in a 40-ml glass centrifuge tube, add 40 mg of zirconium as standardized carrier, 20 to 30 mg of tantalum carrier, and a few drops of niobium hold-back carrier. Add several milliliters of conc HF and a few drops of HClO<sub>4</sub> to dissolve any tantalum that has precipitated.

*Step 2.* Take the solution to near dryness and transfer it to an erlenmeyer flask with conc HNO<sub>3</sub>. Add conc HNO<sub>3</sub> and take the solution to near dryness (1 to 2 ml) again.

*Step 3.* Transfer the solution to a 40-ml glass centrifuge tube and centrifuge for 15 min (Note 1). Save the supernate.

*Step 4.* Wash the Ta<sub>2</sub>O<sub>5</sub> precipitate with 6M HCl, centrifuge for 15 min, and add the supernate to the previous supernate. Wash the precipitate with H<sub>2</sub>O, centrifuge for 20 to 25 min, and add the wash to the previous supernates.

*Step 5.* Centrifuge the combined supernates for 20 min and transfer to an erlenmeyer flask. Add conc NH<sub>4</sub>OH until precipitation occurs. Centrifuge the precipitate and then dissolve it in 6M HCl.

*Step 6.* Add 10M NaOH until precipitation occurs and then add a few drops in excess. (Aluminum remains in solution.) Centrifuge and dissolve the hydroxide precipitate in 6M HCl.

*Step 7.* Precipitate hydroxides with conc NH<sub>4</sub>OH. Centrifuge and redissolve the precipitate in 6M HCl.

*Step 8.* Repeat *Steps 6* and *7* and transfer the solution to a 40-ml plastic (but not polycarbonate) centrifuge tube.

*Step 9.* Add sufficient 6M HCl to make the volume ~15 ml. Then add a small amount of NH<sub>2</sub>OH•HCl, 3 drops of niobium hold-back carrier, and a minimum of 5 ml of conc HF. Heat on a steam bath for ~30 min to ensure exchange with the niobium carrier.

*Step 10.* Add 0.4 ml of lanthanum carrier, stir, and centrifuge. Add another 0.4 ml of lanthanum carrier, stir, and centrifuge. Transfer the supernate to a clean plastic centrifuge tube.

*Step 11.* Repeat *Step 10* twice.

*Step 12.* To the supernate add 2.2 ml of barium carrier, stir, and let stand for 10 min. Centrifuge and discard the supernate.

*Step 13.* To the Ba[ZrF<sub>6</sub>] precipitate add 2 ml of saturated H<sub>3</sub>BO<sub>3</sub> solution and slurry. Add 2 ml of conc HNO<sub>3</sub>, stir, and heat on a steam bath for 10 to 15 min. Add 12 ml of H<sub>2</sub>O and heat on a steam bath until the solution is clear. Centrifuge and decant the supernate to a clean plastic tube.

*Step 14.* Add 2 ml of barium carrier and 2 ml of conc HF. Stir, let stand for 1 min, centrifuge, and discard the supernate. Dissolve the precipitate in H<sub>3</sub>BO<sub>3</sub> as in the previous step.

*Step 15.* Add 2 ml of barium carrier and 2 ml of conc HF, stir, and let stand for 1 min. Centrifuge and discard the supernate. Dissolve the precipitate in 4 ml of H<sub>3</sub>BO<sub>3</sub> and 4 ml of conc HCl. Add 10 ml of H<sub>2</sub>O.

*Step 16.* Add 3 drops of conc H<sub>2</sub>SO<sub>4</sub>. Stir and let stand for 10 min. Centrifuge and discard the BaSO<sub>4</sub> precipitate.

*Step 17.* Add conc NH<sub>4</sub>OH, stir, centrifuge, and discard the supernate. Wash the precipitate in 5 ml of H<sub>2</sub>O.

*Step 18.* Dissolve the precipitate in 4 ml of 9M HCl-0.004M HF solution and transfer to a pretreated Dowex AG1-8X anion-exchange column, 50 to 100 mesh. Save the effluent. Wash the column with two 5-ml portions of the 9M HCl-0.004M HF solution and combine the three effluents.

*Step 19.* To the combined effluents, add ~10 ml of H<sub>2</sub>O, and precipitate the hydroxide with conc NH<sub>4</sub>OH. Stir, centrifuge, and discard the supernate. Dissolve the precipitate in 10 ml of conc HCl, centrifuge, and decant the solution into a clean 40-ml glass centrifuge tube.

*Step 20.* Add 10 ml of mandelic acid solution (15 g of the racemic acid in 100 ml of H<sub>2</sub>O) to precipitate zirconium mandelate. Add paper pulp and heat the mixture on a steam bath for 45 min; stir every 10 min (Note 2).

*Step 21.* Filter the precipitate on filter paper. Wash the precipitate with a solution of mandelic acid (2 g of the acid in 100 ml of 1M HCl). Record the time of filtration (*t<sub>sep</sub>*). Ignite the zirconium mandelate to the oxide in a porcelain crucible at 900°C for 30 min.

*Step 22.* Transfer the oxide with ethanol to a weighed filter paper (1-in. diam), dry, weigh, and mount. Ge(Li) count if it is too hot for NaI.

## B. In the Absence of Tantalum Carrier

*Step 1.* To the sample in a 40-ml plastic (but not polycarbonate) centrifuge tube, add 4.0 ml of zirconium carrier and enough 6M HCl to make the volume of solution ~15 ml. Add a small amount of NH<sub>2</sub>OH•HCl, 3 drops of niobium hold-back carrier, and a minimum of 5 ml of conc HF. Heat on a steam bath for ~1 h.

*Step 2.* Carry out Steps 10 through 22 of Sec. 3.A.

## Notes

1. The <sup>205</sup>Ta precipitate is extremely fine and requires long, high-speed centrifugation to bring it down. Use glass centrifuge tubes and float them with water in the centrifuge cups.

2. The zirconium mandelate is easier to remove from glass than from plastic centrifuge tubes.

(October 1989)

# NIOBIUM

J. S. Gilmore

## 1. Introduction

In the separation of niobium from other fission activities, zirconium is removed as  $\text{Ba}[\text{ZrF}_6]$ ; any uranium(IV) present, as well as lanthanide activities, is carried down as the fluoride at this stage. Niobium is then converted to its cupferron derivative that is extracted into  $\text{CHCl}_3$ . This step gives an effective separation from uranium(VI). The cupferron complex is destroyed and the niobium precipitated as the hydrous oxide,  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ , by means of  $\text{NH}_3$  water; molybdenum remains in solution as a molybdate. The oxide is dissolved in  $\text{H}_2\text{SO}_4$  and decontamination from tin and antimony is effected by means of a sulfide precipitation. Further decontamination is obtained by additional precipitations of the oxide, extractions of the cupferron derivative, and acid sulfide scavengings. Niobium is finally precipitated as the cupferrate and ignited to the oxide, in which form it is weighed and counted. The chemical yield is 40 to 50%. If the sample solution contains large quantities of uranium, the chemical yields are likely to be low; at present there is no explanation for this fact.

## 2. Reagents

Niobium carrier: 10 mg niobium/ml, added as niobium(V) in oxalic acid solution; standardized

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Copper carrier: 10 mg copper/ml, added as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

HCl: 6M; conc

$\text{HNO}_3$ : 6M; conc

$\text{H}_2\text{SO}_4$ : conc

HF: conc

Tartaric acid: 25% aqueous solution

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{H}_2\text{C}_2\text{O}_4$ : saturated aqueous solution

$\text{NH}_4\text{OH}$ : 6M; conc

$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ : saturated aqueous solution

$\text{NH}_4\text{NO}_3$ : 2% aqueous solution

$\text{BaCl}_2$ : 50 mg/ml

$\text{KClO}_3$ : solid

$\text{H}_2\text{S}$ : gas

Cupferron reagent: 6% aqueous solution (kept refrigerated)

Methyl red indicator solution

Chloroform

## 3. Preparation and Standardization of Carrier

Dissolve 26.0 g of potassium hexaniobate,  $\text{K}_8\text{Nb}_6\text{O}_{19} \cdot 16\text{H}_2\text{O}$ , in ~200 ml of  $\text{H}_2\text{O}$ , heat the solution nearly to boiling, and add 15 ml of conc  $\text{HNO}_3$  slowly with stirring. Continue heating and stirring for 2 to 3 min and centrifuge. Wash the precipitate three times, while centrifuging, with 50 ml of hot 2%  $\text{NH}_4\text{NO}_3$  solution. Add 200 ml of saturated  $\text{H}_2\text{C}_2\text{O}_4$ , and heat with stirring until  $\text{Nb}_2\text{O}_5$  dissolves. Cool and dilute with  $\text{H}_2\text{O}$  to 1 l. Filter the solution if it is not clear.

Pipette exactly 5 ml of the carrier solution into a 100-ml beaker. Add 30 ml of 6M  $\text{HNO}_3$  and ~1 g of  $\text{KClO}_3$  and carefully heat the solution to boiling. Boil gently with occasional stirring for ~5 min. Cool the mixture and add ~15 ml conc  $\text{NH}_4\text{OH}$  with stirring to make the pH value 8 to 10. Filter quantitatively through filter paper, returning the first portion of the filtrate if it is not clear, and wash with hot  $\text{H}_2\text{O}$ . Ignite in a porcelain crucible at ~800°C for 15 to 20 min and weigh as  $\text{Nb}_2\text{O}_5$ .

Four standardizations performed as described above gave results agreeing within 0.5%.

## 4. Procedure

*Step 1.* To exactly 4 ml of niobium carrier in a 40-ml plastic centrifuge tube, add 3 ml of conc HF, 10 ml of the sample in 4M HCl, 1 ml of zirconium carrier, and 4 ml of  $\text{BaCl}_2$  solution (50 mg/ml). Centrifuge the  $\text{Ba}[\text{ZrF}_6]$  precipitate, transfer the supernate to a clean 40-ml plastic tube, and discard the precipitate. Repeat the

Ba[ZrF<sub>6</sub>] precipitation three times; after the third time, transfer the supernate to a 125-ml separatory funnel.

*Step 2.* To the supernate add 30 ml of a saturated H<sub>3</sub>BO<sub>3</sub> to decompose the niobium-fluoride complex and make the solution 1M in HCl. Add 4 ml of cold 6% cupferron reagent and let the mixture stand for 1 min. Extract the niobium-cupferron complex into 20 ml of CHCl<sub>3</sub> and transfer the CHCl<sub>3</sub> layer into a 125-ml erlenmeyer flask.

*Step 3.* To the aqueous phase still in the separatory funnel, add 2 ml of cupferron reagent, extract with 10 ml of CHCl<sub>3</sub>, and combine the extract with the previous one. Wash the aqueous phase with 10 ml of CHCl<sub>3</sub> and combine the washings with the previous extracts.

*Step 4.* Heat the CHCl<sub>3</sub> extract with 3 ml of conc H<sub>2</sub>SO<sub>4</sub> and ~20 ml of HNO<sub>3</sub> to destroy organic matter.

*Step 5.* Transfer the solution to a 40-ml glass centrifuge tube and make the solution alkaline by the addition of conc NH<sub>4</sub>OH. Centrifuge and discard the supernate. Dissolve the precipitate (Nb<sub>2</sub>O<sub>5</sub>•XH<sub>2</sub>O) in 3.3 ml of conc H<sub>2</sub>SO<sub>4</sub> and dilute the solution to 20 ml with H<sub>2</sub>O. Add 1 ml of copper carrier and saturate the solution with H<sub>2</sub>S. Centrifuge and filter into a clean 40-ml centrifuge tube.

*Step 6.* Make the supernate alkaline by adding conc NH<sub>4</sub>OH to precipitate Nb<sub>2</sub>O<sub>5</sub>•XH<sub>2</sub>O. Centrifuge, discard the supernate, and wash the precipitate with a mixture of 5 ml of 6M NH<sub>4</sub>OH, 3 ml of 6M HNO<sub>3</sub>, and 5 ml of H<sub>2</sub>O (Note 1). Dissolve the precipitate by warming in 0.5 ml of 25% tartaric acid solution. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard any residue.

*Step 7.* Add 1 ml of conc HNO<sub>3</sub> to the supernate and heat the mixture on a steam bath for ~15 min. Centrifuge, discard the supernate,

and dissolve the Nb<sub>2</sub>O<sub>5</sub>•XH<sub>2</sub>O precipitate in 1 ml of conc HF and 3 drops of 6M HCl.

*Step 8.* Transfer the solution to a 125-ml separatory funnel, add 10 ml of saturated H<sub>3</sub>BO<sub>3</sub>, and make the solution 1M in HCl. Add 4 ml of cold cupferron reagent and extract the solution with 20 ml of CHCl<sub>3</sub>. Transfer the CHCl<sub>3</sub> layer to a 125-ml erlenmeyer flask.

*Step 9.* Repeat Steps 3, 4, 5, 6, and 7.

*Step 10.* Repeat Steps 8, 9, 4, 5, 6, and 7, but dissolve the Nb<sub>2</sub>O<sub>5</sub>•XH<sub>2</sub>O precipitate formed in Step 7 in 5 ml of saturated (NH<sub>4</sub>)<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> solution and sufficient conc NH<sub>4</sub>OH to make the solution alkaline.

*Step 11.* Cool the solution in an ice bath and add 4 ml of cupferron reagent. Add 6M HCl dropwise to acidify (2 drops past a methyl red end point). Filter the niobium-cupferron complex onto a filter circle. Ignite at 800°C for 15 to 20 min. Cool the Nb<sub>2</sub>O<sub>5</sub>, mount, and beta-count (Note 2).

## Notes

1. The Nb<sub>2</sub>O<sub>5</sub>•XH<sub>2</sub>O precipitate is washed with NH<sub>4</sub>NO<sub>3</sub> solution to prevent peptization.
2. The isotopes counted are 72-min <sup>97</sup>Nb, 23.3-h <sup>96</sup>Nb, and 35-d <sup>95</sup>Nb.

(October 1989)



# TANTALUM

B. P. Bayhurst

## 1. Introduction

In the separation of tantalum from niobium and other fission products, decontamination is effected by  $\text{LaF}_3$  and  $\text{Sb}_2\text{S}_3$  scavenges,  $\text{Ba}[\text{ZrF}_6]$  precipitation, and extraction of tantalum into hexone from a solution 2.88M in  $\text{HNO}_3$  and 1.1M in HF. The tantalum is back-extracted from hexone by means of a 1.5%  $\text{H}_2\text{O}_2$  solution and precipitated as the hydrous oxide,  $\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ , which is ignited to the anhydrous compound. The chemical yield is 60 to 70%.

## 2. Reagents

Tantalum carrier: 10 mg tantalum/ml, prepared by dissolving the pure metal in a minimum of a mixture of conc  $\text{HNO}_3$  and HF and diluting to the appropriate volume with  $\text{H}_2\text{O}$ .

Antimony(III) carrier: 10 mg antimony(III)/ml, added as  $\text{SbCl}_3$  in 1M HCl

Lanthanum carrier: 10 mg lanthanum/ml, added as aqueous  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as purified  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 0.1M HCl

$\text{HNO}_3$ : conc; fuming

HF: conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{H}_2\text{S}$ : gas

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : solid

$\text{HNO}_3$ -HF solution: 2.88M in  $\text{HNO}_3$  and 1.1M in HF

$\text{NH}_4\text{OH}$ : dilute; conc

$\text{BaCl}_2$ : 1M

$\text{NH}_4\text{NO}_3$ : saturated aqueous solution

Hexone (4-methyl-2-pentanone)

$\text{H}_2\text{O}_2$ : 1.5% by volume

Ethanol: absolute

Phenolphthalein indicator solution

## 3. Procedure

*Step 1.* To the sample in a 40-ml plastic centrifuge tube, add 4.0 ml of tantalum carrier and 3 ml each of saturated  $\text{NH}_4\text{NO}_3$  and  $\text{H}_3\text{BO}_3$ . Make the solution alkaline to phenolphthalein with conc  $\text{NH}_4\text{OH}$ , centrifuge, and discard the supernate. Wash the precipitate with 30 ml of dilute  $\text{NH}_4\text{OH}$  (1 ml of conc  $\text{NH}_4\text{OH}$  and 29 ml of  $\text{H}_2\text{O}$ ) and 2 ml of saturated  $\text{NH}_4\text{NO}_3$ , centrifuge, and discard the wash.

*Step 2.* Add 10 ml of fuming  $\text{HNO}_3$ , place on a steam bath, and permit the  $\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  to coagulate. Centrifuge, and discard the supernate. Dissolve the precipitate in 7 drops of conc HF, dilute to 10 ml with  $\text{H}_2\text{O}$ , and add 100 mg of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . Add 3 drops of lanthanum carrier, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean plastic tube. Repeat the  $\text{LaF}_3$  scavenge twice.

*Step 3.* To the supernate from the final  $\text{LaF}_3$  scavenge, add 4 drops of antimony(III) carrier and saturate with  $\text{H}_2\text{S}$  on a steam bath. Remove the tube from the bath, cap it, and permit the  $\text{Sb}_2\text{S}_3$  to coagulate. Centrifuge, transfer the supernate to a clean plastic tube, and repeat the  $\text{Sb}_2\text{S}_3$  scavenge. In this scavenge, add 1 ml of filter pulp to bring down "floaters."

*Step 4.* Transfer the supernate to a clean plastic tube and heat on a steam bath to expel  $\text{H}_2\text{S}$ . Add 6 drops of conc HF and 2.75 ml of conc  $\text{HNO}_3$  and bring the volume to 15 ml with  $\text{H}_2\text{O}$ . Add 2 drops of zirconium holdback carrier and 4 drops of 1M  $\text{BaCl}_2$  and heat on a steam bath until  $\text{Ba}[\text{ZrF}_6]$  coagulates. Centrifuge, transfer the supernate to a clean plastic tube, and repeat the  $\text{Ba}[\text{ZrF}_6]$  scavenge. Transfer the supernate to a 1-oz plastic bottle.

*Step 5.* Add 10 ml of hexone and extract tantalum (as fluorocomplex) into the organic solvent (upper layer). Wash the hexone layer five times with  $\text{HNO}_3$ -HF solution (2.88M in  $\text{HNO}_3$  and 1.1M in HF) and discard the washings.

*Step 6.* Extract the tantalum from the hexone solution with ~25% of its volume of 1.5% H<sub>2</sub>O<sub>2</sub>. Repeat the extraction three times, combining all extracts in a Teflon beaker and discarding the hexone layer.

*Step 7.* Add 5 ml of conc HNO<sub>3</sub> and boil the solution to a volume of 2 to 3 ml. Repeat. Add 5 ml of conc HNO<sub>3</sub>, boil down the solution to ~2 to 3 ml, and use conc HNO<sub>3</sub> to transfer the mixture to a 40-ml plastic centrifuge tube. Centrifuge and discard the supernate. Wash the precipitate twice with conc HNO<sub>3</sub>, each time centrifuging and discarding the supernate.

*Step 8.* To the precipitate, add a slurry of filter paper pulp, stir, and filter through filter paper. Transfer the paper to a porcelain crucible and ignite at 900°C for 20 min. Permit the crucible to cool.

*Step 9.* Add 1 to 2 ml of ethanol to the Ta<sub>2</sub>O<sub>5</sub> in the crucible and with the polished end of a stirring rod, crush the oxide to a fine powder. Use a stream of ethanol from a plastic squeeze bottle to transfer the oxide onto a weighed filter circle. Filter, wash the precipitate with ethanol, and dry at 110°C. Cool, weigh, and mount for counting.

(October 1989)

# CHROMIUM

W. H. Burgus

Ethanol: 95%

Ethyl ether

## 1. Introduction

In the analysis for radiochromium, exchange between active chromium and  $\text{Cr}_2\text{O}_7^{2-}$  carrier is promoted by reduction of the latter to the +3 state. Some decontamination of the sample is then effected by acid sulfide scavenging when chromium is in the +3 state. After sulfide scavenging, chromium is oxidized to the +6 state and precipitated as  $\text{BaCrO}_4$ , which is then converted to the blue peroxo compound,  $\text{CrO}_5$ , by treatment with  $\text{H}_2\text{O}_2$  in HCl medium in the presence of ethyl ether. The peroxo compound is extracted into the ether layer (effecting further decontamination), then back-extracted into aqueous  $\text{NH}_3$ , and  $\text{BaCrO}_4$  is again precipitated. After removal of any remaining radiobarium as the sulfate, followed by  $\text{Fe}(\text{OH})_3$  scavenging steps and precipitation of excess sulfate as  $\text{BaSO}_4$ , chromium is finally precipitated and counted as  $\text{BaCrO}_4$ . The chemical yield is 40 to 50%.

## 2. Reagents

Chromium carrier: 10 mg chromium/ml, 56.6 g

$\text{K}_2\text{Cr}_2\text{O}_7$  per liter, primary standard

Palladium carrier: 10 mg palladium/ml, added as

$\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in very dilute HCl

Copper carrier: 10 mg copper/ml, added as

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ml, added as

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute HCl

HCl: conc; dilute (3 ml conc HCl/l)

$\text{H}_2\text{SO}_4$ : 3M

$\text{HNO}_3$ : 6M

$\text{HC}_2\text{H}_3\text{O}_2$ : 1M

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{S}$ : gas

$\text{H}_2\text{O}_2$ : 30%

$\text{Ba}(\text{NO}_3)_2$ : saturated solution

$\text{NaBrO}_3$ : 1M

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ : 1M

Aqueous  $\text{SO}_2$  solution: saturated

## 3. Procedure

*Step 1.* To the sample in a 40-ml glass centrifuge tube, add 2 ml of standard chromium carrier. Dilute the solution to 15 ml, add 3 ml of conc HCl, and heat to boiling. Add saturated  $\text{SO}_2$  solution dropwise until all of the  $\text{Cr}_2\text{O}_7^{2-}$  has been reduced to  $\text{Cr}^{3+}$  ion. Boil off the excess  $\text{SO}_2$ .

*Step 2.* To the hot solution add conc  $\text{NH}_4\text{OH}$  dropwise to precipitate  $\text{Cr}(\text{OH})_3$ . Caution: Do not use a great excess of  $\text{NH}_4\text{OH}$  (Note 1). Centrifuge the  $\text{Cr}(\text{OH})_3$  and discard the supernate.

*Step 3.* Dissolve the  $\text{Cr}(\text{OH})_3$  in 6 to 8 drops of conc HCl, dilute to 20 ml, heat to boiling, and reprecipitate  $\text{Cr}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 4.* Dissolve the  $\text{Cr}(\text{OH})_3$  in 6 to 8 drops of conc HCl, dilute to 20 ml, and add 4 drops each of palladium and copper carriers. Heat to boiling and pass in  $\text{H}_2\text{S}$  for 5 min. Filter and discard the sulfide scavenger precipitate, retaining the  $\text{Cr}^{3+}$ -containing filtrate in a 40-ml centrifuge tube.

*Step 5.* Precipitate  $\text{Cr}(\text{OH})_3$  from the filtrate (*Step 2*), centrifuge, and discard the supernate.

*Step 6.* Dissolve the  $\text{Cr}(\text{OH})_3$  in 8 drops of conc HCl, boil out remaining  $\text{H}_2\text{S}$ , and dilute to 20 ml. Add 4 drops each of palladium and copper carriers and remove another sulfide scavenging precipitate as in *Step 4*. Filter and collect the filtrate in a 40-ml centrifuge tube.

*Step 7.* Repeat *Step 5*.

*Step 8.* Redissolve the  $\text{Cr}(\text{OH})_3$  from *Step 7* in 8 drops of conc HCl, heat to boiling to remove  $\text{H}_2\text{S}$ , and reprecipitate  $\text{Cr}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 9.* Dissolve the  $\text{Cr}(\text{OH})_3$  in 4 to 6 drops of conc HCl (Note 2). Add 15 ml of  $\text{H}_2\text{O}$  and  $\sim 6$  ml of 1M  $\text{NaBrO}_3$ . Transfer to a 125-ml erlenmeyer flask and heat over a flame until all the  $\text{Cr}^{3+}$  ion is oxidized to  $\text{Cr}_2\text{O}_7^{2-}$ . If the oxidation does not appear to be complete, additional  $\text{NaBrO}_3$  should be added (Note 3).

*Step 10.* Add 3 to 4 ml of saturated  $\text{Ba}(\text{NO}_3)_2$  solution and 3 to 4 ml of 1M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . This will result in the precipitation of  $\text{BaCrO}_4$ . If precipitation appears to be incomplete, 1 drop of conc  $\text{NH}_4\text{OH}$  should be added. Transfer to a 40-ml centrifuge tube centrifuge, and discard the supernate. Wash the precipitate with 30 ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the washings.

*Step 11.* Dissolve the  $\text{BaCrO}_4$  in  $\sim 6$  drops of conc HCl and 10 ml of  $\text{H}_2\text{O}$ . (Heating may be required.) Dilute to  $\sim 30$  ml and reprecipitate  $\text{BaCrO}_4$  with 1M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  as in *Step 10*. Centrifuge, wash the precipitate with 30 ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the washings.

*Step 12.* Dissolve the  $\text{BaCrO}_4$  in 10 ml of  $\text{H}_2\text{O}$  and 5 drops of conc HCl. Cool to 0 to  $5^\circ\text{C}$  in an ice bath. Transfer to a 125-ml separatory funnel to which 90 to 100 ml of cold (below  $5^\circ\text{C}$ ) ethyl ether has been added. Add 3 drops of cold (below  $5^\circ\text{C}$ ) 30%  $\text{H}_2\text{O}_2$  and immediately extract the blue peroxo compound  $\text{CrO}_5$  into cold ether (Note 4). Discard the aqueous layer.

*Step 13.* Wash the ether layer four times with 10-ml portions of cold ( $\sim 5^\circ\text{C}$ )  $\text{H}_2\text{O}$  that contains 3 ml of conc HCl/l. Discard the washings.

*Step 14.* Back-extract into  $\text{H}_2\text{O}$  by shaking the ether with  $\sim 15$  ml of  $\text{H}_2\text{O}$  that contains 3 to 4 drops of conc  $\text{NH}_4\text{OH}$ . Transfer the aqueous layer to a 40-ml centrifuge tube.

*Step 15.* Add 2 to 3 ml of saturated  $\text{Ba}(\text{NO}_3)_2$  solution to precipitate  $\text{BaCrO}_4$ . Centrifuge and wash with 30 ml of  $\text{H}_2\text{O}$ ; discard the supernate and washings.

*Step 16.* Dissolve the  $\text{BaCrO}_4$  in 15 ml of  $\text{H}_2\text{O}$  and 8 drops of conc HCl. Heat to boiling and add 3 drops of 3M  $\text{H}_2\text{SO}_4$ . Centrifuge and discard the  $\text{BaSO}_4$  precipitate. Transfer the supernate to a 40-ml centrifuge tube.

*Step 17.* Add 6 drops of iron carrier to the supernate containing the  $\text{Cr}_2\text{O}_7^{2-}$  ion and precipitate  $\text{Fe}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the  $\text{Fe}(\text{OH})_3$ ; transfer the supernate to a 40-ml centrifuge tube. Acidify the supernate with  $\text{HNO}_3$ .

*Step 18.* Repeat *Step 17* and heat the supernate to boiling.

*Step 19.* Add  $\sim 3$  ml of saturated  $\text{Ba}(\text{NO}_3)_2$  solution to remove  $\text{SO}_4^{2-}$  ion. Centrifuge the  $\text{BaSO}_4$ , discard the precipitate, and transfer the supernate to a 40-ml centrifuge tube.

*Step 20.* Precipitate  $\text{BaCrO}_4$  from the supernate by the addition of conc  $\text{NH}_4\text{OH}$ . Dissolve in 6 to 8 drops of conc HCl and precipitate from 20 ml of solution by adding 3 to 4 ml of 1M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . Centrifuge and discard the supernate.

*Step 21.* Dissolve the  $\text{BaCrO}_4$  in 5 drops of conc HCl. Dilute to 30 ml and add 1 ml of 1M  $\text{HC}_2\text{H}_3\text{O}_2$ . Heat to boiling and add 2 ml of 1M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  dropwise to precipitate  $\text{BaCrO}_4$ . Filter onto a weighed filter circle. Wash the precipitate three times with 15- to 20-ml portions of hot  $\text{H}_2\text{O}$  and then with ethanol. Dry for 10 min at  $110^\circ\text{C}$ . Weigh, mount, and count immediately.

## Notes

1. It is important to avoid using a large excess of conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{Cr}(\text{OH})_3$  because some of the  $\text{Cr}(\text{OH})_3$  will complex with  $\text{NH}_3$  and go into solution.

2. The  $\text{Cl}^-$  and  $\text{H}^+$  ion concentrations must be kept low to avoid reduction of the  $\text{Cr}_2\text{O}_7^{2-}$  that is formed by oxidation of  $\text{Cr}^{3+}$  ion with  $\text{BrO}_3^-$ .

3. It is possible to visually determine whether oxidation of  $\text{Cr}^{3+}$  ion to  $\text{Cr}_2\text{O}_7^{2-}$  is complete.

4. The formation and ether extraction of the blue peroxo compound,  $\text{CrO}_5$ , must be carried out in the cold; otherwise the  $\text{Cr}_2\text{O}_7^{2-}$  will merely oxidize the  $\text{H}_2\text{O}_2$ . Only a transient blue color is then observed.

(October 1989)

# MOLYBDENUM I

J. W. Barnes and E. J. Lang

## 1. Introduction

The separation of molybdenum from fission products is based on its behavior in the +6 oxidation state on an anion-exchange resin. Molybdenum(VI) is adsorbed on the resin from HCl solutions of concentrations 5 to 9M. Resin washes with a mixture of dilute HCl and HF and with 3M NH<sub>4</sub>OH remove most of the interfering ions. Molybdenum is eluted from the column with 6M NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, precipitated with alpha-benzoinoxime, and converted by ignition to MoO<sub>3</sub>, in which form it is weighed and counted. The chemical yield is ~75%.

## 2. Reagents

Molybdenum carrier: 10 mg molybdenum/ml

(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O solution; standardized

Iron carrier: 10 mg iron/ml, added as aqueous

FeCl<sub>3</sub>•6H<sub>2</sub>O

Copper carrier: 10 mg copper/ml, added as

aqueous CuSO<sub>4</sub>•5H<sub>2</sub>O

H<sub>2</sub>SO<sub>4</sub>: conc

H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>: saturated aqueous solution

NH<sub>4</sub>Cl: 3M

NaBrO<sub>3</sub>: 0.5M

HNO<sub>3</sub>: 1M; conc

HCl: 6M; conc

HClO<sub>4</sub>: conc

HCl-HF: 0.1M in HCl and 0.05M in HF

NH<sub>4</sub>OH: 3M; conc

NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>: 6M

Alpha-benzoinoxime: 2% in ethanol

H<sub>2</sub>S: gas

Br<sub>2</sub>-H<sub>2</sub>O

Anion-exchange resin: Dowex 1-X8 (50 to 100 mesh); stored in 6M HCl

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 18.4 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O in H<sub>2</sub>O, add 1 ml of 0.5M NaBrO<sub>3</sub>, and dilute to 1 l with 6M HCl. Pipette 5.0 ml of the solution into a porcelain crucible that has been heated in a muffle furnace at 550°C, cooled, and weighed. Add 0.5 ml of conc HNO<sub>3</sub> and 0.5 ml of conc HClO<sub>4</sub>. Carefully dry the sample under an infrared lamp, and ensure that no spattering occurs. Ignite in the furnace for 1 h at 550°C. Cool and weigh as MoO<sub>3</sub>.

## 4. Procedure

*Step 1.* Add the sample to 3.0 ml of molybdenum carrier in a 125-ml erlenmeyer flask. Then add 1 ml of Br<sub>2</sub>-H<sub>2</sub>O, 4 drops of copper carrier, and 1 to 5 ml of conc H<sub>2</sub>SO<sub>4</sub>, depending upon the amount of uranium in the sample (~2 ml of the acid is sufficient for 1 g of uranium). Fume to dryness over a burner, add 30 ml of H<sub>2</sub>O, and warm to dissolve the residue. While the solution is kept warm, saturate with H<sub>2</sub>S. Pour the mixture into a 40-ml conical centrifuge tube, centrifuge, and save the supernate for the recovery of uranium (Note 1).

*Step 2.* Wash the precipitate by stirring with 5 ml of 3M NH<sub>4</sub>Cl and 10 ml of H<sub>2</sub>O. Centrifuge and discard the washings. Dissolve the precipitate in 1 ml of conc HCl and a few drops of conc HNO<sub>3</sub>. Add 10 ml of H<sub>2</sub>O, boil to remove excess H<sub>2</sub>S, and then add 3 to 4 drops of iron carrier. Precipitate Fe<sub>2</sub>O<sub>3</sub>•xH<sub>2</sub>O by adding 2 to 3 ml of conc NH<sub>4</sub>OH. Warm to coagulate the precipitate, centrifuge, transfer the supernate to a 125-ml erlenmeyer flask, and discard the precipitate.

*Step 3.* Take the supernate to half-volume over a burner. Add 1 ml of conc HCl and again take to half-volume. Add 1 ml of conc HCl, take the solution almost to dryness, and then add 10 ml of 6M HCl and 1 ml of Br<sub>2</sub>-H<sub>2</sub>O.

*Step 4.* Heat the solution to boiling, transfer it to the Dowex 1-X8 anion-exchange resin column

(Note 2), and permit it to run through under gravity. Wash the sides of column with 1 to 2 ml of 6M HCl and, when the level of acid reaches the top of the resin, add 10 ml of hot HCl-HF solution (Note 3). When the level of the HCl-HF solution reaches the top of the resin, add 5 ml of 3M NH<sub>4</sub>OH.

*Step 5.* As soon as the level of the NH<sub>4</sub>OH reaches the top of the resin, all effluents collected to this point are placed in the appropriate waste bottle. Add 10 ml of hot 6M NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to the resin and permit the solution to pass through; catch the molybdenum eluate in a clean 40-ml centrifuge tube.

*Step 6.* To the eluate add 2 ml of conc NH<sub>4</sub>OH, stir, and then add 4 drops of iron carrier. Boil for 1 min while stirring. Centrifuge.

*Step 7.* Add the supernate to an ice-cold mixture of 6 ml of conc HNO<sub>3</sub>, 1 ml of Br<sub>2</sub>-H<sub>2</sub>O, and 1 ml of saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in a 40-ml centrifuge tube. Cool in an ice bath for 5 min, add 10 ml of alpha-benzoinoxime solution, and stir vigorously. Filter onto filter paper and complete the transfer with 1M HNO<sub>3</sub>.

*Step 8.* Place the filter paper and contents in a porcelain crucible and ignite to MoO<sub>3</sub> at 550°C for ~1 h (Note 4).

*Step 9.* After ignition, allow the crucible to cool and grind the MoO<sub>3</sub> to a fine consistency with the end of a stirring rod. Add 2 drops of ethanol and slurry; then add an additional 5 ml of ethanol, stir, and filter onto a washed, dried, and weighed filter circle. Wash with ethanol and dry at 110°C for ~10 min. Cool, weigh, and mount (Note 5).

## Notes

1. This step is used only when the amount of uranium in the sample is >~50 mg or if plutonium or tungsten are present in appreciable amounts. If the amount of uranium is <50 mg and if relatively

little plutonium is present, add the sample to 3.0 ml of molybdenum carrier, and then add 1 ml of conc H<sub>2</sub>SO<sub>4</sub> and 1 ml of Br<sub>2</sub>-H<sub>2</sub>O. Fume to dryness, cool, add 10 ml of H<sub>2</sub>O and 3 drops of iron carrier, and precipitate Fe<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O as in *Step 2*. Then continue the usual procedure.

2. To prepare the resin column for use (a) place a small plug of glass wool in the tip of the column, (b) add enough resin slurry to obtain a bed height of 4 to 5 cm, and (c) allow the acid to drain off. (The column is fabricated by fusing a 15-ml conical centrifuge tube to an 8-cm length of 1-cm tubing drawn to a tip.)

3. The HCl-HF wash removes moderate quantities of uranium and plutonium.

4. A stream of air through the muffle furnace helps convert the molybdenum(VI)-benzoinoxime complex to MoO<sub>3</sub>.

5. The sample is permitted to stand for 18 h before counting to allow the 6-h <sup>99</sup>Tc daughter to grow into equilibrium. The individual counts are corrected to zero time using a half-life of 66.4 h; a correction for self-absorption in the sample is also applied.

(October 1989)

## MOLYBDENUM II

J. S. Gilmore and H. L. Smith

### 1. Introduction

The procedure described below, devised originally for the rapid determination of  $^{101}\text{Mo}$  in the presence of large quantities of foreign material, has proved to be suitable for the removal of molybdenum from 120 g of uranium, 1 g of plutonium, or ~20 g of iron. It also gives excellent decontamination from niobium and fission products.

The chief decontamination step is an extraction of the precipitate of molybdenum(VI) with alpha-benzoinoxime into  $\text{CHCl}_3$ . This step may be omitted and decontamination effected by extraction of molybdenum from HCl solution into hexone if the sample contains <10 g of uranium. If the original sample has a volume >1 l, the hexone extraction is essential as a volume-reducing step.

Additional decontamination steps include adsorption of molybdenum(VI) from HCl solution on an anion-exchange resin and an  $\text{Fe}(\text{OH})_3$  scavenger. The molybdenum is finally precipitated as the 8-quinolate, in which form it is counted. The chemical yield is 60 to 70%.

### 2. Reagents

Molybdenum carrier: 10 mg molybdenum/ml,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ; standardized as described in the MOLYBDENUM I procedure.

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$

Alpha-benzoinoxime: 2% in ethanol

8-quinolinol (8-hydroxyquinoline): 5% in 2M  $\text{HC}_2\text{H}_3\text{O}_2$

HCl: conc; 6M; 1M

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HC}_2\text{H}_3\text{O}_2$ : 6M

NaOH: 0.6M

HCl-HF: 0.1M in HCl and 0.1M in HF

$\text{NH}_4\text{OH}$ : 3M; conc

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ : 6M

Acetone

Ethanol: 95%

Chloroform

Methyl red indicator solution

Anion-exchange resin: Dowex 1-X10 (200 to 400 mesh); stored in 6M HCl

### 3. Procedure

*Step 1.* Make the sample 6 to 7M in HCl and add 1 to 2 ml of molybdenum carrier (Note 1). Boil the solution briefly and dilute with ice and  $\text{H}_2\text{O}$  to 750 ml (Note 2). Transfer the solution to a 1-l pear-shaped separatory funnel and precipitate molybdenum with 25 ml of alpha-benzoinoxime reagent.

*Step 2.* Add 50 ml of chloroform and shake vigorously. Permit the phases to separate and the precipitate to move from the aqueous to the chloroform phase (Note 3). Transfer the chloroform phase to a 250-ml pear-shaped separatory funnel. Extract the aqueous phase with 10 ml of alpha-benzoinoxime and 30 ml of chloroform; combine the chloroform layer with that separated previously. Discard the aqueous phase.

*Step 3.* Wash the chloroform layer with a mixture of 80 ml of 1M HCl and 20 ml of ethanol; discard the washings. Transfer the chloroform layer to a 125-ml separatory funnel. Add 25 ml of 0.6M NaOH and shake vigorously to remove the molybdenum. Discard the chloroform and transfer the aqueous layer to a 250-ml Vycor or quartz erlenmeyer flask.

*Step 4.* Boil the solution briefly to expel any chloroform present. Add 10 ml of conc  $\text{HNO}_3$  and boil the solution to half its original volume. Add 4 ml of conc  $\text{HClO}_4$  and 2 ml of conc  $\text{H}_2\text{SO}_4$ , and boil carefully until the exothermic reaction subsides. Then boil until strong fumes of  $\text{SO}_3$  are evolved. (This step removes organic material.)



*Step 5.* Dilute the solution with 20 ml of 6M HCl and place on a Dowex 1-X10 (200 to 400 mesh) resin column (4-ml bed volume). Wash the resin successively with 10 ml of 6M HCl, 15 ml of 0.1M HCl-HF, and 10 ml of 3M NH<sub>4</sub>OH.

*Step 6.* Elute the molybdenum from the column with 15 ml of 6M NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> solution. To the eluate add 3 ml of conc NH<sub>4</sub>OH and 4 drops of iron carrier. Boil and filter through filter paper in a 2-in. 60° funnel. Discard the precipitate (Note 4).

*Step 7.* To the filtrate add methyl red indicator solution, acidify with 6M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, then add 2 ml in excess, boil, and add 2 ml of 8-quinolinol reagent (Note 5). Filter onto a filter circle and discard the filtrate. Wash the precipitate with H<sub>2</sub>O and then with acetone.

*Step 8.* Dry the molybdenum quinolate for 30 s at 140°C, weigh, mount, and beta-count.

#### Notes

1. Hexone (4-methyl-2-pentanone) extraction may be performed at this point instead of or in addition to the precipitation and extraction of molybdenum as the alpha-benzoinoximate. Hexone extraction is advisable if the sample contains <10 g uranium; the extraction is essential as a volume-reducing step if the sample has a volume >1 l. The solution, which is 6 to 7M in HCl, is extracted with an equal volume of hexone that has been preequilibrated with 6M HCl to remove molybdenum. The hexone layer is washed with an equal volume of 6M HCl that has been preequilibrated with hexone, and is then shaken with 20 to 50% of its volume of H<sub>2</sub>O to back-extract the molybdenum. If the original sample contained >100 mg of iron, proceed with the precipitation of molybdenum by means of alpha-benzoinoxime; otherwise, go directly to *Step 5*. If no iron is present at this point, the H<sub>2</sub>O back-extract may be diluted with an equal volume of conc HCl and the solution put directly on a Dowex-1, 40-ml reservoir, anion-exchange column.

2. Precipitation of molybdenum with alpha-benzoinoxime is more nearly complete if the solution is cold.

3. Allow at least 15 min to elapse after irradiation before performing any molybdenum chemistry to avoid possible separation of <sup>99</sup>Nb and <sup>99</sup>Mo before the molybdenum has grown in.

4. The Fe(OH)<sub>3</sub> scavenge removes niobium, which otherwise contaminates the final sample.

5. The 8-quinolate precipitation constitutes the last technetium separation from molybdenum. Therefore, the time of addition of the 8-quinolinol should be accurately observed and recorded.

(October 1989)

# TUNGSTEN I

R. J. Prestwood

## 1. Introduction

In its separation from fission products, tungsten is initially precipitated as the hydrous oxide ("tungstic acid"),  $\text{WO}_3 \cdot \text{XH}_2\text{O}$ . The tungsten is then further decontaminated by a series of  $\text{Fe}(\text{OH})_3$  and acid sulfide scavenging steps. The latter steps, performed in the presence of tartaric acid, which strongly complexes tungsten(VI), remove the troublesome molybdenum activity. Niobium is effectively removed from  $\text{HCl}$  medium by extraction into  $\text{CHCl}_3$  with cupferron; this is an excellent decontamination step for other activities also. The tungsten, present as a tartrate complex, is unaffected by cupferron and is finally precipitated from a buffered  $\text{HC}_2\text{H}_3\text{O}_2$  solution as the 8-quinolinol (8-hydroxyquinoline) derivative, in which form it is weighed and counted. The chemical yield is ~50%.

## 2. Reagents

Tungsten carrier: 10 mg tungsten/ml, added as  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ; standardized

Bismuth carrier: 10 mg bismuth/ml, added as  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Molybdenum carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Niobium carrier: 10 mg niobium/ml, added as  $\text{Nb}_2\text{O}_5$  in  $\text{H}_2\text{C}_2\text{O}_4$  solution

$\text{HCl}$ : conc

$\text{HNO}_3$ : conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HC}_2\text{H}_3\text{O}_2$ : glacial

Tartaric acid: 50% aqueous solution

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ : 6M

Chloroform

Buffer solution: 1M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 3.6M in  $\text{NaC}_2\text{H}_3\text{O}_2$

$\text{H}_2\text{S}$ : gas

Cupferron reagent: 6% aqueous solution (kept in refrigerator)

8-quinolinol (8-hydroxyquinoline) reagent: 5% in 2M  $\text{HC}_2\text{H}_3\text{O}_2$

Aerosol: 0.1% in  $\text{H}_2\text{O}$

Ethanol: absolute

## 3. Preparation and Standardization of Carrier

Dissolve 17.94 g of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  and make the solution up to a volume of 1 l.

Pipette exactly 10 ml of the carrier solution into a 125-ml erlenmeyer flask, add 2 ml of glacial  $\text{HC}_2\text{H}_3\text{O}_2$  and 8 ml of 6M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , and heat the solution on a steam bath to ~80°C. Add a few drops of aerosol solution and 5 ml of 5% (in 2M  $\text{HC}_2\text{H}_3\text{O}_2$ ) 8-quinolinol reagent. Heat on a steam bath until the 8-quinolinol derivative coagulates. (The coagulation may be aided by bringing the solution to a boil over an open flame.) Filter the precipitate into a weighed 60-ml sintered glass crucible of medium porosity; wash three times with 5-ml portions of  $\text{H}_2\text{O}$  and once with a 5-ml portion of absolute ethanol. Dry the precipitate at 110°C for 30 min. Cool and weigh.

To determine the quantity of tungsten contained in 1 ml of the standard solution, a known volume of the solution contained in a 125-ml erlenmeyer flask is digested on a steam bath with 6M  $\text{HNO}_3$  for 12 h. The  $\text{WO}_3 \cdot \text{XH}_2\text{O}$  formed is filtered into a weighed Gooch crucible that is covered with a thin mat of asbestos. The precipitate is ignited at 850°C for 1 h. (Caution: at 900°C  $\text{WO}_3$  begins to volatilize.) It is then cooled and weighed as  $\text{WO}_3$ .

Four standardizations were run, and results agreed within ~1%. In one series of standardizations, 20.0 mg of tungsten gave 54.8 mg of the tungsten-derivative of 8-quinolinol.

#### 4. Procedure

*Step 1.* To a 40-ml glass centrifuge tube add 2.0 ml of standard tungsten carrier and an aliquot of the sample. Then add 10 ml of conc HNO<sub>3</sub> and digest on a steam bath for 10 min. Remove, centrifuge, and discard the supernate.

*Step 2.* To the WO<sub>3</sub>•XH<sub>2</sub>O residue add 6 drops of conc NH<sub>4</sub>OH and dilute to 15 ml with H<sub>2</sub>O. Add, while swirling, 3 drops of iron carrier solution (Note 1) and 2 drops of aerosol solution. Centrifuge and decant the supernate into a clean centrifuge tube.

*Step 3.* To the solution add 10 drops of 50% tartaric acid solution, 10 drops of conc H<sub>2</sub>SO<sub>4</sub>, and 5 drops each of bismuth and molybdenum carriers. Place on steam bath and bubble in H<sub>2</sub>S rather vigorously for at least 2 min (Note 2). (Some time is required for MoS<sub>3</sub> to coagulate, but coagulation is aided by the precipitation of Bi<sub>2</sub>S<sub>3</sub>.) Filter the hot mixture containing the sulfide precipitates through filter paper in a 2-in. 60° funnel (Note 3), and collect the filtrate in a clean centrifuge tube. Wash the centrifuge tube and the precipitate with 2 to 3 ml of H<sub>2</sub>O and pour the washings through the filter funnel. To the filtrate add 10 ml of conc HNO<sub>3</sub> and digest on a steam bath for 10 min. Remove, centrifuge, and discard the supernate.

*Step 4.* Repeat Steps 2 and 3.

*Step 5.* Dissolve the WO<sub>3</sub>•XH<sub>2</sub>O precipitate in 6 drops of conc NH<sub>4</sub>OH and add 15 drops of 50% tartaric acid solution. With 10 ml H<sub>2</sub>O, transfer the solution to a 60-ml separatory funnel. Add 10 drops of conc HCl, 1 ml of niobium carrier, and 10 ml of chloroform. Shake briefly and add 5 ml of 6% cupferron reagent. Shake for 30 s and allow to stand for 1 to 2 min. Drain off the chloroform layer and discard. Extract again with 5 ml of chloroform. Drain the H<sub>2</sub>O layer into clean 40-ml centrifuge tube.

*Step 6.* Repeat Step 3 but do not add the tartaric acid solution. Caution: When the mixture is heated on a steam bath, there is a vigorous evolution of nitrogen oxides from reaction between the tartaric acid present in solution and the added HNO<sub>3</sub>.

*Step 7.* To the WO<sub>3</sub>•XH<sub>2</sub>O precipitate obtained in Step 6, add 6 drops of conc NH<sub>4</sub>OH. Using H<sub>2</sub>O from a wash bottle, transfer the resulting solution to a 125-ml erlenmeyer flask. The volume of solution should be ~15 ml. Add 6 drops of glacial HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 10 ml of the buffer solution (see reagents). Heat to boiling and add 1 ml of 5% 8-quinolinol reagent dropwise. Boil for ~30 s, let stand for a few minutes, and filter through a weighed filter circle. Dry at 120°C for 10 min. Allow to stand for 20 min and weigh. Mount and beta-count immediately.

#### Notes

1. The percentage of tungsten lost in this step is almost exactly equal to the number of drops of iron carrier added.

2. It is necessary to keep the solution hot to avoid formation of sulfur when HNO<sub>3</sub> is added to decompose tartrate.

3. Filtration is superior to centrifugation because "floaters" are invariably present after centrifugation.

(October 1989)

## TUNGSTEN II

R. J. Prestwood

### 1. Introduction

This procedure was developed for the separation of tungsten from fission products in samples obtained from underground nuclear explosions. These samples had large quantities of debris associated with them, and the TUNGSTEN I procedure did not remove niobium adequately.

There are three major differences between this procedure and the original: the  $\text{CHCl}_3$  extraction has been eliminated; fuming with conc  $\text{H}_2\text{SO}_4$  has been introduced; and the final weighing form of the tungsten is  $\text{WO}_3$ .

### 2. Reagents

Tungsten carrier: 10 mg tungsten/ml, added as  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ; standardized

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Molybdenum carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2$  in 1M  $\text{HCl}$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : conc

$\text{HNO}_3$ : conc

$\text{H}_2\text{SO}_4$ : conc

Tartaric acid: 50% aqueous solution

$\text{NH}_4\text{OH}$ : conc

$\text{NaOH}$ : 10M

$\text{H}_2\text{S}$ : gas

Ethanol: absolute

### 3. Preparation and Standardization of Carrier

See TUNGSTEN I procedure.

### 4. Procedure

*Step 1.* To a 40-ml glass centrifuge tube add 2.0 ml of standard tungsten carrier and an aliquot of the sample. Then add 10 ml of conc  $\text{HNO}_3$  and digest on a steam bath for 10 min. Centrifuge and discard the supernate. If the original sample is in a large volume of solution (the author has processed as much as 200 ml of sample-containing solution that was 4M in  $\text{HCl}$ ), the acidic solution is added to the standard carrier in an erlenmeyer flask and digested on a hot plate for 24 h. The  $\text{WO}_3 \cdot \text{XH}_2\text{O}$  precipitates and coagulates during the digestion. The mixture is then centrifuged in portions in a single centrifuge tube; the supernates are discarded.

*Step 2.* To the precipitate add 3 to 4 ml of conc  $\text{H}_2\text{SO}_4$  and, while stirring, fume until  $\text{SO}_3$  fumes appear only above the mouth of the centrifuge tube (Note 1). Cool the tube in air until it is safe to cool further with  $\text{H}_2\text{O}$ . When cool, carefully add 20 ml of  $\text{H}_2\text{O}$ , stir, and heat on a steam bath for 5 to 10 min. Centrifuge and discard the supernate.

*Step 3.* To the precipitate add 10 drops of 10M  $\text{NaOH}$ , dilute to 15 ml with  $\text{H}_2\text{O}$ , and then add 1 drop each of iron and lanthanum carriers. Heat on a steam bath until the precipitate coagulates. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 4.* Repeat the iron-lanthanum scavenge on the supernate. Centrifuge and transfer the supernate to a clean centrifuge tube and discard the precipitate.

*Step 5.* To the supernate add 10 drops of tartaric acid, 10 drops of conc  $\text{H}_2\text{SO}_4$ , 1 ml of iron carrier (Note 2), and 1 drop of molybdenum and 5 drops of palladium carrier. Place on a steam bath and saturate with  $\text{H}_2\text{S}$  for at least 5 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 6.* To the supernate add 5 drops of palladium carrier, place on a steam bath, and saturate with  $\text{H}_2\text{S}$  for 5 min. Centrifuge and filter the supernate through filter paper into a clean centrifuge tube. Discard the precipitate.

*Step 7.* To the supernate add 10 ml of conc  $\text{HNO}_3$ , heat on a steam bath for 10 min, centrifuge, and discard the supernate.

*Step 8.* Repeat *Step 2*.

*Step 9.* Repeat *Steps 3* and *4*, but use conc  $\text{NH}_4\text{OH}$  rather than  $\text{NaOH}$ .

*Step 10.* To the supernate add 10 drops of tartaric acid, 10 drops of conc  $\text{H}_2\text{SO}_4$ , and 5 drops of palladium carrier. Saturate with  $\text{H}_2\text{S}$  on a steam bath for 5 min. Centrifuge and filter the supernate through filter paper into a clean centrifuge tube. Discard the precipitate.

*Step 11.* To the supernate add 10 ml of conc  $\text{HNO}_3$ , digest for 10 min on a steam bath, centrifuge, and discard the supernate. To the precipitate add 3 ml of conc  $\text{H}_2\text{SO}_4$  and fume as in *Step 2*. Cool, add 20 ml of  $\text{H}_2\text{O}$ , and heat on a steam bath for 10 min. Centrifuge and discard the supernate.

*Step 12.* Dissolve the precipitate in 1 ml of conc  $\text{NH}_4\text{OH}$  and repeat one iron-lanthanum scavenge. Centrifuge and transfer the supernate to a clean centrifuge tube.

*Step 13.* To the supernate add 5 ml of paper pulp mixture (Note 3) and 10 ml of conc  $\text{HCl}$ . Digest for 10 min on a steam bath. Filter the hot mixture onto a Millipore filter (pore size  $\leq 1.2 \mu\text{m}$ ). Do not wash the precipitate. Transfer the precipitate and filter paper to a porcelain crucible and ignite for 5 to 10 min at  $800^\circ\text{C}$ . Cool and powder gently with a polished glass rod. Using absolute ethanol, transfer the powdered material onto a weighed filter circle. Weigh as  $\text{WO}_3$ .

## Notes

1. This treatment seems to ensure subsequent decontamination from niobium.

2. The presence of  $\text{Fe}^{3+}$  delays the reduction of molybdenum by  $\text{H}_2\text{S}$  and therefore facilitates its complete precipitation.

3. The pulp mixture is made by adding six Whatman No. 42 (9-cm) filter papers to 500 ml of  $\text{H}_2\text{O}$  in a Waring blender and macerating for  $\sim 5$  min. The pulp mixture is transferred to a Pyrex container and made slightly acidic with  $\text{HCl}$  to inhibit mold formation.

(October 1989)

## TUNGSTEN III

B. P. Bayhurst and R. J. Prestwood

### 1. Introduction

In this procedure, the alkaloid cinchonine ( $C_{19}H_{22}N_2O$ ) is used to precipitate tungsten from a medium 3M in HCl. After dissolution of the precipitate in 10M NaOH,  $La(OH)_3$  scavenges are carried out, and the tungsten is then precipitated as the 8-quinolinate in the presence of EDTA. The precipitate is wet washed, the  $WO_3$  formed is dissolved in 10M NaOH, and  $La(OH)_3$  scavenges are repeated. Niobium is further removed by extraction with cupferron into  $CHCl_3$ . Molybdenum is removed from the aqueous layer by precipitating PdS. The hydrous oxide,  $WO_3 \cdot xH_2O$ , is then precipitated by conc  $HNO_3$  and ignited to the anhydrous form for weighing and counting. The chemical yield is 60 to 70%.

### 2. Reagents

Tungsten carrier: 10 mg tungsten/ml, added as  $Na_2WO_4 \cdot 2H_2O$  in  $H_2O$ ; standardized

Molybdenum carrier: 10 mg molybdenum/ml, added as  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in  $H_2O$

Palladium carrier: 10 mg palladium/ml, added as  $PdCl_2$  in 1M HCl

Lanthanum carrier: 10 mg lanthanum/ml, added as  $La(NO_3)_3 \cdot 6H_2O$  in  $H_2O$

HCl: conc

$HNO_3$ : conc

$H_2SO_4$ : conc

Tartaric acid: 50% aqueous solution

$HC_2H_3O_2$ : conc

$H_2S$ : gas

NaOH: 10M

EDTA solution: 0.2M solution of disodium ethylenediamine tetraacetate

Cinchonine ( $C_{19}H_{22}N_2O$ ) solution: 125 g diluted to 1 l with 6M HCl

Cinchonine wash solution: 25 ml of cinchonine solution and 30 ml of conc HCl; diluted to 1 l with  $H_2O$

8-quinolinol (8-hydroxyquinoline) reagent: 5% solution in 2M  $HC_2H_3O_2$

Cupferron reagent: 6% aqueous solution (freshly prepared and kept in a refrigerator)

Ethanol: absolute

$CHCl_3$

### 3. Preparation and Standardization of Carrier

See TUNGSTEN I procedure.

### 4. Procedure

*Step 1.* To the sample in 3M HCl, add 4.0 ml of tungsten carrier and warm on a hot plate overnight. Boil down to ~30 ml, add 100 ml of hot  $H_2O$ , and keep at low heat on a hot plate for 30 min. Add 6 ml of cinchonine solution and heat for an additional 30 min. Centrifuge portions of the mixture in a 40-ml glass centrifuge tube and discard the supernates. Wash the precipitate with 30 ml of hot cinchonine wash solution and discard the wash.

*Step 2.* Dissolve the precipitate in 10 drops of 10M NaOH and dilute to 10 ml with  $H_2O$ . Centrifuge off any insoluble material and transfer the supernate to a clean centrifuge tube. Add 3 drops of lanthanum carrier, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean centrifuge tube. Repeat the  $La(OH)_3$  scavenge.

*Step 3.* To the supernate add 5 ml of 0.2M EDTA solution, adjust the pH to between 5.0 and 5.6 with conc  $HC_2H_3O_2$ , and heat on a steam bath for 5 min. Add 5 ml of 8-quinolinol reagent and permit the precipitate to coagulate. Centrifuge, discard the supernate, and wash the precipitate with 30 ml of  $H_2O$ .

*Step 4.* Dissolve the precipitate in 6 ml of conc  $HNO_3$  and transfer the solution to a 125-ml erlenmeyer flask. Add 4 ml of conc  $H_2SO_4$  and boil to  $SO_3$  fumes. Cool, dilute to 15 ml with  $H_2O$ ,

transfer to a clean centrifuge tube, centrifuge, and discard the supernate.

*Step 5.* Dissolve the  $\text{WO}_3 \cdot \text{XH}_2\text{O}$  precipitate in 10 drops of 10M NaOH and dilute to 15 ml with  $\text{H}_2\text{O}$ . Add 3 drops of lanthanum carrier, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean tube. Repeat the  $\text{La}(\text{OH})_3$  scavenge twice.

*Step 6.* Repeat Steps 3 to 5.

*Step 7.* Transfer the supernate to a 60-ml separatory funnel and add 10 drops of tartaric acid solution and 10 drops of conc HCl. Add 10 ml of  $\text{CHCl}_3$  and shake vigorously for ~1 min. Add 5 ml of 6% cupferron reagent, shake for 1 min, and discard the  $\text{CHCl}_3$  (lower) layer. To the aqueous layer add 10 ml of  $\text{CHCl}_3$  and 3 ml of cupferron reagent, shake for 1 min, and discard the  $\text{CHCl}_3$  layer. Wash the aqueous layer with 5 ml of  $\text{CHCl}_3$  and discard the wash.

*Step 8.* Transfer the aqueous layer to a 40-ml glass centrifuge tube and place on a steam bath. Add 10 drops of conc  $\text{H}_2\text{SO}_4$ , 5 drops of palladium carrier, and 1 drop of molybdenum carrier; saturate the solution with  $\text{H}_2\text{S}$ . Heat for a few minutes, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 9.* Add 5 drops of palladium carrier and saturate with  $\text{H}_2\text{S}$  on a steam bath. Centrifuge and filter the precipitate onto a filter paper. Collect the filtrate in a clean centrifuge tube.

*Step 10.* To the filtrate add 10 ml of conc  $\text{HNO}_3$ , and then heat on a steam bath to coagulate the  $\text{WO}_3 \cdot \text{XH}_2\text{O}$  formed. Centrifuge, discard the supernate, and slurry the precipitate with 6 ml of filter paper pulp and 4 ml of conc HCl. Filter through a Millipore filter (AAWP, 0.8- $\mu\text{m}$ ) and ignite for 15 min at 800°C. Weigh and mount the  $\text{WO}_3$ .

(October 1989)

## MANGANESE

B. P. Bayhurst and R. J. Prestwood

### 1. Introduction

In this procedure for separating manganese from fission-product solutions, manganese is finally precipitated as  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  after standard decontamination steps. No detectable contamination was found in the manganese separated from  $2.5 \times 10^{14}$  fissions 1-h old.

### 2. Reagents

Manganese carrier: 10 mg manganese/ml, added as  $\text{MnCl}_2$  in  $\text{H}_2\text{O}$ ; standardized

Tungsten carrier: 10 mg tungsten/ml, added as  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3$  in 1M HCl

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in 1M HCl

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 1M HCl

HCl: conc; 6M

$\text{HNO}_3$ : conc

$\text{HC}_2\text{H}_3\text{O}_2$ : glacial

$\text{NH}_4\text{OH}$ : conc; 0.1M

NaOH: 10M

$\text{H}_2\text{S}$ : gas

$\text{NaBrO}_3$ : saturated solution

$(\text{NH}_4)_2\text{S}$ : 20% solution

$(\text{NH}_4)_2\text{HPO}_4$ : 1.5M

Aerosol: 0.1% in  $\text{H}_2\text{O}$

Dowex AG 50-X4, 100 to 200 mesh, cation-exchange resin; slurry in  $\text{H}_2\text{O}$

Dowex AG 1-X8, 50 to 100 mesh, anion-exchange resin; slurry in 6M HCl

Ethanol: absolute

### 3. Preparation and Standardization of Carrier

Dissolve 22.9 g of  $\text{MnCl}_2$  in  $\text{H}_2\text{O}$  and dilute the solution to 1 l. Pipette exactly 2 ml of the solution into a 40-ml glass centrifuge tube, add 5 drops

of conc HCl, 3 ml of 1.5M  $(\text{NH}_4)_2\text{HPO}_4$ , and make alkaline with conc  $\text{NH}_4\text{OH}$ . Heat to boiling, let stand for 10 min, and filter the precipitate into a weighed sintered glass crucible. Wash the precipitate first with 0.1M  $\text{NH}_4\text{OH}$  and then with ethanol. Dry at 110°C, cool, and weigh as  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ .

Four standardizations using the above procedure gave results with a total spread of 1%.

### 4. Procedure

*Step 1.* Add the sample to 2.0 ml of manganese carrier in a 40-ml glass centrifuge tube and adjust the volume to ~20 ml with conc  $\text{HNO}_3$ .

*Step 2.* Add 5 drops of tungsten carrier and heat on a steam bath for 5 to 10 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and repeat the tungsten scavenge.

*Step 3.* To the supernate from the second tungsten scavenge, add 3 ml of saturated  $\text{NaBrO}_3$  and heat on a steam bath. ( $\text{MnO}_2$  begins to precipitate and the solution fizzes.) Carefully add another 3 ml of  $\text{NaBrO}_3$  and heat on a steam bath until the total time of heating is ~10 min. Cool the solution, add  $\text{H}_2\text{O}$  to fill the tube, and centrifuge. Discard the supernate, wash the precipitate twice with  $\text{H}_2\text{O}$ , and discard the washings.

*Step 4.* To the precipitate add 2 drops of iron carrier and 6 ml of conc HCl and boil over a burner until the volume of solution is ~3 ml. Dilute to 20 ml with  $\text{H}_2\text{O}$ , add conc  $\text{NH}_4\text{OH}$  dropwise until  $\text{Fe}(\text{OH})_3$  precipitates, and then add 1 to 2 drops in excess. Heat on a steam bath for ~2 min and centrifuge. Transfer the supernate to a clean centrifuge tube and repeat the iron scavenge. Centrifuge and transfer the supernate to a clean centrifuge tube.

*Step 5.* Add 2 ml of 20%  $(\text{NH}_4)_2\text{S}$ , heat for 1 to 2 min on a steam bath, and centrifuge. Discard the supernate. The precipitate is  $\text{MnS}$ .



*Step 6.* To the precipitate add 5 ml of glacial  $\text{HC}_2\text{H}_3\text{O}_2$  and boil over a flame. Add 5 drops of palladium carrier, dilute to 20 ml with  $\text{H}_2\text{O}$ , place on a steam bath, and bubble in  $\text{H}_2\text{S}$ . Centrifuge and transfer the supernate to a clean centrifuge tube. To the supernate add 5 drops of palladium carrier, repeat the sulfide scavenge, and transfer the supernate to a clean centrifuge tube.

*Step 7.* To the supernate add 3 ml of 1.5M  $(\text{NH}_4)_2\text{HPO}_4$  and ~5 drops of conc HCl and boil. Add 2 drops of zirconium carrier, centrifuge, and transfer the supernate to a clean tube. Add 2 drops of zirconium carrier to the supernate, centrifuge, and transfer the supernate into a clean tube.

*Step 8.* To the supernate add conc  $\text{NH}_4\text{OH}$  dropwise until  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  precipitates and then heat on a steam bath for 3 to 5 min. Centrifuge and discard the supernate. Wash the precipitate with a full tube of  $\text{H}_2\text{O}$ , centrifuge, and discard the washings.

*Step 9.* Dissolve the precipitate in 2 to 3 drops of conc HCl, dilute to 5 to 7 ml with  $\text{H}_2\text{O}$ , and place on a Dowex AG 50-X4, 100 to 200 mesh, cation-exchange resin column (6-mm diam. and 3-cm length). Rinse the centrifuge tube with  $\text{H}_2\text{O}$  and add the rinsings to the resin. Wash the resin with several 2- to 3-ml portions of  $\text{H}_2\text{O}$  and discard all washings. Place the column on top of a Dowex AG 1-X8, 50 to 100 mesh, anion-exchange resin column (8-mm diam. and 4- to 5-cm length) so that the eluate from the cation column drips into the anion column. Add 6 to 9 ml of 6M HCl to the cation resin column. To the eluate from the anion column, which contains the manganese and is collected in a clean centrifuge tube, add 10M NaOH dropwise to precipitate  $\text{Mn}(\text{OH})_2$ . Centrifuge and discard the supernate.

*Step 10.* To the precipitate, add 10 ml of conc  $\text{HNO}_3$ , bring to a boil over a flame, and boil until the solution has lost any color. Repeat the tungsten scavenge (*Step 2*).

*Step 11.* Repeat *Step 9*.

*Step 12.* Repeat the iron scavenge (*Step 4*).

*Step 13.* Repeat the MnS precipitation (*Step 5*).

*Step 14.* Repeat the PdS scavenge (*Step 6*).

*Step 15.* Repeat the  $\text{Zr}_3(\text{PO}_4)_4$  precipitation (*Step 7*).

*Step 16.* To the supernate add conc  $\text{NH}_4\text{OH}$  dropwise until  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  precipitates and then heat on a steam bath for 3 to 5 min. Centrifuge, discard the supernate, and dissolve the precipitate in 4 to 5 drops of conc HCl. Dilute to 20 ml with  $\text{H}_2\text{O}$ , add a few drops of aerosol, and centrifuge. Transfer the supernate to a clean centrifuge tube and reprecipitate  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ . Filter onto a weighed filter circle. Wash the precipitate first with 0.1M  $\text{NH}_4\text{OH}$  and then with ethanol. Dry at 110°C, cool, weigh, and mount.

(October 1989)

# RHENIUM

B. P. Bayhurst

Ethanol: absolute  
Methyl red indicator solution

## 1. Introduction

This procedure was designed for the separation of rhenium from underground nuclear debris samples containing fission products. Steps in the analysis include (1)  $\text{LaF}_3$  and  $\text{La}(\text{OH})_3$  scavenges, (2)  $\text{Re}_2\text{S}_7$  precipitations, (3) passage of rhenium(VII) in 0.1M HCl solution through a cation-exchange resin column, (4) copper(II)- and iron(III)-8-quinolinate scavenges, and (5) removal of ruthenium(III) by precipitation of the hydroxide. The rhenium is finally precipitated as  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$ . The chemical yield is ~50%.

## 2. Reagents

Rhenium(VII) carrier:  $\text{KReO}_4$  in  $\text{H}_2\text{O}$ , corresponding to ~15 mg of  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4/\text{ml}$ ; standardized (see procedure for SEPARATION OF RHENIUM FROM TUNGSTEN)

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Copper(II) carrier: 10 mg copper/ml, added as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron(III) carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in dilute HCl

Ruthenium(III) carrier: 10 mg ruthenium/ml, added as  $\text{RuCl}_3$  in 0.1M HCl; probably contains some ruthenium(IV)

$\text{HNO}_3$ : fuming, conc

HCl: conc; 6M; 0.2M; 0.1M

HF: conc

HF-HCl solution: 5M in each

$\text{HC}_2\text{H}_3\text{O}_2$ : 6M

$\text{NH}_4\text{OH}$ : conc

NaOH: 10M

$\text{H}_2\text{S}$ : gas

$\text{H}_2\text{O}_2$ : 30%

8-quinolinol (8-hydroxyquinoline) reagent:  
5% solution in 2M  $\text{HC}_2\text{H}_3\text{O}_2$

$[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$  reagent: 1% aqueous solution

Cation-exchange resin: Dowex 50-X8, 100 to 200 mesh ( $\text{H}^+$  form)

## 3. Procedure

*Step 1.* Dissolve ~2 g of sample in a Teflon beaker by the successive addition of fuming  $\text{HNO}_3$ , conc HCl, and conc HF. The process is aided by heating, but the mixture is never taken to dryness (the  $\text{Re}_2\text{O}_7$  formed is volatile). Make the final solution ~4M in HF and transfer to a 40-ml plastic centrifuge tube. Centrifuge, transfer the supernate to a Teflon beaker, and discard the precipitate.

*Step 2.* To the supernate, add 20 ml of conc HCl and evaporate nearly to dryness. Add 20 ml of conc HF and again evaporate nearly to dryness. Repeat the HCl and HF treatments and then transfer the solution to a 40-ml plastic centrifuge tube. Dilute to 15 ml with  $\text{H}_2\text{O}$ .

*Step 3.* Add 3 drops of lanthanum carrier and heat on a steam bath for a few minutes. Centrifuge, transfer the supernate to a clean plastic tube, and discard the precipitate. Repeat the  $\text{LaF}_3$  scavenge until the precipitate no longer contains activity. Transfer the supernate from the final scavenge to a clean plastic tube.

*Step 4.* Heat the solution on a steam bath and saturate with  $\text{H}_2\text{S}$  for ~15 min. Stopper the tube and permit it to stand until the  $\text{Re}_2\text{S}_7$  formed has coagulated. Centrifuge and discard the supernate. Add 30 ml of HF-HCl solution to the  $\text{Re}_2\text{S}_7$  and saturate with  $\text{H}_2\text{S}$  on a steam bath. Centrifuge and discard the supernate. Add 30 ml of 6M HCl to the  $\text{Re}_2\text{S}_7$ , saturate again with  $\text{H}_2\text{S}$ , centrifuge, and discard the supernate.

*Step 5.* To the precipitate, add 1 ml of 10M NaOH and 5 to 6 drops of 30%  $\text{H}_2\text{O}_2$ . Heat on a steam bath until a clear solution ( $\text{ReO}_4^-$ ) is formed. Dilute with  $\text{H}_2\text{O}$  to 15 ml, add 2 drops of lanthanum carrier, and centrifuge. Transfer the supernate to a 40-ml glass centrifuge tube and discard the  $\text{La}(\text{OH})_3$  precipitate. Repeat

the  $\text{La}(\text{OH})_3$  scavenge three more times, each time transferring the supernate to a clean glass centrifuge tube.

*Step 6.* Evaporate the supernate to  $\sim 2$  ml and neutralize to a methyl red end point with conc HCl. Add an equal volume of 0.2M HCl and pass the solution through a Dowex 50-X8, 100 to 200 mesh, cation-exchange resin column ( $\text{H}^+$  form). Collect the effluent in a glass centrifuge tube. Wash the column with 20 ml of 0.1M HCl and collect the effluent in the same tube.

*Step 7.* Evaporate the solution to  $\sim 2$  ml and dilute to 15 ml with  $\text{H}_2\text{O}$ . Add 2 ml of 8-quinolinol reagent and adjust the pH to 6 with 10M NaOH. Add 2 drops of copper(II) carrier and heat to coagulate the precipitate. [The copper(II)-8-quinolate carries down a substantial amount of contaminant activity.] Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate. Repeat the copper(II)-8-quinolate scavenge, but after centrifugation, filter the supernate through filter paper and collect the filtrate in a clean glass tube.

*Step 8.* To the filtrate, add 2 ml of 6M  $\text{HC}_2\text{H}_3\text{O}_2$  and 2 drops of iron(III) carrier; heat on a steam bath until the precipitate coagulates. [The precipitate of iron(III)-8-quinolate carries down molybdenum activity.] Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate. Repeat the iron(III)-8-quinolate scavenge twice. After the last centrifugation, filter the supernate through filter paper and collect the filtrate in a 40-ml plastic centrifuge tube.

*Step 9.* To the filtrate, add 5.5 ml of conc HF and 8 ml of conc HCl. Heat on a steam bath and saturate with  $\text{H}_2\text{S}$  for 15 min. Stopper the centrifuge tube and permit the  $\text{Re}_2\text{S}_7$  to coagulate. Treat the precipitate with HF-HCl solution and 6M HCl as described in *Step 4*.

*Step 10.* Dissolve the  $\text{Re}_2\text{S}_7$  with 10M NaOH and 30%  $\text{H}_2\text{O}_2$  as in *Step 5*. Use  $\text{H}_2\text{O}$  to transfer the perrhenate solution to a 125-ml erlenmeyer flask. Boil the solution until all the  $\text{H}_2\text{O}_2$  has been decomposed. Add 5 ml of absolute ethanol and 2 ml of 10M NaOH; heat on a hot plate and then add 2 drops of ruthenium(III) carrier. Boil on a hot plate until  $\text{Ru}(\text{OH})_3$  has precipitated completely and the solution has no color. Transfer the mixture to a glass centrifuge tube, centrifuge, and pour the supernate into a clean erlenmeyer flask. Discard the precipitate. Repeat the  $\text{Ru}(\text{OH})_3$  scavenge twice, adding ethanol each time to ensure that any ruthenium(IV) in the carrier is reduced to ruthenium(III).

*Step 11.* Evaporate the perrhenate solution in a glass centrifuge tube to  $\sim 2$  ml, make it 9 to 10M in HCl, and heat for 30 min on a steam bath (to convert any technetium to the +4 oxidation state). Saturate with  $\text{H}_2\text{S}$  for 15 min, centrifuge, and discard the supernate. Wash the  $\text{Re}_2\text{S}_7$  precipitate with 20 ml of 6M HCl and discard the wash.

*Step 12.* Add 1 ml of conc  $\text{NH}_4\text{OH}$  and 5 to 6 drops of 30%  $\text{H}_2\text{O}_2$  to the sulfide. Heat on a steam bath until the solution is completely clear and dilute it to 15 ml with  $\text{H}_2\text{O}$ . Add 4 ml of  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$  reagent, boil the mixture for 2 min, then cool in an ice bath. Filter the  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$  through a weighed filter circle. Wash the precipitate with cold  $\text{H}_2\text{O}$  and then with cold absolute ethanol. Dry in an oven at  $110^\circ\text{C}$  for 5 min, cool, weigh, and mount for counting.

(October 1989)

# THE SEPARATION OF RHENIUM FROM TUNGSTEN

B. P. Bayhurst

## 1. Introduction

In this procedure for the separation of rhenium activity from radioactive tungsten (which has already been decontaminated), the major purification step is the precipitation of  $\text{Re}_2\text{S}_7$  from a medium that is  $\sim 5M$  in both  $\text{HCl}$  and  $\text{HF}$ . The chemical yield is  $\sim 80\%$ .

## 2. Reagents

Rhenium carrier:  $\text{KReO}_4$  in  $\text{H}_2\text{O}$ , corresponding to  $\sim 15$  mg of  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4/\text{ml}$ ; standardized

Tungsten carrier: 10 mg tungsten/ml, added as  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : conc;  $6M$

$\text{HF}$ : conc

$\text{HF-HCl}$ :  $5M$  in each

$\text{H}_2\text{S}$ : gas

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{O}_2$ : 30%

$\text{NaCl}$ :  $5M$

$[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$ : 1% aqueous solution

Ethanol: absolute

## 3. Preparation and Standardization of Carrier

Dissolve 6.85 g of  $\text{KReO}_4$  in  $\text{H}_2\text{O}$  and dilute the solution to 1 l. Pipette 5.0 ml of the solution into a 40-ml glass centrifuge tube, dilute to 20 ml with  $\text{H}_2\text{O}$ , and make the solution  $0.5M$  in  $\text{NaCl}$ . Add 7 ml of 1%  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$ , bring the solution to a boil, and then cool it overnight in a refrigerator. Filter through a weighed, fritted glass crucible and wash the precipitate with ice water. Dry in an oven at  $110^\circ\text{C}$  for 20 min, cool, and weigh as  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$ .

Four standardizations agreed with each other within  $<1\%$ .

## 4. Procedure

*Step 1.* To  $\sim 10$  ml of a slightly alkaline solution of the tungsten in a 40-ml glass centrifuge tube, add 2.0 ml of rhenium carrier and allow the solution to stand for the desired growth period. Make the solution  $6M$  in  $\text{HCl}$  and heat on a steam bath for 15 min to permit the precipitated  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  to coagulate. Centrifuge and transfer the supernate to a clean centrifuge tube.

*Step 2.* To the supernate, add 2 ml of tungsten holdback carrier, heat on a steam bath for 5 to 10 min, centrifuge, and transfer the supernate to a clean 40-ml plastic centrifuge tube. Discard the precipitate.

*Step 3.* Make the solution  $\sim 5M$  in both  $\text{HF}$  and  $\text{HCl}$ . Add 2 ml of tungsten carrier and saturate with  $\text{H}_2\text{S}$  for at least 10 min while heating the solution on a steam bath. Centrifuge and discard the supernate. To the  $\text{Re}_2\text{S}_7$  precipitate add 30 ml of  $\text{HF-HCl}$  mixture, saturate with  $\text{H}_2\text{S}$ , centrifuge, and discard the supernate.

*Step 4.* To the precipitate add 1 ml of conc  $\text{NH}_4\text{OH}$  and 5 to 6 drops of 30%  $\text{H}_2\text{O}_2$ . Let the mixture stand on a steam bath, while stirring, until solution is complete. Add 30 ml of the  $\text{HF-HCl}$  mixture and heat on a steam bath for 5 min.

*Step 5.* Saturate the solution, still on the steam bath, for at least 5 min with  $\text{H}_2\text{S}$ . Centrifuge and discard the supernate. Wash the precipitate with 20 to 30 ml of  $6M$   $\text{HCl}$  and discard the washings.

*Step 6.* To the precipitate add 1 ml of conc  $\text{NH}_4\text{OH}$  and 5 to 6 drops of 30%  $\text{H}_2\text{O}_2$ . Heat on a steam bath to dissolve the  $\text{Re}_2\text{S}_7$  and transfer the solution to a clean 40-ml glass centrifuge tube. Make the solution acidic with  $\text{HCl}$  and boil over a burner for a few min to ensure complete removal of  $\text{H}_2\text{O}_2$ .

*Step 7.* Add 4 drops of lanthanum carrier, make the solution alkaline with conc  $\text{NH}_4\text{OH}$ , centrifuge, and transfer the supernate to a clean centrifuge tube. Discard the precipitate.

*Step 8.* To the supernate add 1 to 2 ml of 5M NaCl, 3 ml of 1%  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$ , and bring the solution to a boil. Cool and filter the  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$  through a weighed filter circle. Wash the precipitate with  $\text{H}_2\text{O}$  and a small amount of absolute ethanol. Dry in an oven at  $110^\circ\text{C}$  for 5 min, cool, weigh, mount, and count.

(October 1989)

# IRON

J. S. Gilmore

## 1. Introduction

In the separation of radioiron from fission products, high-order decontamination is obtained by the precipitation of FeS from an ammoniacal medium containing tartrate as a complexing ion. Further decontamination is effected by acid sulfide scavenging, followed by extraction of iron(III) into isopropyl ether from HCl solution. Iron is finally electroplated from solution. The chemical yield is ~50%.

## 2. Reagents

Iron carrier: 10 mg iron/ml, added as FeCl<sub>3</sub>•6H<sub>2</sub>O in 1M HCl; standardized

Antimony(III) carrier: 100 mg antimony/ml, added as SbCl<sub>3</sub> in 3M HCl

Tin(II) carrier: 100 mg tin/ml, added as SnCl<sub>2</sub> in 3M HCl

Tellurium(IV) carrier: 10 mg tellurium/ml, added as TeCl<sub>4</sub> in 3M HCl

Thallium(III) carrier: 10 mg thallium/ml, added as TlCl<sub>3</sub> in H<sub>2</sub>O

I<sup>-</sup> carrier: 100 mg I<sup>-</sup>/ml, added as KI in H<sub>2</sub>O

HCl: 0.2M; 8M; conc

HNO<sub>3</sub>: conc

Tartaric acid: saturated aqueous solution

NH<sub>4</sub>OH: conc

(NH<sub>4</sub>)<sub>2</sub>S: saturated solution

(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> reagent: 392.5 g of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in 175 ml of conc NH<sub>4</sub>OH; diluted to 1 l

NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> reagent: 230 g NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>/l

Br<sub>2</sub>: liquid

Aerosol: 0.1% aqueous solution

Isopropyl ether (alcohol-free)

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Weigh out 48.4 g of FeCl<sub>3</sub>•6H<sub>2</sub>O and make up to 1 l in 1M HCl. Pipette 5.0 ml into an electroplating cell and add conc NH<sub>4</sub>OH dropwise until Fe(OH)<sub>3</sub> begins to precipitate. Add 1 ml of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> reagent and 10 ml of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> reagent. Plate onto a weighed 1-in. platinum disk at 2 A and 70°C for 90 min. Wash the plate with H<sub>2</sub>O and with 95% ethanol. Dry in an oven at 100°C for 5 min, cool, and weigh.

Four standardizations were performed; results agreed within 1%.

## 4. Procedure

*Step 1.* To the sample in a 40-ml glass centrifuge tube, add 4.0 ml of standard iron carrier. Make the solution ammoniacal with conc NH<sub>4</sub>OH and add 5 ml of (NH<sub>4</sub>)<sub>2</sub>S solution. Centrifuge and discard the supernate.

*Step 2.* Dissolve the FeS precipitate in 3 to 4 drops of conc HCl and boil the solution to drive off H<sub>2</sub>S. Add 1 ml of tellurium(IV) carrier, 1 drop each of tin(II) and antimony(III) carriers, and 20 ml of 0.2M HCl. Add 1 drop of aerosol solution and saturate with H<sub>2</sub>S. Filter into a clean 40-ml centrifuge tube and discard the precipitate.

*Step 3.* To the filtrate add 1 to 2 ml of saturated tartaric acid and 5 ml of (NH<sub>4</sub>)<sub>2</sub>S solution. Centrifuge and discard the supernate.

*Step 4.* Dissolve the precipitate in 3 to 4 drops of conc HCl and oxidize the Fe<sup>2+</sup> ion with 1 to 2 drops of conc HNO<sub>3</sub>. Evaporate the solution to dryness; add 3 to 4 drops of conc HCl, and again evaporate to dryness. Use 10 ml of 8M HCl to transfer the FeCl<sub>3</sub> to a 125-ml separatory funnel. Add 30 ml

of isopropyl ether, shake for 1 min, and discard the aqueous phase. Add 10 ml of H<sub>2</sub>O to the ether phase and shake for 1 min. Transfer the aqueous phase to a 40-ml centrifuge tube and discard the ether layer.

*Step 5.* To the aqueous phase add 1 ml of saturated tartaric acid and 5 ml of (NH<sub>4</sub>)<sub>2</sub>S solution. Centrifuge and discard the supernate.

*Step 6.* To the FeS precipitate add 3 to 4 drops of conc HCl and boil to remove H<sub>2</sub>S. Add 1 drop of antimony(III) carrier and 3 to 4 drops of liquid Br<sub>2</sub>. Boil off excess Br<sub>2</sub>, and add 1 ml of thallium(III) carrier and 1 ml of I<sup>-</sup> carrier (Note 1). Make the solution up to a volume of 20 ml with 0.2M HCl, add 1 drop of aerosol solution, and saturate with H<sub>2</sub>S. Filter into a 40-ml centrifuge tube and discard the precipitate.

*Step 7.* Repeat Steps 3 through 5.

*Step 8.* Dissolve the FeS precipitate in 1 ml of conc HCl. Boil, add 1 ml of tellurium(IV) carrier, and boil again (Note 2). Dilute the solution to 20 ml with 0.2M HCl. Add 1 drop each of tin(II) and antimony(III) carriers and 1 drop of aerosol solution; saturate with H<sub>2</sub>S. Filter into a 40-ml centrifuge tube and discard the precipitate.

*Step 9.* Repeat Steps 3 through 6.

*Step 10.* Repeat Steps 3 and 4.

*Step 11.* Filter the aqueous layer into a clean 40-ml centrifuge tube and precipitate Fe(OH)<sub>3</sub> with conc NH<sub>4</sub>OH. Centrifuge and discard the supernate.

*Step 12.* To the precipitate add 1 ml of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> reagent and 10 ml of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> reagent; warm to dissolve the Fe(OH)<sub>3</sub>. Transfer the solution to a plating cell.

*Step 13.* Plate on a 1-in. platinum disk for 1 h at 2 A and 70°C. Wash the plate with H<sub>2</sub>O and with 95% ethanol. Dry in oven at 100°C for 5 min. Cool, weigh, and beta-count.

## Notes

1. To promote exchange between radioantimony and carrier, antimony(III) is first oxidized to antimony(V) by Br<sub>2</sub>, and the pentapositive antimony is then reduced by I<sup>-</sup> ion. In the next operation, H<sub>2</sub>S reduces thallium(III) to thallium(I), which is then precipitated as the iodide.

2. When the solution containing tellurium carrier is boiled with conc HCl, any tellurium(VI) present is reduced to the +4 state. This operation promotes exchange.

(October 1989)

# RUTHENIUM

M. A. Melnick

## 1. Introduction

Radioruthenium is separated from other fission products by oxidation to the tetroxide,  $\text{RuO}_4$ , and distillation of this volatile oxide. The oxidation is effected by means of a mixture of  $\text{HClO}_4$  and  $\text{NaBiO}_3$  in the presence of red fuming  $\text{HNO}_3$ . The bismuthate converts the halogens to their nonvolatile oxoacids. The  $\text{RuO}_4$  is distilled into  $\text{NaOH}$  solution and the ruthenium is precipitated as a mixture of oxides,  $\text{Ru}_2\text{O}_3$  and  $\text{RuO}_2$ , by reduction with ethanol. These oxides are dissolved in  $\text{HCl}$  and elementary ruthenium is precipitated by means of magnesium metal. The chemical yield is  $\sim 70\%$ .

## 2. Reagents

Ruthenium carrier: 10 mg ruthenium/ml, added as a mixture of  $\text{RuCl}_3$  and  $\text{RuCl}_4$  in 0.1M  $\text{HCl}$ ; standardized

$\text{I}^-$  carrier: 10 mg  $\text{I}^-$ /ml, added as  $\text{KI}$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : 0.1M; 1M; 6M; conc

$\text{HNO}_3$ : red fuming

$\text{HClO}_4$ : 70%

$\text{H}_3\text{PO}_4$ : 85%

$\text{NaOH}$ : 6M

$\text{NaBiO}_3$ : solid

Magnesium metal: powder

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 26 g of commercial ruthenium chloride (a mixture of the hydrated trichloride and tetrachloride) in 1 l of 0.1M  $\text{HCl}$ .

Pipette 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask and add  $\sim 0.4$  g of powdered magnesium metal in portions; shake after each addition. Dissolve the excess magnesium metal in conc  $\text{HCl}$  and decant the resulting supernate carefully. Add 20 ml of 1M  $\text{HCl}$  and

swirl. Filter the ruthenium metal onto a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate twice with 5-ml portions of  $\text{H}_2\text{O}$  and twice with 5-ml portions of 95% ethanol. Dry for 15 min at  $110^\circ\text{C}$ , cool, and weigh.

Four standardizations were performed, and results agreed within 0.5%.

## 4. Procedure

*Step 1.* Pipette an aliquot of the sample into the distillation flask (see Fig. 1). Add 2.0 ml of ruthenium carrier, 1 ml of  $\text{I}^-$  holdback carrier, 6 ml of red fuming  $\text{HNO}_3$ , 0.4 g of  $\text{NaBiO}_3$ , 1 ml of 85%  $\text{H}_3\text{PO}_4$  (Note 1), and 10 ml of 70%  $\text{HClO}_4$ . Keep the flask in a hot  $\text{H}_2\text{O}$  bath until the solution is a light amber color.

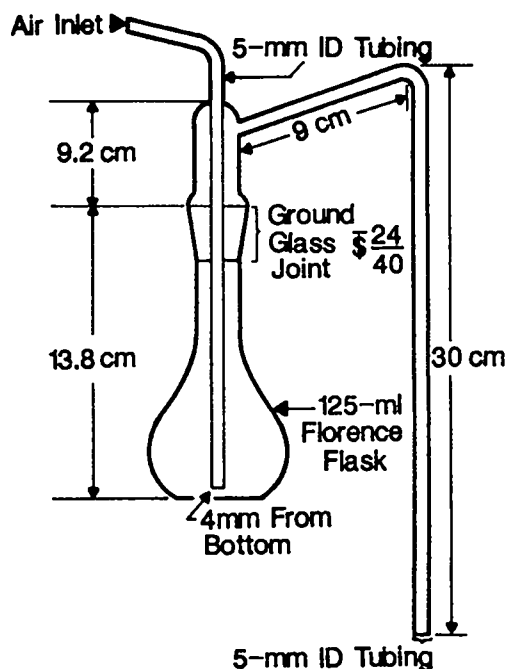


Fig. 1. Ruthenium distilling flask.

*Step 2.* Heat the distilling flask over a Bunsen burner and catch the first 2 ml of distillate in a 40-ml glass centrifuge tube containing 10 ml of 6M  $\text{NaOH}$ . Discard this portion of the distillate.



*Step 3.* Place as the receiver a clean 40-ml centrifuge tube that contains 20 ml of 6M NaOH and is cooled in an ice bath. Continue the distillation until all the RuO<sub>4</sub> has come over. (At this stage, the solution in the distilling flask will be colorless.)

*Step 4.* To the distillate add 3 ml of 95% ethanol, heat to boiling, and centrifuge the mixture of precipitated ruthenium oxides (Note 2). Discard the supernate.

*Step 5.* Dissolve the precipitate by heating with 2 ml of 6M HCl. Transfer the resulting solution to a 125-ml erlenmeyer flask and add ~0.3 g of magnesium powder in portions. Dissolve unreacted magnesium powder in a minimum of conc HCl and carefully decant the supernate. Add 20 ml of H<sub>2</sub>O.

*Step 6.* Filter the ruthenium metal onto a weighed filter circle. Wash the metal twice with 5-ml portions of 95% ethanol. Dry at 110°C for 15 min, cool, weigh, and mount (Note 3).

#### Notes

1. The H<sub>3</sub>PO<sub>4</sub> is added to the distilling flask to prevent the slight volatilization of molybdenum by HClO<sub>4</sub>.

2. Technetium is volatilized, probably as Tc<sub>2</sub>O<sub>7</sub>. However, technetium(VII) is not reduced by ethanol; therefore, this element does not contaminate the ruthenium. Moreover, technetium activity is usually absent from most solutions because 5.9-h <sup>99</sup>Tc (daughter of 67-h <sup>99</sup>Mo) is the longest-lived technetium isotope prominent in fission.

3. The 42-d <sup>103</sup>Ru activity can be separated conveniently from 1-y <sup>106</sup>Ru because the <sup>103</sup>Ru activity is ~43 times as abundant as <sup>106</sup>Ru as a result of half-life and fission-yield factors. Ruthenium-103 also has about three times as many gamma rays as <sup>106</sup>Ru does. By using a scintillation counter and a 2000-mg aluminum absorber to

eliminate the 3.55-MeV beta from <sup>106</sup>Ru, it is possible to determine <sup>103</sup>Ru. Ruthenium-106 may be counted on a beta proportional counter that uses a 210-mg aluminum absorber to cut out the 0.68-MeV beta of <sup>103</sup>Ru. The 0.55-MeV gamma from <sup>103</sup>Ru is counted also, and must be corrected for by counting through a series of heavy aluminum absorbers (1600 to 2500 mg/cm<sup>2</sup>) and extrapolating the activity to 210-mg aluminum.

(October 1989)

# COBALT

W. H. Burgus

## 1. Introduction

Cobalt is separated from most fission products and specifically from nickel by precipitations: as potassium hexanitrocobaltate(III),  $K_3[Co(NO_2)_6]$ , from an  $HC_2H_3O_2$  medium. The  $NO_2^-$  ion, in this acid medium, is not only the complexing agent but also serves to oxidize cobalt(II) to the +3 state. A second precipitation of cobalt as the hexanitro complex is followed by appropriate scavenging steps, and cobalt is then extracted as the blue  $Co(SCN)_4^{2-}$  complex into an amyl alcohol-ethyl ether mixture; the extraction provides additional decontamination. The cobalt is back-extracted into an  $NH_3-H_2O$  solution and is precipitated as the sulfide. The sulfide is then dissolved, and cobalt is plated from strongly ammoniacal solution and is counted as the metal. Some decontamination occurs during the plating process. The chemical yield is 70 to 75%.

## 2. Reagents

Cobalt carrier: 10 mg cobalt/ml, added as  $Co(NO_3)_2 \cdot 6H_2O$  in very dilute  $HNO_3$ ; standardized

Nickel carrier: 10 mg nickel/ml, added as  $Ni(NO_3)_2 \cdot 6H_2O$  in very dilute  $HNO_3$

Palladium carrier: 10 mg palladium/ml, added as  $PdCl_2 \cdot 2H_2O$  in very dilute  $HCl$

Copper carrier: 10 mg copper/ml, added as  $CuCl_2 \cdot 2H_2O$  in  $H_2O$

Iron carrier: 10 mg iron/ml, added as  $FeCl_3 \cdot 6H_2O$  in very dilute  $HCl$

$HCl$ : conc

$HNO_3$ : conc

$H_2SO_4$ : conc

$HC_2H_3O_2$ : 6M; 3M

$KOH$ : 10M

$NH_4OH$ : conc

$NH_4SCN$ : solid; 1 g/2 ml  $H_2O$

$(NH_4)_2SO_4$ : solid

$KNO_2$ : solid

$H_2S$ : gas

Amyl alcohol-ethyl ether mixture: equal parts by volume

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 49.3 g of  $Co(NO_3)_2 \cdot 6H_2O$  in  $H_2O$ , add 1 ml of  $HNO_3$ , and dilute to 1 l with  $H_2O$ .

Pipette 5.0 ml of the above carrier solution into a 125-ml erlenmeyer flask, and add 5 ml of  $H_2O$  and 3 ml of conc  $H_2SO_4$ . Carefully boil down to copious  $SO_3$  fumes to remove  $NO_3^-$  ion. Cool, dilute to 8 to 10 ml with  $H_2O$ , and allow the solution to come to room temperature. Cautiously neutralize with conc  $NH_4OH$ , then add 1 ml in excess and allow to cool to room temperature. Transfer the solution quantitatively to a plating cell that contains a rotating platinum anode and a weighed, square platinum cathode; dilute to 15 ml with  $H_2O$ . Add ~2 g of solid  $(NH_4)_2SO_4$  and stir until the  $(NH_4)_2SO_4$  has dissolved. Plate out cobalt by continuous stirring. The current is initially kept at 0.10 A at ~3 V. During the first 30 min of plating, the current is gradually increased to 0.20 A and maintained at that level for the remainder of the plating process. (The optimum plating time is at least 3 h.) The cell is dismantled, and the cathode plate is removed and washed several times with distilled  $H_2O$  and once with ethanol. It is then air-dried and weighed.

Four standardizations were made and results agreed within ~0.2%.

## 4. Procedure

*Step 1.* To the sample in a 40-ml glass centrifuge tube, add sufficient  $H_2O$  to bring the volume to 20 ml. Add 3 ml of standard cobalt carrier and 1 ml of nickel carrier. Precipitate cobalt and nickel hydroxides by the addition of 10M  $KOH$  (Note 1). Centrifuge and wash the hydroxides with 15 ml of  $H_2O$ ; discard the supernate and washings.

*Step 2.* Dissolve the precipitate by warming with 3 ml of 6M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Dilute to 25 ml with H<sub>2</sub>O and cool to room temperature.

*Step 3.* Precipitate K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] by the addition of a reagent made by saturating 6 ml of 3M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with KNO<sub>2</sub>. Allow ~3 min for complete precipitation. Centrifuge, discard the supernate, wash the precipitate once with 30 ml of H<sub>2</sub>O, and discard the washings.

*Step 4.* Dissolve the K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] by the addition of several milliliters of conc HCl. Boil off the decomposition products. Add 1 ml of nickel carrier and dilute to 25 ml with H<sub>2</sub>O.

*Step 5.* Precipitate cobalt and nickel hydroxides with 10M KOH as in *Step 1*. Dissolve the hydroxides as in *Step 2*.

*Step 6.* Repeat *Step 3*.

*Step 7.* Dissolve the K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] in 4 to 5 ml of conc HCl, boiling almost to dryness. Add 2 drops of palladium and 4 drops of copper carriers. Dilute to 20 ml with H<sub>2</sub>O and make ~0.1M in HCl. Heat to boiling and pass in H<sub>2</sub>S for 5 min. Filter onto filter paper and catch the filtrate in a 125-ml erlenmeyer flask; discard the sulfide scavenging precipitate.

*Step 8.* Boil out H<sub>2</sub>S from the filtrate. Add 2 drops of palladium and 4 drops of copper carriers and dilute to 20 ml with H<sub>2</sub>O. Make 0.1M in HCl, heat to boiling, and pass in H<sub>2</sub>S for 5 min. Again remove sulfides by filtration (*Step 7*).

*Step 9.* Boil out H<sub>2</sub>S from the filtrate. This will require concentration almost to dryness (Note 2). Dilute to 25 ml with H<sub>2</sub>O and transfer quantitatively to 40-ml centrifuge tube. Add 4 drops of iron carrier and precipitate Fe(OH)<sub>3</sub> by addition of conc NH<sub>4</sub>OH; add ~0.5 ml of NH<sub>4</sub>OH in excess. Centrifuge and discard the Fe(OH)<sub>3</sub> scavenger; retain the supernate.

*Step 10.* Acidify the supernate with HCl. Add 4 drops of iron carrier and remove Fe(OH)<sub>3</sub> again by the addition of conc NH<sub>4</sub>OH (0.5 ml in excess). Centrifuge and discard the precipitate.

*Step 11.* Repeat *Step 10*.

*Step 12.* Acidify the supernate from *Step 10* with conc HCl, and add 1 ml in excess. Transfer to a 125-ml separatory funnel. Add 15 g of NH<sub>4</sub>SCN and shake until all the solid has dissolved. Extract the complex into 50 ml of amyl alcohol-ethyl ether mixture. Wash the organic layer twice with 10-ml portions of NH<sub>4</sub>SCN solution. Discard washings.

*Step 13.* Back-extract the cobalt into 20 ml of H<sub>2</sub>O to which 4 to 6 ml of conc NH<sub>4</sub>OH has been added. Discard the organic layer and transfer the aqueous layer to a 40-ml centrifuge tube.

*Step 14.* Precipitate CoS from solution by passing in H<sub>2</sub>S for 1 min. Centrifuge and discard the supernate.

*Step 15.* Transfer the CoS precipitate with 5 to 10 ml of H<sub>2</sub>O to a 125-ml erlenmeyer flask. Add 10 ml of conc HNO<sub>3</sub>. Boil nearly to dryness (1 to 2 ml). Add 3 ml of conc H<sub>2</sub>SO<sub>4</sub> and heat to SO<sub>3</sub> fumes. Cool and slowly add 5 to 10 ml of H<sub>2</sub>O. Cool again. Neutralize with conc NH<sub>4</sub>OH and add 1 ml in excess. Add 2 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, transfer to a plating cell, and electroplate cobalt on a weighed platinum foil. (For a circular foil of ~ $\frac{7}{8}$ -in. diam, begin plating at 3 to 4 V and 0.10 A. After the first 30 min, increase the current to 0.20 A. Plate for 2.5 to 3 h.) After plating, wash the platinum foil with distilled water and then with ethanol. Dry at room temperature, weigh, and count. The counting procedure depends on the isotope involved.

## Notes

1. The purpose of the initial precipitation by means of KOH is to remove the cobalt from the strongly acidic solution. For as complete a

precipitation of  $K_3[Co(NO_2)_6]$  as possible, mineral acids and oxidizing agents must be absent.

2. The  $H_2S$  is removed by boiling to prevent precipitation of cobalt as  $CoS$  when the  $Fe(OH)_3$  scavenging step is performed.

(October 1989)

# RHODIUM

J. S. Gilmore

## 1. Introduction

In the determination of radiorhodium, the principal decontamination steps include (a) removal of ruthenium as the volatile  $\text{RuO}_4$ , (b) extraction of iridium and platinum chlorides into TBP(tributyl phosphate) solution in *n*-hexane, (c) precipitation of  $\text{RhI}_3$ , and (d)  $\text{Fe}(\text{OH})_3$  and acid sulfide scavenges from solutions containing the extremely stable  $[\text{Rh}(\text{CN})_6]^{3-}$  complex ion. The rhodium is finally electroplated from  $\text{H}_2\text{SO}_4$  solution after destruction of the complex. The chemical yield is ~60%.

## 2. Reagents

Rhodium carrier: 10 mg rhodium/ml, added as  $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ ; standardized

Platinum carrier: 10 mg platinum/ml, added as  $\text{H}_2\text{PtCl}_6$  in dilute HCl

Cobalt carrier: 10 mg cobalt/ml, added as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1M HCl

Molybdenum carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$

Barium carrier: 10 mg barium/ml, added as  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Antimony(III) carrier: 10 mg antimony/ml, added as  $\text{SbCl}_3$  in 1M HCl

Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 1M HCl

HCl: 3M; 6M; conc

$\text{HNO}_3$ : conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HClO}_4$ : conc

$\text{NaOH}$ : 6M

$\text{NH}_4\text{OH}$ : conc

KCN: 3M

$\text{NaNO}_2$ : 5M

$\text{Na}_2\text{CO}_3$ : 0.5M

KCl: solid

$\text{Cu}(\text{NO}_3)_2$  solution: 100 mg copper/ml

KI: solid

$\text{H}_2\text{S}$ : gas

TBP (tributyl phosphate) solution: 5% solution in *n*-hexane

Ethanol: 95%

Methyl red indicator solution

## 3. Preparation and Standardization of Carrier

Weigh out 27.34 g of  $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$  and make up to 1 l in 0.01M HCl. Pipette 3 ml of the solution into a 125-ml erlenmeyer flask and add 3 ml of conc  $\text{H}_2\text{SO}_4$ , 2 ml of conc  $\text{HClO}_4$ , and 1 ml of conc  $\text{HNO}_3$ . Heat until  $\text{SO}_3$  fumes appear. Transfer the solution with 20 ml of  $\text{H}_2\text{O}$  to a plating cell that uses a weighed platinum disk as the cathode. Electroplate at room temperature and 0.1 A for 16 h (Note). Wash the cathode with  $\text{H}_2\text{O}$  and then with 95% ethanol. Dry at 110°C for 15 min, cool, and weigh.

Four standardizations gave results agreeing within 0.3%.

## 4. Procedure

*Step 1.* To a 125-ml erlenmeyer flask, add 3 ml of standard rhodium carrier, 1 ml each of platinum, molybdenum, and cobalt carriers and an aliquot of the sample.

*Step 2.* Add 5 ml of conc  $\text{HClO}_4$ , 1 ml of conc  $\text{HNO}_3$ , and heat to near dryness. Add 30 ml of 6M HCl.

*Step 3.* Add 1 to 2 g of solid KI and boil for 20 min; add 3M HCl as needed to keep the volume of solution approximately constant. Transfer to a 40-ml centrifuge tube, centrifuge, and discard the supernate. Wash the  $\text{RhI}_3$  precipitate with 20 ml of warm 3M HCl and discard the supernate.

*Step 4.* To the precipitate add 3 ml of 3M KCN, and heat until solution occurs. Add 1 ml of tellurium(IV) carrier and 2 ml of 6M HCl; heat to boiling. While heating, add 5M  $\text{NaNO}_2$  dropwise until  $\text{I}_2$  fumes are no longer visible.

*Step 5.* Dilute to 20 ml with H<sub>2</sub>O, add 3 drops of iron carrier, then add conc NH<sub>4</sub>OH until a precipitate barely forms. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

*Step 6.* Add 2 ml of conc NH<sub>4</sub>OH, 1 ml of barium carrier, and 3 ml of 0.5M Na<sub>2</sub>CO<sub>3</sub>; warm on a steam bath for 5 min. Add 3 drops of iron carrier, stir, and centrifuge. Transfer the supernate to a clean centrifuge tube and discard the precipitate.

*Step 7.* Add 2 drops of methyl red indicator solution and then add conc HCl dropwise until the solution is acidic. Add 1 ml of 6M HCl and 1 ml each of tellurium(IV) and antimony(III) carriers; saturate with H<sub>2</sub>S. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 8.* Boil the solution for ~30 s to remove H<sub>2</sub>S. Add 7 ml of conc HCl and 2 ml of Cu(NO<sub>3</sub>)<sub>2</sub> solution; cool in an ice bath. (The rhodium is precipitated, presumably as the compound Cu<sub>3</sub>[Rh(CN)<sub>6</sub>]<sub>2</sub>.) Centrifuge and discard the supernate.

*Step 9.* To the precipitate add 20 ml of H<sub>2</sub>O, warm the mixture, and then add sufficient 6M NaOH to convert all the copper to the insoluble oxide; this treatment leaves the rhodium cyano complex in solution as the sodium salt. When conversion is complete (the precipitate will be black and the solution colorless), centrifuge, transfer the supernate to a 125-ml erlenmeyer flask, and discard the precipitate.

*Step 10.* Add 3 ml of conc H<sub>2</sub>SO<sub>4</sub> and evaporate the solution to near dryness to destroy the rhodium-cyanide complex.

*Step 11.* Use 20 ml of H<sub>2</sub>O to transfer the solution to a 40-ml glass centrifuge tube. Add 6M NaOH dropwise to precipitate Rh(OH)<sub>3</sub> (pH~8). Centrifuge and discard the supernate.

*Step 12.* Add 3 drops of platinum carrier, 40 mg of KCl, 3 drops of conc HNO<sub>3</sub>, 1 ml of conc HCl, heat to effect solution, and then evaporate to dryness on a steam bath. Dissolve the residue in 20 ml of 6M HCl and transfer the solution to a 60-ml separatory funnel. Add 20 ml of TBP solution, shake for 1 min, let the phases separate, and discard the organic (upper) phase. Repeat the extraction with 20 ml of TBP solution.

*Step 13.* Repeat Steps 3 through 9.

*Step 14.* Repeat Steps 6 through 10.

*Step 15.* Add 2 ml of conc HClO<sub>4</sub> and 1 ml of conc HNO<sub>3</sub>; heat until SO<sub>3</sub> fumes evolve. Transfer to the plating cell with 20 ml of H<sub>2</sub>O. Electroplate at room temperature and 0.1 A for 16 h on a weighed platinum cathode disk. Wash the cathode with H<sub>2</sub>O and then with 95% ethanol. Dry in an oven at 110°C for 15 min. Cool, weigh, mount, and beta-count.

#### Note

The components of the plating cell must be extremely clean to obtain a smooth, adherent cathode deposit.

(October 1989)

## IRIDIUM

J. S. Gilmore

### 1. Introduction

This procedure describes the major steps for the analysis of radioactive iridium in underground nuclear test debris samples. The sample is fumed with conc  $\text{HClO}_4$ , a process that converts the iridium to polynuclear cationic species in which the element is in at least the +4 oxidation state. The complexed iridium is absorbed on a cation-exchange resin column and eluted with 4.5M HCl. After the element is converted to anionic chloro complexes in 0.05M HCl, it is passed again through a cation-exchange resin column. (The two exchange resin steps essentially remove all contaminants except the other platinum metals, molybdenum, and tellurium.) After molybdenum is extracted from solution in 7M HCl into diisopropyl ether, tellurium is reduced to the element state with  $\text{SO}_2$  and ruthenium is distilled as  $\text{RuO}_4$ . Iridium is oxidized to the tetrapositive state by means of  $\text{HNO}_3$  and extracted into TBP (tributyl phosphate) in *n*-hexane; Rh(III) is left behind. Iridium is reduced to the +3 state, and iodide complexes of dipositive palladium and platinum are extracted into TBP-*n*-hexane. Iridium is oxidized to the +4 condition and precipitated as  $\text{Cs}_2[\text{IrCl}_6]$ , in which form it is mounted for counting. Chemical yields of ~50% are obtained.

### 2. Reagents

Iridium carrier: yields 10 mg of  $\text{Cs}_2[\text{IrCl}_6]/\text{ml}$ .

Weigh out 3.596 g of  $\text{K}_2[\text{IrCl}_6]$  (dried to constant weight at 110°C) and dissolve in 500 ml of 2M HCl

Molybdenum carrier: 10 mg molybdenum/ml, added as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 6M HCl

Tellurium carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in dilute HCl

Rhodium carrier: 10 mg rhodium/ml, added as  $\text{Na}_3[\text{RhCl}_6]$  in 1M HCl

HCl: 0.05M; 1M; 4.5M; 6M; conc  
1M HCl-0.1M HF

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc; 1M

HF: conc

NaOH: 6M

KI: 4% aqueous solution

CsCl reagent: 4 g in 60 ml of 6M HCl

KCl: solid

TBP reagent: 50% by volume in *n*-hexane  
*n*-Hexane

Diisopropyl ether

$\text{SO}_2$ : gas

Ethanol: absolute

Dowex AG 50W-X8 cation-exchange resin, 100 to 200 mesh

### 3. Procedure

*Step 1.* To the pulverized sample (1 to 25 g) in a Teflon beaker, add 3 ml of iridium carrier and dissolve the material in a mixture of conc  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and HF. Fume down to a low volume of  $\text{HClO}_4$ , and to the cooled mixture add sufficient  $\text{H}_2\text{O}$  to make the solution 2M in  $\text{HClO}_4$ .

*Step 2.* Prepare a cation-exchange resin bed, 8 mm by 10 cm, in a plastic column that is fitted with a plug of Teflon turnings to support the resin. Wash the resin successively with 4.5M HCl,  $\text{H}_2\text{O}$ , and 1M  $\text{HClO}_4$ ; transfer the solution from *Step 1* to the top of the column. Permit the solution to pass through, and wash the column with 60 ml of 1M HCl-0.1M HF and then with 10 ml of 1M HCl. Discard the effluent. Add 40 ml of warm 4.5M HCl to the resin column and collect the effluent in a 150-ml beaker.

*Step 3.* Add 3 drops of molybdenum carrier and 1 ml of tellurium carrier and heat on a hot plate for 10 min. Transfer the solution to a 125-ml separatory funnel with sufficient HCl to make the final solution ~7M in acid. Extract twice with 50 ml of diisopropyl ether, discard the organic (upper) phase, and transfer the aqueous layer to a 150-ml beaker. Using an air jet, evaporate to a small volume on a hot plate, add 2 to 3 drops of conc  $\text{HNO}_3$ , and then evaporate to dryness on a steam bath.

*Step 4.* Prepare an 8-mm by 15-cm cation-exchange resin bed in a glass column. Wash the resin with 4.5M HCl and then with 0.05M HCl. Transfer the residue from *Step 3* to the resin with 15 ml of 0.05M HCl, and collect the effluent in a 125-ml erlenmeyer flask. Wash the resin with 5 ml of 0.05M HCl and combine the effluent with the previous one.

*Step 5.* Add 10 ml of conc HCl and 1 ml of tellurium carrier to the combined effluents and saturate the hot solution with SO<sub>2</sub>. Filter off the tellurium precipitate and collect the filtrate in a 125-ml erlenmeyer flask. Boil to expel SO<sub>2</sub>.

*Step 6.* Add 5 ml of conc HClO<sub>4</sub> and 2 ml of conc HNO<sub>3</sub>; evaporate to dense fumes of HClO<sub>4</sub>. (RuO<sub>4</sub> volatilizes.)

*Step 7.* Dilute the solution to 2M in HClO<sub>4</sub> and repeat *Step 2*.

*Step 8.* Add 2 drops of rhodium carrier and ~40 mg of KCl. Heat to effect solution and then evaporate to dryness in a steam bath. Add 3 ml of conc HCl and 3 drops of conc HNO<sub>3</sub>; evaporate to dryness again. Repeat the last evaporation process. (Iridium is converted to IrCl<sub>6</sub><sup>2-</sup>.) Dissolve the residue in 10 ml of 6M HCl and transfer the solution to a 60-ml separatory funnel by adding another 10 ml of 6M HCl. Add 20 ml of TBP reagent, shake for 1 min, and transfer the organic (upper) layer to a 40-ml glass centrifuge tube. Add 2 drops of conc HNO<sub>3</sub> to the aqueous phase, repeat the extraction with TBP, combine the organic phases, and discard the aqueous. Centrifuge and remove the trace of aqueous layer with a transfer pipette. To the combined organic phases add 2 ml of 6M HCl, let the mixture settle, and remove and discard the aqueous layer.

*Step 9.* Transfer the organic layer to a 125-ml separatory funnel, add 1 ml of 4% KI, shake, and allow to stand for 10 min. Add 20 ml of 6M HCl, shake well, and discard the organic phase. Wash the

aqueous phase with two 30-ml portions of *n*-hexane and discard the washes.

*Step 10.* Repeat *Step 8* but omit the addition of rhodium carrier and KCl.

*Step 11.* Transfer the organic layer to a 125-ml separatory funnel. Back-extract the iridium with two 40-ml H<sub>2</sub>O washes and discard the organic phase. Wash the aqueous phase twice with 30-ml portions of *n*-hexane and discard the washes. Transfer the aqueous phase to a 150-ml beaker, add 5 ml of conc HCl and a few drops of conc HNO<sub>3</sub>, and use an air jet to evaporate to near dryness on a hot plate. Then evaporate to dryness in a steam bath.

*Step 12.* Prepare and wash a cation-exchange resin column as in *Step 4*. Transfer the residue from *Step 11* to the column with 10 ml of 0.5M HCl, and collect the effluent in a 40-ml Vycor centrifuge tube. Wash the column with 10 ml of 0.05M HCl and combine the effluent with the previous one. Stir well and transfer half of the solution to a second 40-ml Vycor tube. To each tube add 10 ml of conc HCl and 1 ml of CsCl reagent. Heat for 2 h in a steam bath; add HCl as needed to prevent evaporation to <10 ml, and occasionally add 1 drop of conc HNO<sub>3</sub>. Centrifuge and discard the supernates. Wash each precipitate with 10 ml of 6M HCl, wash each twice with ethanol, and discard the washes. Using ethanol as the transfer agent, filter one of the precipitates onto a weighed filter circle. Dry the precipitate at 110°C for 10 min, weigh, mount, and count on an L x-ray counter. Carefully evaporate the last traces of ethanol from the second precipitate, dry in centrifuge tube at 110°C for 15 min, transfer to a previously weighed Teflon vial for NaI-well counting, and weigh (Note).



## Note

The isotope of mass 190 is determined from the part of the gamma spectrum with energy  $>1.4$  MeV. The isotope of mass 192 is calculated from the region between 0.32 and 1.4 MeV by subtracting the contribution from  $^{190}\text{Ir}$ . Similarly,  $^{193}\text{Ir}$  and  $^{189}\text{Ir}$  are derived from the L and K x-rays, respectively, by subtracting the other three isotopes.

(October 1989)

# NICKEL

W. H. Burgus

## 1. Introduction

Nickel is separated from fission products by precipitation with dimethylglyoxime (DMG) from an ammoniacal medium in the presence of a large quantity of citrate ion. Three precipitations are carried out in the presence of cobalt as a holdback carrier. After appropriate scavenging steps, the nickel is again precipitated with DMG, and the nickel-DMG complex is extracted into chloroform. The nickel is then back-extracted into dilute HCl solution and is finally plated out of strongly ammoniacal solution. The chemical yield is ~75%.

## 2. Reagents

Nickel carrier: 10 mg nickel/ml, added as  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$ ; standardized

Cobalt carrier: 10 mg cobalt/ml, added as  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$  in very dilute HCl

Copper carrier: 10 mg copper/ml, added as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute HCl

HCl: conc; 6M

$\text{HNO}_3$ : conc

$\text{H}_2\text{SO}_4$ : conc

$\text{NH}_4\text{OH}$ : conc

$(\text{NH}_4)_2\text{SO}_4$ : solid

Sodium citrate: 10% in  $\text{H}_2\text{O}$

$\text{H}_2\text{S}$ : gas

Dimethylglyoxime (DMG) reagent: .1% in 95% ethanol

Chloroform

Ethanol: 95%

## 3. Preparation and Standardization of Carrier

Dissolve 49.5 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , add 1 ml of  $\text{HNO}_3$ , and dilute to 1 l with  $\text{H}_2\text{O}$ .

Pipette 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask, add 3 ml of conc  $\text{H}_2\text{SO}_4$ , boil down to  $\text{SO}_3$  fumes to remove  $\text{NO}_3^-$  ion, and cool to room temperature. Dilute to 8 to 10 ml with  $\text{H}_2\text{O}$ , and cautiously neutralize with conc  $\text{NH}_4\text{OH}$ ; add 1 ml in excess. Add 1 g of  $(\text{NH}_4)_2\text{SO}_4$ , transfer quantitatively to a plating cell that contains a weighed platinum cathode and a platinum anode, and plate for 3 h at 0.10 A and ~3 V. Add 1 drop of conc  $\text{NH}_4\text{OH}$  about every 30 min. When the plating is complete, wash the cathode several times with distilled  $\text{H}_2\text{O}$  and once with ethanol. Air dry and weigh.

Four standardizations were carried out and results agreed within ~0.2%.

## 4. Procedure

*Step 1.* To 5 to 10 ml of the sample in a 40-ml centrifuge tube, add 2 ml of the standard nickel carrier, 10 drops of cobalt holdback carrier, and 10 ml of 10% sodium citrate solution (Note 1). Make ammoniacal by addition of conc  $\text{NH}_4\text{OH}$ . (A deep blue-violet color indicates that sufficient  $\text{NH}_4\text{OH}$  has been added.) Dilute to 25 ml with  $\text{H}_2\text{O}$ . Precipitate nickel by the addition of 15 ml of 1% alcoholic DMG reagent. Centrifuge and wash the precipitate with 30 ml of  $\text{H}_2\text{O}$  that contains 1 drop of conc  $\text{NH}_4\text{OH}$ . Discard the supernate and washings.

*Step 2.* Dissolve the nickel-DMG precipitate in 2 ml of conc HCl and dilute to 15 ml with  $\text{H}_2\text{O}$ . (Disregard any DMG that precipitates.) Add 10 ml of 10% sodium citrate, 2 drops of cobalt carrier, and 5 ml of DMG reagent. Precipitate nickel-DMG by adding conc  $\text{NH}_4\text{OH}$ . Centrifuge and wash as in *Step 1.*

*Step 3.* Repeat *Step 2*.

*Step 4.* Dissolve the nickel-DMG precipitate in 10 ml of conc HNO<sub>3</sub>, and transfer to a 125-ml erlenmeyer flask. Boil to dryness and heat to destroy all organic matter (Note 2). Dissolve NiO (black) in a few milliliters of conc HCl by heating. The solution process is aided by adding 1 to 2 drops of conc HNO<sub>3</sub>. Boil until NiCl<sub>2</sub> precipitates and then dilute to 20 ml with H<sub>2</sub>O. (Be certain that the heating is continued for sufficient time to remove HNO<sub>3</sub>.)

*Step 5.* Add 3 drops of conc HCl and 4 drops each of copper and palladium carriers. Heat to boiling and pass in H<sub>2</sub>S for 5 min. Filter the sulfide scavenger precipitate and discard.

*Step 6.* Boil out H<sub>2</sub>S, add 2 drops of conc HCl, add 4 drops each of copper and palladium carriers, dilute to 20 ml with H<sub>2</sub>O, heat, and remove another sulfide scavenger precipitate with H<sub>2</sub>S. Boil out H<sub>2</sub>S from the filtrate and transfer to a 40-ml centrifuge tube.

*Step 7.* Dilute to 20 ml with H<sub>2</sub>O. Add 8 drops of iron carrier and precipitate Fe(OH)<sub>3</sub> from a hot solution by the addition of conc NH<sub>4</sub>OH (1 ml in excess). Centrifuge and discard Fe(OH)<sub>3</sub> scavenger precipitate.

*Step 8.* Acidify the supernate with HCl or HNO<sub>3</sub>. Add 8 drops of iron carrier and remove a second Fe(OH)<sub>3</sub> scavenge. Transfer the supernate to a 100-ml beaker.

*Step 9.* To the supernate from the Fe(OH)<sub>3</sub> scavenge, add 10 ml of 10% sodium citrate and 1 drop of cobalt carrier. Add 15 ml of DMG solution and transfer to a 600-ml separatory funnel. Add 500 ml of CHCl<sub>3</sub> and extract nickel-DMG (Note 3).

*Step 10.* Wash the CHCl<sub>3</sub> layer twice with 50-ml portions of H<sub>2</sub>O that each contain 1 drop of conc NH<sub>4</sub>OH. Discard washings.

*Step 11.* Back-extract nickel into 20 ml of 6M HCl. Transfer the H<sub>2</sub>O layer to a 125-ml erlenmeyer flask (Note 4), and boil nearly to dryness. Add 4 to 5 ml of conc HNO<sub>3</sub>. Boil nearly to dryness. Add ~3 ml of conc H<sub>2</sub>SO<sub>4</sub> and heat to SO<sub>3</sub> fumes (Note 5). Cool to room temperature.

*Step 12.* Add 8 ml of H<sub>2</sub>O and cautiously neutralize with conc NH<sub>4</sub>OH (1 ml in excess). Add 1 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, dilute to 20 ml with H<sub>2</sub>O, and transfer to the plating cell. Plate nickel on a weighed platinum foil. (For a circular foil of  $\frac{7}{8}$ -in. diam, plate for 2 h at 0.10 A. Add 1 drop of conc NH<sub>4</sub>OH about every 30 min.) After plating, wash with H<sub>2</sub>O and then with ethanol. Air dry, weigh, and count (Note 6).

### Notes

1. Citrate is added to complex ions that give insoluble hydroxides and would, therefore, be coprecipitated with nickel.

2. When boiling down with conc HNO<sub>3</sub>, be certain to take to dryness, and then heat a little longer. All citrate and decomposition products of DMG must be removed; otherwise, it is impossible to precipitate Fe(OH)<sub>3</sub> in *Step 7*.

3. Freshly precipitated nickel-DMG ordinarily extracts rapidly into CHCl<sub>3</sub>. If it does not do so, add a further 50 ml of CHCl<sub>3</sub> and shake the separatory funnel vigorously. The CHCl<sub>3</sub> and H<sub>2</sub>O layers do not separate quickly, and at least 5 min should be allowed for the emulsion to break and the separation to occur.

4. The complete disappearance of the yellow-orange color of nickel-DMG in the CHCl<sub>3</sub> layer indicates that back-extraction is complete.

5. For successful plating, all organic material and nitrates must be removed.

6. If 36-h <sup>57</sup>Ni is being counted, mount the sample and cover with 1-mil Dural to absorb the radiations of 2 × 10<sup>5</sup>-yr <sup>59</sup>Ni and 300-yr <sup>63</sup>Ni.

(October 1989)

# PALLADIUM

E. J. Lang

## 1. Introduction

Radiopalladium is separated from fission products by three times carrying out the sequence of PdS precipitation, palladium dimethylglyoximate precipitation, and AgCl and Fe(OH)<sub>3</sub> scavenges. The palladium is then precipitated as the sulfide and converted again to the dimethylglyoxime complex, Pd(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>, in which form it is weighed. The chemical yield is 60 to 70%.

## 2. Reagents

Palladium carrier: 10 mg palladium/ml, added as PdCl<sub>2</sub> in H<sub>2</sub>O; standardized

Silver carrier: 10 mg silver/ml, added as AgNO<sub>3</sub> in H<sub>2</sub>O

Iron carrier: 10 mg iron/ml, added as FeCl<sub>3</sub>•6H<sub>2</sub>O in very dilute HCl

HCl: 0.4M; 6M; conc

HNO<sub>3</sub>: conc

NH<sub>4</sub>OH: conc

H<sub>2</sub>S: gas

Dimethylglyoxime (DMG) reagent: 1% solution in 95% ethanol

Aerosol: 0.1% in H<sub>2</sub>O

Ethanol: absolute

## 3. Preparation and Standardization of Carrier

Dissolve 16.65 g of PdCl<sub>2</sub> in H<sub>2</sub>O and dilute the solution to a volume of 1 l. Pipette 5.0 ml of the carrier solution into a 40-ml glass centrifuge tube and make the solution 0.4M in HCl. Add 5 ml of 1% DMG reagent and stir thoroughly. Filter the palladium-DMG precipitate through a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate with small quantities of H<sub>2</sub>O and absolute ethanol. Dry at 110°C for 15 min, cool, and weigh as Pd(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>.

Four standardizations were carried out. Results agreed within 0.5%.

## 4. Procedure

*Step 1.* Pipette an aliquot of the sample into a 40-ml glass centrifuge tube, add 2.0 ml of palladium carrier, and make the solution 6M in HCl.

*Step 2.* Heat and pass in H<sub>2</sub>S to precipitate PdS. Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate by boiling with 0.8 ml of conc HNO<sub>3</sub> and add 0.15 to 0.5 ml of conc HCl.

*Step 4.* Take the solution close to dryness by heating over a flame.

*Step 5.* Add 20 ml of 0.4M HCl and stir. (The solution should be clear. Heating may be necessary to effect complete solution.)

*Step 6.* Add 5 ml of DMG reagent and 1 drop of aerosol. Centrifuge and discard the supernate.

*Step 7.* Dissolve the precipitate in 1 ml of conc HNO<sub>3</sub>, boil nearly to dryness, add 2 ml of conc HCl, and boil nearly to dryness. Add 15 ml of H<sub>2</sub>O, heat to boiling, and hold at boiling for 1 min.

*Step 8.* Add 1 drop of conc HCl and 2 ml of silver carrier. Heat and stir to coagulate the AgCl precipitate. Centrifuge and transfer the supernate to a clean centrifuge tube.

*Step 9.* To the supernate add 1 ml of iron carrier, make the solution alkaline with conc NH<sub>4</sub>OH, centrifuge, and transfer the supernate to a clean centrifuge tube.

*Step 10.* Make the supernate 6M in HCl by addition of the conc acid.

*Step 11.* Repeat Steps 2 through 10 twice.

*Step 12.* Heat the solution and pass in  $\text{H}_2\text{S}$ . Centrifuge and discard the supernate.

*Step 13.* Dissolve the PdS precipitate in 1 ml of conc  $\text{HNO}_3$  and take the solution almost to dryness by heating over a flame. Add 20 ml of 0.4M HCl, stir, and centrifuge. Transfer the supernate to a clean centrifuge tube.

*Step 14.* To the supernate add 5 ml of DMG reagent and 1 drop of aerosol. Centrifuge and discard the supernate. Wash the precipitate by centrifugation first with 30 ml of 0.4M HCl and then with 30 ml of absolute ethanol. With the aid of ethanol, transfer the precipitate onto a weighed filter circle. Wash with small portions of  $\text{H}_2\text{O}$  and absolute ethanol. Dry at  $110^\circ\text{C}$  for 5 min, cool, weigh, and mount. Count the betas from  $^{109}\text{Pd}$  and  $^{112}\text{Pd}$ .

(October 1989)

## SILVER

E. J. Lang

### 1. Introduction

Silver is initially separated from other fission products by the specific precipitation of the chloride from HNO<sub>3</sub> solution. The silver is then purified by Fe(OH)<sub>3</sub> scavenging and Ag<sub>2</sub>S precipitation, both of which are performed in ammoniacal solution. After repetition of the scavenging-precipitation cycle, the silver is converted to the oxide and finally to the iodate, AgIO<sub>3</sub>, in which form it is counted. The chemical yield exceeds 80%.

### 2. Reagents

Silver carrier: primary standard, 10 mg silver/ml,  
added as AgNO<sub>3</sub> in very dilute HNO<sub>3</sub>  
Iron carrier: 10 mg iron/ml, added as  
FeCl<sub>3</sub>•6H<sub>2</sub>O in very dilute HCl  
HCl: conc  
HNO<sub>3</sub>: conc  
H<sub>2</sub>SO<sub>4</sub>: conc  
HIO<sub>3</sub>: 2M  
NaOH: 6M  
NH<sub>4</sub>OH: conc  
(NH<sub>4</sub>)<sub>2</sub>S: saturated solution  
Ethanol: 95%

### 3. Preparation of Carrier

Dissolve 15.75 g of AgNO<sub>3</sub>, primary standard grade, in a minimum amount of H<sub>2</sub>O, add a few drops of HNO<sub>3</sub>, and dilute the solution to 1 l.

### 4. Procedure

*Step 1.* (Note 1.) To the sample in a 40-ml glass centrifuge tube, add exactly 2 ml of silver carrier and 5 ml of conc HNO<sub>3</sub> and dilute the solution to 20 ml with H<sub>2</sub>O. Heat to boiling and precipitate AgCl by the addition of 4 drops of conc HCl. Heat until the AgCl has coagulated; cool, centrifuge, and discard the supernate.

*Step 2.* Dissolve the AgCl in 2 ml of conc NH<sub>4</sub>OH, dilute to 20 ml with H<sub>2</sub>O, and add 1 ml of iron carrier. Stir, centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

*Step 3.* To the solution add 1 ml of saturated (NH<sub>4</sub>)<sub>2</sub>S solution. Stir vigorously, centrifuge (Note 2), and discard the supernate.

*Step 4.* Dissolve the Ag<sub>2</sub>S precipitate by heating with 1 ml of conc HNO<sub>3</sub>. Dilute to 20 ml with H<sub>2</sub>O and precipitate AgCl by the addition of 4 drops of conc HCl as in *Step 1*. Centrifuge and discard the supernate.

*Step 5.* Repeat *Steps 2* and *3*.

*Step 6.* Dissolve the Ag<sub>2</sub>S by heating with 1 ml of conc HNO<sub>3</sub>. Dilute with 20 ml of H<sub>2</sub>O, make the solution alkaline with 6M NaOH, and then add 3 drops in excess. Centrifuge the Ag<sub>2</sub>O precipitate and discard the supernate. Add 4 drops of conc H<sub>2</sub>SO<sub>4</sub> and heat over a burner until a clear solution is obtained. Cool.

*Step 7.* While stirring, add 20 ml of H<sub>2</sub>O and then 1 ml of 2M HIO<sub>3</sub>. Centrifuge and discard the supernate.

*Step 8.* Dissolve the AgIO<sub>3</sub> in 4 drops of conc NH<sub>4</sub>OH and dilute to 20 ml with H<sub>2</sub>O. Centrifuge and transfer the supernate to a clean 40-ml centrifuge tube.

*Step 9.* Add 3 drops of conc H<sub>2</sub>SO<sub>4</sub> to the solution, stir, and filter the AgIO<sub>3</sub> precipitate onto a weighed filter circle. Wash the precipitate with a large amount of H<sub>2</sub>O and then with 5 ml of 95% ethanol. Dry for 10 min at 110°C, cool, weigh, and mount (Note 3).

## Notes

1. Wait 1 d after bombardment before beginning the procedure; this delay allows  $^{111}\text{Pd}$  and  $^{111\text{m}}\text{Pd}$  to decay to  $^{111}\text{Ag}$ . The additional silver resulting from this waiting period is only  $\sim 0.5\%$  of the total.

2. Although the precipitation of  $\text{AgCl}$  from acidic solution is specific for  $\text{Ag}^+$  among the cations in fission products, it is possible that the precipitate may be contaminated by bromide and iodide. The  $\text{Ag}_2\text{S}$  precipitations are performed to remove any contaminating halogen activities.

3. Beta-counting for 7.4-d  $^{111}\text{Ag}$  activity is begun  $\sim 16$  h after the chemistry is completed; this delay permits 3.2-h  $^{112}\text{Ag}$  to decay sufficiently so that it will not interfere.

### Electroplating of Silver

R. J. Prestwood and B. P. Bayhurst

#### 1. Introduction

The procedure for electroplating silver after it is separated from fission products provides for the isolation and counting of silver in its elemental form rather than as the usual compound such as  $\text{AgIO}_3$ . There are two major advantages to this method: (a) the superior stability and reproducibility of the final product as the metal, and (b) an  $\sim 40\%$  increase in counting efficiency.

#### 2. Procedure

After silver is separated from fission products,  $\text{Ag}_2\text{O}$  should be precipitated with  $\text{NaOH}$ . The precipitated oxide is washed thoroughly twice with  $\text{H}_2\text{O}$ , and then the following procedure is followed.

*Step 1.* To the precipitate in a 40-ml glass centrifuge tube add 5 ml of 2M NaCN and stir until solution is effected; heat if necessary. Transfer the solution to a plating cell, the cathode of which is a weighed, polished platinum disk of 1-in. diam.

Wash the centrifuge tube with 5 ml 2M NaCN and transfer the washings to the plating cell.

*Step 2.* Plate the silver on the platinum disk at 15 mA at room temperature for 1 h and 10 min; maintain a constant amperage by using a variable resistance in series with the plating cell. After the plating is complete, remove the cell, discard the electrolyte, wash the cell with distilled  $\text{H}_2\text{O}$ , and disassemble it. Wash the silver-plated platinum disk thoroughly with absolute ethanol, allow to dry at room temperature, weigh, and mount.

(October 1989)

# GOLD

G. A. Cowan

## 1. Introduction

Gold is separated from most fission-product activities by reduction to the metal by means of HI in HCl solution in the presence of sulfosalicylic acid. The latter complexes strongly and therefore holds back many of the ions found in fission-product solutions. The precipitated gold is further decontaminated by dissolution in aqua regia, followed by AgCl and Fe(OH)<sub>3</sub> scavenging precipitations. Last traces of contaminating activities are removed by extracting AuCl<sub>3</sub> from 1M HCl into ethyl acetate. The tripositive gold is finally converted by HI reduction to the metallic state, in which form it is counted. The chemical yield is ~75%.

## 2. Reagents

Gold carrier: 10 mg gold/ml, added as AuCl<sub>3</sub> in ~0.1M HCl; used as a primary standard

Silver carrier: 10 mg silver/ml, added as AgNO<sub>3</sub> in H<sub>2</sub>O

Tellurium(VI) carrier: 10 mg tellurium/ml, added as H<sub>2</sub>TeO<sub>4</sub> • 2H<sub>2</sub>O in H<sub>2</sub>O

Iron carrier: 10 mg iron/ml, added as FeCl<sub>3</sub> • 6H<sub>2</sub>O in 1M HCl

HCl: 0.1M; 1M; 2M; conc

HNO<sub>3</sub>: conc

HI: conc

Aqua regia: three parts by volume of conc HCl + one part conc HNO<sub>3</sub>

NaOH: conc

Sulfosalicylic acid: 5% in H<sub>2</sub>O

Ethyl acetate

## 3. Preparation of Gold Carrier Solution

Dissolve 10.0 g of pure gold metal in a minimum quantity of aqua regia. Evaporate the solution nearly to dryness in the presence of excess HCl and dilute to 1 l with 0.1M HCl. The solution is used without further standardization.

## 4. Procedure

*Step 1.* To the sample (Note 1) contained in 20 ml of 1M HCl in a 40-ml glass centrifuge tube, add 2 ml of 5% sulfosalicylic acid solution, 2.0 ml of gold carrier, 1 drop of tellurium(VI) holdback carrier (Note 2), and 1.5 ml of conc HI. Heat on a steam bath for 10 to 15 min. Centrifuge and discard the supernate.

*Step 2.* Wash out chloride ion by filling the centrifuge tube with H<sub>2</sub>O and decanting. Repeat. Digest the gold precipitate with 1 ml of conc HNO<sub>3</sub> by boiling for 1 min in the hood. Centrifuge and discard the supernate.

*Step 3.* Fill the tube with H<sub>2</sub>O and decant. Dissolve the precipitate in 2 ml of conc HCl and 3 or 4 drops of conc HNO<sub>3</sub>. Boil off all the HNO<sub>3</sub>.

*Step 4.* Dilute to 20 ml with 1M HCl and repeat *Steps 1, 2, and 3* twice.

*Step 5.* Dilute the solution to 20 ml with 1M HCl and add 3 drops of silver carrier. Centrifuge and transfer the supernate to another 40-ml centrifuge tube; discard the AgCl precipitate.

*Step 6.* Add 4 drops of iron carrier and then a slight excess of conc NaOH. Without delay, centrifuge and transfer the supernate to a clean 40-ml centrifuge tube and discard the Fe(OH)<sub>3</sub> precipitate. Immediately reacidify the supernate with conc HCl (Note 3).

*Step 7.* Add 1.5 ml of conc HI and reprecipitate metallic gold as in *Step 1*. Dissolve the precipitate in a minimum amount of aqua regia.

*Step 8.* Wash the solution into a 125-ml separatory funnel with ~40 ml of 1M HCl. Extract with 25 ml of ethyl acetate. Wash the ethyl acetate layer twice with 5-ml portions of 2M HCl.

*Step 9.* Transfer the ethyl acetate extract to a 125-ml erlenmeyer flask and remove the ethyl



acetate on a steam bath. Add 25 ml of 1M HCl and 1.5 ml of conc HI. Heat on a steam bath for 10 to 15 min to precipitate metallic gold.

*Step 10.* Filter the gold on a weighed filter circle. Wash the precipitate with 1M HCl and then with acetone. Dry for 15 min at 110°C. Cool, weigh, and mount (Note 4).

## Notes

1. If any oxidizing acids are present in the original sample, they must be removed before the reduction with HI.

2. Tellurium(VI) carrier is added because reduction to the +4 state by HI promotes exchange with active species.

3. Although gold(III) is amphoteric, considerable gold is lost by precipitation of the hydrous oxide if the solution is kept strongly alkaline for 1 h or more after the Fe(OH)<sub>3</sub> scavenging step.

4. This procedure has been used to determine 2.69-d <sup>198</sup>Au. Counting is begun immediately upon completion of the chemistry.

(October 1989)

SEPARATION OF GOLD, ARSENIC,  
NICKEL, AND SCANDIUM  
INC-11 Radiochemistry Group

### 1. Introduction

In the separation of radioactive gold, arsenic, nickel, and scandium, gold is first removed by extraction into ethyl acetate from a solution 1 to 4M in HCl. Arsenic is then precipitated as the sulfide from HCl solution. Following this step, scandium is thrown down as the hydroxide by means of conc NH<sub>4</sub>OH; nickel remains in solution.

### 2. Reagents

Gold carrier: 10 mg gold/ml (see GOLD procedure)

Arsenic carrier: 10 mg arsenic/ml (see ARSENIC procedure)

Nickel carrier: 10 mg nickel/ml (see NICKEL procedure)

Scandium carrier: 20 mg ScO<sub>3</sub>/ml (see the procedure for SCANDIUM I)

HCl: conc

NH<sub>4</sub>OH: conc

H<sub>2</sub>S: gas

Ethyl acetate

### 3. Procedure

*Step 1.* To an aliquot of the sample in a 40-ml centrifuge tube, add 20 mg of gold, arsenic, and nickel carriers and 15 mg of scandium carrier. Adjust the solution to an HCl concentration of 1 to 4M. Add a volume of ethyl acetate equal to that of the solution and stir with a motor-driven stirrer. Using a pipette, transfer the ethyl acetate phase containing the gold to a 125-ml erlenmeyer flask. Evaporate the ethyl acetate on a steam bath. For analysis of gold, start with *Step 1* of the GOLD procedure, but do not add additional gold carrier.

*Step 2.* To the aqueous phase from *Step 1*, add 8 ml of conc HCl and pass in H<sub>2</sub>S until As<sub>2</sub>S<sub>3</sub> precipitation is complete. Heat on a steam bath

for 5 min. Centrifuge and transfer the supernate to a clean centrifuge tube. For analysis of arsenic in the sulfide precipitate, proceed from *Step 2* of the ARSENIC procedure.

*Step 3.* Boil the supernate to remove H<sub>2</sub>S and add conc NH<sub>4</sub>OH dropwise until the solution is alkaline and Sc(OH)<sub>3</sub> is completely precipitated. Centrifuge and transfer the supernate to a clean centrifuge tube. To determine scandium in the hydroxide precipitate, begin with *Step 2* of the SCANDIUM I procedure.

*Step 4.* For analysis of nickel in the supernate, start with *Step 1* of the NICKEL procedure, but do not add additional nickel carrier or NH<sub>4</sub>OH.

- (October 1989)

## CADMIUM

B. P. Bayhurst and R. J. Prestwood

### 1. Introduction

This procedure is designed for the rapid separation of cadmium from fission products. Decontamination steps include scavenging with CdS, acid sulfide, and  $\text{Fe}(\text{OH})_3$ . The cadmium, in 4M HCl, is then placed on an anion-exchange resin (Dowex AG 1-X8) and eluted with 1.5M  $\text{H}_2\text{SO}_4$ . Finally, the cadmium is converted to the elemental form by electroplating. The chemical yield is ~80%.

### 2. Reagents

Cadmium carrier: 10 mg cadmium/ml, added as  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in very dilute HCl; standardized

Silver carrier: 10 mg silver/ml, added as  $\text{AgNO}_3$  in very dilute  $\text{HNO}_3$

Iron carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in very dilute HCl

Palladium carrier: 10 mg palladium/ml, added as  $\text{PdCl}_2$  in  $\text{H}_2\text{O}$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

HCl: conc; 6M; 3M; 0.1M

$\text{H}_2\text{SO}_4$ : 1.5M; conc

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_4\text{Cl}$ : 3M

$(\text{NH}_4)_2\text{HPO}_4$ : 1.5M

$\text{NaCN}$ : 2M

$\text{NaOH}$ : 10M

$\text{H}_2\text{S}$ : gas

Dowex AG 1-X8: 50 to 100 mesh, anion-exchange resin, slurry in 6M HCl

Methyl red indicator solution

Ethanol: 95%; absolute

### 3. Preparation and Standardization of Carrier

Dissolve 27.4 g of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , make the solution slightly acidic with HCl, and dilute to 1 l with  $\text{H}_2\text{O}$ . Pipette exactly 5.0 ml of the

above carrier solution into a 40-ml glass centrifuge tube and evaporate to dryness. Dissolve the residue in 20 ml of  $\text{H}_2\text{O}$ , add 2 ml of 3M  $\text{NH}_4\text{Cl}$  and 2 ml of 1.5M  $(\text{NH}_4)_2\text{HPO}_4$ , and bring the solution to a boil. Permit the mixture to come to room temperature, and filter through a 60-ml sintered glass crucible of medium porosity. Wash the precipitate with water and then with 95% ethanol. Dry for 15 min at 110°C, cool, and weigh as  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ .

### 4. Procedure

*Step 1.* Add the sample to 2.0 ml of cadmium carrier in a 40-ml glass centrifuge tube. Add sufficient 6M HCl to make the solution 0.1M with respect to this acid. Bubble in  $\text{H}_2\text{S}$  for ~3 min, centrifuge, and discard the supernate.

*Step 2.* To the precipitate add 2 ml of conc HCl and boil to expel  $\text{H}_2\text{S}$ . Dilute to 20 ml with  $\text{H}_2\text{O}$ , add 2 drops of iron carrier, and make alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. Add 2 drops of lanthanum carrier, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 3.* Add 1 ml of silver carrier and then conc  $\text{H}_2\text{SO}_4$  dropwise until the solution is acid to methyl red indicator. Add 10 drops of 6M HCl and place on a steam bath for ~3 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

*Step 4.* Saturate the supernate with  $\text{H}_2\text{S}$ , centrifuge, and discard the supernate.

*Step 5.* Dissolve the CdS precipitate in a few drops of conc HCl, boil briefly, and add 10 ml of 3M HCl and 3 drops of palladium carrier. While the solution is being heated on a steam bath, saturate it with  $\text{H}_2\text{S}$ . Centrifuge, filter the supernate through filter paper into a 125-ml erlenmeyer flask, and discard the precipitate.

*Step 6.* Boil the solution to expel  $H_2S$  and then place it on top of a Dowex AG 1-X8, 50 to 100 mesh, anion-exchange resin column (0.8-cm by 5-cm resin bed). Wash the flask with 2 ml of 3M HCl and add the washings to the column. Wash the column with 10 to 15 ml of 0.1M HCl. Discard all effluents. Add 10 ml of 1.5M  $H_2SO_4$  to the column and when this has passed through, add 20 ml of  $H_2O$ . Collect the eluates in a clean centrifuge tube.

*Step 7.* Make the solution alkaline with 10M NaOH, centrifuge, discard the supernate, and proceed with the electroplating of cadmium metal.

variable resistance in series with the plating cell. After the plating is complete, remove the cell, discard the electrolyte, wash the cell with distilled  $H_2O$ , and disassemble it. Wash the cadmium-plated platinum disk thoroughly with absolute ethanol, allow to dry at room temperature, weigh, and mount.

(October 1989)

## Electroplating of the Metal

### 1. Introduction

The procedure for electroplating cadmium after it is separated from fission products provides for the isolation and counting of cadmium in its elemental form rather than as the usual compound such as  $CdNH_4PO_4 \cdot H_2O$ . There are two major advantages to this method: (a) the superior stability and reproducibility of the final product as the metal, and (b) an ~40% increase in counting efficiency.

### 2. Procedure

After cadmium is separated from fission products,  $Cd(OH)_2$  is precipitated with NaOH. The precipitate is thoroughly washed twice with  $H_2O$  before the following procedure is begun.

*Step 1.* To the precipitate in a 40-ml glass centrifuge tube add 5 ml of 2M NaCN and stir until solution is effected; heat the solution if necessary. Transfer the solution to a plating cell, the cathode of which is a weighed, polished platinum disk of 1-in. diam. Wash the centrifuge tube with 5 ml of 2M NaCN and transfer the washings to the plating cell.

*Step 2.* Plate the cadmium onto the platinum disk at 25 mA at room temperature for 1 h and 10 min. Maintain a constant amperage by using a

# SCANDIUM I

J. E. Sattizahn

With Modifications by R. J. Prestwood  
and B. P. Bayhurst

## 1. Introduction

The initial step in the procedure for determining radioscandium is the extraction of the element from a solution 10M in HNO<sub>3</sub> by 0.5M HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The scandium is then back-extracted into water as a complex fluoride. After destruction of the complex, scandium is precipitated as the simple fluoride. Other decontamination steps are LaF<sub>3</sub> scavenging while the scandium is complexed, and La(OH)<sub>3</sub>-Fe(OH)<sub>3</sub> scavenging. Scandium is finally precipitated as the hydroxide, ignited, and counted as the oxide. The chemical yield is ~65%.

## 2. Reagents

Scandium carrier: 13 mg scandium/ml, added as ScCl<sub>3</sub> in very dilute HCl; standardized

Iron carrier: 10 mg iron/ml, added as FeCl<sub>3</sub>•6H<sub>2</sub>O in very dilute HCl

Lanthanum carrier: 10 mg lanthanum/ml, added as La(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O in very dilute HNO<sub>3</sub>

Cerium(IV) carrier: 10 mg cerium/ml, added as Ce(NO<sub>3</sub>)<sub>4</sub>

HCl: 6M

HNO<sub>3</sub>: conc; 10M

HClO<sub>4</sub>: conc

H<sub>2</sub>SO<sub>4</sub>: conc

NH<sub>4</sub>OH: conc

NH<sub>2</sub>OH•HCl: solid

H<sub>3</sub>BO<sub>3</sub>: saturated aqueous solution

NH<sub>4</sub>HF<sub>2</sub>: mixture of two volumes of 6M NH<sub>4</sub>OH and one volume of 27M HF

NH<sub>4</sub>NO<sub>3</sub>: 2% aqueous solution

NH<sub>4</sub>Cl: 0.1M

Methyl red indicator solution: 0.5% in 90% ethanol

Ethanol: absolute

Rubber cement: 6% in benzene

HDEHP: 0.5M solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane.

## 3. Preparation and Standardization of Carrier

Dissolve 20.0 g of Sc<sub>2</sub>O<sub>3</sub> in a minimum of conc HCl, add 5 ml of HCl, and make the solution up to a volume of 1 l with H<sub>2</sub>O.

Pipette 5.0 ml of the above carrier solution into a 100-ml beaker and dilute to 20 ml with H<sub>2</sub>O. Add 5 ml of conc NH<sub>4</sub>OH to precipitate Sc(OH)<sub>3</sub>. Filter the solution through filter paper. Rinse the beaker with 5 ml of 0.1M NH<sub>4</sub>Cl and filter the washings through the paper containing the Sc(OH)<sub>3</sub>. Transfer the precipitate to a weighed porcelain crucible and ignite at 900°C for 1 h. Cool and weigh as Sc<sub>2</sub>O<sub>3</sub>.

Two standardizations gave results that agreed within 0.3%.

## 4. Procedure

*Step 1.* Add 2.0 ml of scandium carrier and then an aliquot of sample to a 60-ml separatory funnel. Make the solution 10M in HNO<sub>3</sub>, add 5 drops of cerium(IV) carrier [as Ce(NO<sub>3</sub>)<sub>4</sub>], and make the volume ~40 ml by the addition of 10M HNO<sub>3</sub>. Add ~100 to 200 mg of NH<sub>2</sub>OH•HCl to reduce cerium(IV) to cerium(III). (The reduction is evident by the yellow color.) Add 10 ml of HDEHP, stir vigorously for 5 min, and discard the H<sub>2</sub>O layer. Wash the heptane layer with 10 ml of 10M HNO<sub>3</sub> that contains 5 drops of cerium(III) (prepared as described above), and discard the washings. Transfer the heptane layer to a 40-ml quartz tapered centrifuge tube.

*Step 2.* Add 4 ml of NH<sub>4</sub>HF<sub>2</sub> and stir vigorously for 5 min. Add 5 ml of H<sub>2</sub>O, stir for 2 min, add 5 ml of conc HClO<sub>4</sub>, and heat on a steam bath for 10 min. (ScF<sub>3</sub> precipitates at this point.) Centrifuge and discard both the organic and aqueous supernates. To the ScF<sub>3</sub> precipitate add 1 ml of conc H<sub>2</sub>SO<sub>4</sub> and 3 to 4 drops of cerium(IV) carrier; heat to SO<sub>3</sub> fumes. Cool.

*Step 3.* Dilute to 10 ml with H<sub>2</sub>O and heat to dissolve any solid material. Add 100 to 200 mg of NH<sub>2</sub>OH•HCl to reduce cerium(IV), 3 ml of NH<sub>4</sub>HF<sub>2</sub>, and 2 to 3 drops of methyl red indicator solution. Add conc NH<sub>4</sub>OH until the solution is barely acidic. (CeF<sub>3</sub> precipitates and scandium remains in solution as a fluoro complex.) Add 2 drops of lanthanum carrier, centrifuge, and transfer the supernate to a clean 40-ml plastic tapered centrifuge tube.

*Step 4.* To the solution, add 4 drops of lanthanum carrier, 4 drops of iron carrier, and 1.5 ml of conc NH<sub>4</sub>OH. Dilute to 20 ml with H<sub>2</sub>O and heat on a steam bath to coagulate the La(OH)<sub>3</sub>-Fe(OH)<sub>3</sub> precipitate. Centrifuge, transfer the supernate to a clean 40-ml plastic centrifuge tube, and discard the precipitate.

*Step 5.* Add 6 ml of conc HClO<sub>4</sub> to the supernate; heat 5 min on a steam bath. Allow to cool for 10 min, centrifuge, and discard the supernate. (Soluble fluoroscandate is converted to insoluble ScF<sub>3</sub>.) Add 4 drops of cerium(IV) carrier, dissolve the precipitate in 1 ml of conc H<sub>2</sub>SO<sub>4</sub>, and heat to SO<sub>3</sub> fumes. Cool.

*Step 6.* Repeat *Steps 3* through *5* twice; the second time, stop with the formation of ScF<sub>3</sub>.

*Step 7.* Dissolve the ScF<sub>3</sub> precipitate in 2 ml of saturated H<sub>3</sub>BO<sub>3</sub> solution and 3 ml of conc HNO<sub>3</sub>. Dilute to 20 ml and transfer to a clean glass centrifuge tube. Add 10 ml of conc NH<sub>4</sub>OH to precipitate Sc(OH)<sub>3</sub>, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of H<sub>2</sub>O and discard the washings. Add 2 ml of conc H<sub>2</sub>SO<sub>4</sub> and evaporate to fumes of SO<sub>3</sub>. Cool, dilute to 20 ml with H<sub>2</sub>O, and add an excess of NH<sub>4</sub>OH. Centrifuge and discard supernate.

*Step 8.* Dissolve the Sc(OH)<sub>3</sub> in 1 ml of 6M HCl, dilute the solution to 20 ml, and centrifuge. Transfer the supernate to a clean centrifuge tube. Add filter paper pulp and an excess of conc NH<sub>4</sub>OH to precipitate Sc(OH)<sub>3</sub>. Filter onto filter paper and

wash the precipitate with H<sub>2</sub>O. Ignite at 900°C in a porcelain crucible for 20 min. Cool. Powder the Sc<sub>2</sub>O<sub>3</sub> with the fire-polished tip of a glass stirring rod. Transfer the Sc<sub>2</sub>O<sub>3</sub> with ethanol onto a weighed filter circle. Rinse the centrifuge tube with two 10-ml portions of ethanol and pour through the filter. Dry the Sc<sub>2</sub>O<sub>3</sub> at 110°C for 10 min, cool, weigh, and mount.

(October 1989)

## SCANDIUM II

B. P. Bayhurst

Cation-exchange resin: Bio-Rad AG 50W-X4,  
minus 400 mesh ( $\text{NH}_4^+$  form)

### 1. Introduction

In the analysis for scandium in underground nuclear debris samples, the three major decontamination steps are (1) removal of iron and some zirconium on a Dowex AG 1-X8 anion-exchange resin from a solution 10M in HCl, (2)  $\text{Zr}_3(\text{PO}_4)_4$  scavenges, and (3)  $\text{LaF}_3$  scavenges from solutions that contain scandium in the form of fluorocomplexes. Following the decontamination steps, scandium is precipitated as the fluoride and converted to the hydroxide. From dilute  $\text{HNO}_3$  solution, it is then placed on a Bio-Rad AG 50W-X4 cation-exchange resin. Elution from the column is effected with alpha-HIB (alpha-hydroxyisobutyric acid), and the scandium is finally precipitated as the hydroxide and ignited to the oxide. The chemical yield is 60 to 70%.

### 2. Reagents

Scandium carrier: 20 mg  $\text{Sc}_2\text{O}_3/\text{ml}$ , added as  $\text{ScCl}_3$  in very dilute HCl; standardized (see SCANDIUM I procedure)

Zirconium holdback carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

HCl: conc; 10M

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc

$\text{NH}_4\text{OH}$ : conc

NaOH: 10M

$\text{NH}_4\text{H}_2\text{PO}_4$ : 1.5M

$\text{NH}_4\text{HF}_2$ -HF reagent: 4M in  $\text{NH}_4\text{HF}_2$  and 1M in HF

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : solid

Methyl red indicator solution

0.05M alpha-HIB(alpha-hydroxyisobutyric acid): adjusted to pH 5.2 with  $\text{NH}_4\text{OH}$

Anion-exchange resin: Dowex AG 1-X8, 50 to 200 mesh (washed with 10M HCl)

### 3. Procedure

*Step 1.* To the sample in a 40-ml glass centrifuge tube, add 1.0 ml of standard scandium carrier and 5 ml of conc  $\text{HClO}_4$ ; fume nearly to dryness. Dilute to 20 ml with  $\text{H}_2\text{O}$  and precipitate  $\text{Sc}(\text{OH})_3$  with 10M NaOH. Centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, dilute to 20 ml with  $\text{H}_2\text{O}$ , and precipitate  $\text{Sc}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ .

*Step 2.* Dissolve the precipitate in a minimum of conc HCl, dilute to 20 ml with  $\text{H}_2\text{O}$ , and repeat the precipitations of  $\text{Sc}(\text{OH})_3$  with NaOH and  $\text{NH}_4\text{OH}$ . Centrifuge, discard the supernate, and wash the precipitate with 20 ml of  $\text{H}_2\text{O}$ .

*Step 3.* Dissolve the precipitate in 5 ml of conc HCl and place the solution on a Dowex AG 1-X8 anion-exchange resin column (50 to 200 mesh). Collect the effluent in a 125-ml erlenmeyer flask. Pass 15 ml of 10M HCl through the column and combine the effluent with the previous one.

*Step 4.* Add 2 drops of zirconium holdback carrier and evaporate to ~3 ml on a steam bath. Transfer the solution to a 40-ml glass centrifuge tube, dilute to 20 ml with  $\text{H}_2\text{O}$ , and make the solution 2 to 3M in HCl. Add 5 drops of 1.5M  $\text{NH}_4\text{H}_2\text{PO}_4$  solution, heat on a steam bath for a few minutes, and let stand until the  $\text{Zr}_3(\text{PO}_4)_4$  precipitate coagulates. Centrifuge, transfer the supernate to a clean tube, and discard the precipitate. Add another 2 drops of zirconium carrier and again precipitate  $\text{Zr}_3(\text{PO}_4)_4$ . Carry out three to four additional  $\text{Zr}_3(\text{PO}_4)_4$  precipitations. Transfer the supernate (after the final precipitation) to a 40-ml plastic centrifuge tube.

*Step 5.* Add 3 ml of  $\text{NH}_4\text{HF}_2$ -HF reagent and neutralize the solution to a methyl red end point with conc  $\text{NH}_4\text{OH}$ . (The scandium is now

in the form of fluorocomplexes.) Add 100 mg of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , heat on a steam bath, add 3 drops of lanthanum carrier, and heat again on a steam bath for a few minutes. Centrifuge, transfer the supernate to a clean plastic tube, and discard the precipitate. Repeat the  $\text{LaF}_3$  scavenge three times and transfer the final supernate to a clean plastic tube.

*Step 6.* Add 6 ml of conc HCl to precipitate  $\text{ScF}_3$ , centrifuge, and discard the supernate. Add 1 ml of 10M NaOH, stir, and heat to convert  $\text{ScF}_3$  to  $\text{Sc}(\text{OH})_3$ . Dilute to 15 ml with  $\text{H}_2\text{O}$ , centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl and precipitate  $\text{Sc}(\text{OH})_3$  by adding conc  $\text{NH}_4\text{OH}$ . Centrifuge discard the supernate, and wash the precipitate with 30 ml of  $\text{H}_2\text{O}$  to remove  $\text{NH}_4^+$  ion. Centrifuge and discard the supernate.

*Step 7.* Dissolve the precipitate in 4 to 6 drops of conc  $\text{HNO}_3$  and dilute to 30 ml with  $\text{H}_2\text{O}$ . Add 2 to 3 ml of Bio-Rad AG 50W-X4, minus 400 mesh cation-exchange resin, stir for  $\sim 1$  min, centrifuge, and discard the supernate. Use a small amount of  $\text{H}_2\text{O}$  and a transfer pipette to add the resin to the top of a column of the same resin. Use some rubber tubing to connect the top of the column to a reservoir of 0.05M alpha-HIB, for which the pH has been adjusted to 5.2. Maintain an air pressure of 3 psi on the column, and collect the eluate that contains the scandium in 13- by 100-mm glass tubes. The tubes are held in an automatic fraction collector set for 18-min change intervals. The scandium collects in 25 to 40 tubes.

*Step 8.* To the eluate in each tube add 1 drop of methyl red indicator and enough 10M NaOH to precipitate  $\text{Sc}(\text{OH})_3$ . Combine the contents of all tubes that contain  $\text{Sc}(\text{OH})_3$  in a 125-ml erlenmeyer flask and heat to coagulate the precipitate. Centrifuge portions of the solution in a 40-ml glass centrifuge tube and discard the supernates.

*Step 9.* Dissolve the precipitate in a minimum of conc HCl, dilute to 20 ml with  $\text{H}_2\text{O}$ , and add conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{Sc}(\text{OH})_3$ . Centrifuge and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, add filter paper pulp slurry, and again precipitate  $\text{Sc}(\text{OH})_3$  with conc  $\text{NH}_4\text{OH}$ . Filter through filter paper. Transfer the paper to a porcelain crucible and ignite at  $1000^\circ\text{C}$  for 15 min. Weigh and mount the  $\text{Sc}_2\text{O}_3$ .

(October 1989)



## SCANDIUM III

R. J. Prestwood

### 1. Introduction

In this procedure for the determination of radioactive scandium from debris of underground weapons tests, these are the major steps: (1) an anion-exchange resin column step that decontaminates from neptunium, iron, uranium, and other impurities; (2) removal of zirconium by precipitation of  $Zr_3(PO_4)_4$ ; (3)  $LaF_3$  scavenges, during which scandium is kept in solution as a fluoro complex; and (4) precipitation of  $ScF_3$  and ignition to  $Sc_2O_3$ . The latter is  $Ge(Li)$  counted. The chemical yield is 60 to 85%.

### 2. Reagents

Scandium carrier: 10 mg scandium/ml, added as the chloride

Lanthanum carrier: 10 mg lanthanum/ml, added as  $La(NO_3)_3 \cdot 6H_2O$  in very dilute  $HNO_3$

Yttrium carrier: 10 mg yttrium/ml, added as the chloride

Zirconium carrier: 10 mg zirconium/ml, added as the chloride

Neodymium carrier: 10 mg neodymium/ml, added as the chloride

Tellurium carrier: 10 mg tellurium/ml, added as  $Na_2TeO_4$  in dilute HCl

$HClO_4$ : conc

$H_2SO_4$ : conc

HCl: 6M; 8M; conc

$H_3PO_4$ : 85% aqueous solution

HF: conc

$NH_4OH$ : conc

NaOH: 10M

$NH_4HF_2$ -HF reagent: 4M in  $NH_4HF_2$  and 2M in HF

Methyl red indicator: 0.1% in ethanol

Paper pulp: Whatman No. 40 filter paper in  $H_2O$ ; pulped in a blender and a few drops of HCl added

AGMP-1 anion-exchange resin, 50 to 100 mesh; packed in Econo-Column

<sup>TM</sup>Polypropylene Columns; source: Bio-Rad Laboratories, Richmond, California; column dimensions: 4-in. length, ~9-ml reservoir volume, ~2-ml resin bed volume, and  $\sim 1\frac{1}{2}$ -by  $\frac{5}{16}$ -in. bed dimensions

### 3. Procedure

*Step 1.* To a 125-ml erlenmeyer flask, add 2.0 ml of scandium carrier, 3 ml of conc  $H_2SO_4$ , 2 ml of conc  $HClO_4$ , and 1 drop each of lanthanum, tellurium, yttrium, zirconium, and neodymium carriers. Evaporate the solution to dryness and heat the residue for 30 min in a furnace at 550°C.

*Step 2.* Dissolve the residue in a minimum of 6M HCl and transfer the solution to a 40-ml glass centrifuge tube. Precipitate hydroxides by adding a slight excess of conc  $NH_4OH$ . Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in a minimum of 6M HCl. Add 10M NaOH to precipitate hydroxides, then add 1 ml in excess. Place in a steam bath for at least 10 min to ensure coagulation of  $Sc(OH)_3$ . Centrifuge and discard the supernate.

*Step 4.* Dissolve the precipitate in 3 ml of conc HCl. Add 6 ml of 8M HCl and place the solution on the AGMP-1 anion-exchange resin column. (Neptunium, iron, uranium, tellurium, and other contaminants stay on the column.) Collect the effluent in a clean glass centrifuge tube. Wash the resin with 8M HCl and combine the effluents. The total volume should be ~20 ml. (A concentration of 8M for HCl is optimum for the adsorption of neptunium, iron, uranium, tellurium, etc., but still permits scandium to pass through the column.)

*Step 5.* To the combined effluent, add 1 drop of zirconium carrier and place the tube in a steam bath. When the solution is hot, add 3 drops of 85%  $H_3PO_4$  while stirring. After the  $Zr_3(PO_4)_4$  coagulates, centrifuge. Add another drop of zirconium carrier, swirl the tube gently, and place it back in the steam bath to coagulate the  $Zr_3(PO_4)_4$ .

Centrifuge and transfer the supernate to a clean glass tube.

*Step 6.* To the supernate add 1 drop of zirconium carrier, heat in a steam bath, and centrifuge. Add another drop of zirconium carrier, swirl, and place the tube back in the steam bath to coagulate the  $Zr_3(PO_4)_4$ . Centrifuge and transfer the supernate to a clean glass tube.

*Step 7.* Repeat *Step 6*, but transfer the supernate to a 40-ml plastic centrifuge tube after the final centrifugation. To the supernate add 2 ml of conc HF and place the tube in a steam bath until  $ScF_3$  precipitates and coagulates. Centrifuge and discard the supernate.

*Step 8.* To the precipitate, add 4 to 5 ml of  $NH_4HF_2$ -HF reagent and slurry the mixture with a plastic stirring rod. Add 1 drop of methyl red indicator and then add conc  $NH_4OH$  until the solution is slightly alkaline. (At this point, scandium will have dissolved as a complex fluoride and the lanthanides will remain as a precipitate.) Bring the volume to ~20 ml with  $H_2O$  and place the tube in a steam bath for a few minutes. Centrifuge, add 1 drop each of yttrium, lanthanum, and neodymium carriers, swirl gently, and again place the tube in a steam bath for a few minutes. Centrifuge and transfer the supernate to a clean plastic tube.

*Step 9.* Repeat the double lanthanide precipitation from the fluoride medium three more times; keep the solution slightly alkaline by occasional addition of conc  $NH_4OH$ .

*Step 10.* After the final centrifugation, transfer the supernate to a clean plastic centrifuge tube, add ~10 ml of conc HCl, and place the tube in a steam bath to precipitate  $ScF_3$ . Centrifuge and discard the supernate.

*Step 11.* Slurry the  $ScF_3$  with a little paper pulp and, with the aid of  $H_2O$ , filter the slurry through a polycarbonate filter. Ignite the fluoride to  $Sc_2O_3$

at 1100°C, mount, and count in a Ge(Li) counter (Note).

#### Note

If small amounts of neptunium, cerium, and lanthanum activities are present at this stage, they do not interfere with the Ge(Li) counting of any of the scandium isotopes.

(October 1989)

# YTTRIUM I

R. J. Prestwood

## 1. Introduction

In the analysis of radioyttrium in fission products,  $YF_3$  precipitations are carried out in the presence of zirconium holdback carrier. After dissolution of the fluoride and reprecipitation of yttrium as the hydroxide, yttrium is separated from europium, samarium, and the lighter lanthanides by extraction from 0.75M HCl solution with 0.5M HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. Yttrium is finally precipitated as the hydroxide, ignited, and counted as the oxide.

## 2. Reagents

Yttrium carrier: 10 mg yttrium/ml; standardized

Zirconium carrier: 10 mg zirconium/ml, added as

$ZrO(NO_3)_2 \cdot 2H_2O$  in 1M  $HNO_3$

HCl: 0.75M; 1.5M; 6M; conc

$HNO_3$ : 6M

HF: conc; 5M

$H_3BO_3$ : saturated aqueous solution

$NH_4OH$ : conc

Ethanol: absolute

6% rubber cement in benzene

$(NH_4)_2C_2O_4$ : saturated aqueous solution

HDEHP: 0.5M solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane

## 3. Preparation and Standardization of Carrier

Dissolve 12.7 g of  $Y_2O_3$  in 100 ml of conc HCl and dilute the solution to 1 l.

To 5.0 ml of the carrier solution in a 40-ml glass centrifuge tube, add 20 ml of  $H_2O$ , heat to boiling, and add 20 ml of saturated  $(NH_4)_2C_2O_4$  while stirring. Heat for 10 min on a steam bath and then cool in an ice bath for 4 min. Centrifuge the  $Y_2(C_2O_4)_3$  and decant the supernate. Take up the precipitate in 10 ml of  $H_2O$  and filter onto filter paper. Wash the precipitate with  $H_2O$ , transfer to

a weighed porcelain crucible, and ignite at 900°C for 1 h. Cool and weigh as  $Y_2O_3$ .

Four standardizations gave results that agreed within 1%.

## 4. Procedure

*Step 1.* To the sample in a 40-ml plastic, tapered centrifuge tube, add 4.0 ml of standard yttrium carrier and make the solution 2 to 4M in  $HNO_3$ . Add 2 ml of zirconium holdback carrier and make the solution 4M in HF. Centrifuge the  $YF_3$ , decant the supernate, and wash the precipitate with 10 ml of 5M HF.

*Step 2.* Dissolve the  $YF_3$  in 2 ml of saturated  $H_3BO_3$  solution and 2 ml of conc  $HNO_3$ ; dilute to 10 ml. Add 2 ml of zirconium carrier and enough conc HF to make the solution 4M in HF. Centrifuge the  $YF_3$ , decant the supernate, and wash the precipitate with 10 ml of 5M HF.

*Step 3.* Dissolve the precipitate in 2 ml of saturated  $H_3BO_3$  solution and 2 ml of conc  $HNO_3$ . Dilute the solution to 10 ml and precipitate  $Y(OH)_3$  by the addition of conc  $NH_4OH$ . Centrifuge and discard the supernate. Wash the precipitate with 30 ml of  $H_2O$ .

*Step 4.* Dissolve the  $Y(OH)_3$  in 2.0 ml of 1.5M HCl. Transfer the solution with 8 ml of 0.75M HCl to a clean 60-ml separatory funnel. Add 10 ml of HDEHP, shake vigorously for 1 min, and discard the aqueous layer. Wash the heptane layer twice with 10-ml portions of 0.75M HCl and discard the washings. Back-extract the yttrium into 10 ml of 6M HCl, transfer the aqueous layer to a clean plastic centrifuge tube, and discard the heptane layer. Add an excess of conc  $NH_4OH$  to precipitate  $Y(OH)_3$ , centrifuge, and discard the supernate. Wash the precipitate with 30 ml of  $H_2O$  and discard the washings.

*Step 5.* Repeat Step 4 (Note).

*Step 6.* Dissolve the  $Y(OH)_3$  in 1 ml of 6M HCl, dilute the solution to 20 ml, centrifuge, and transfer the supernate to a clean centrifuge tube. Add paper pulp and then add an excess of conc  $NH_4OH$  to precipitate  $Y(OH)_3$ . Filter onto filter paper and wash the precipitate with  $H_2O$ . Ignite at  $900^\circ C$  in a porcelain crucible for 20 min. Cool and powder the  $Y_2O_3$  with the fire-polished tip of a glass stirring rod. Transfer the  $Y_2O_3$  with ethanol onto a weighed filter circle. Rinse the crucible twice with ethanol and pour through the filter. Dry the  $Y_2O_3$  at  $110^\circ C$  for 10 min, cool, weigh, and mount.

#### Note

It probably is not necessary to repeat *Step 4* if  $^{91}Y$  is being determined. Repetition of this step is desirable when  $^{88}Y$  is determined in the presence of large amounts of fission products.

(October 1989)

# YTTRIUM II

R. J. Prestwood

## 1. Introduction

The determination of radioyttrium in fission products as described here involves separation of the element on a cation-exchange resin column. The column step is preceded by two fluoride precipitations. The yttrium is eluted from the column by means of alpha-HIB (alpha-hydroxyisobutyric acid) and is finally precipitated as the oxalate and ignited to the oxide.

The analysis gives excellent separation of yttrium from the lanthanides—cerium through terbium and erbium through lutetium. Separation from dysprosium and holmium is marginal.

## 2. Reagents

Yttrium carrier: 12.67 mg  $Y_2O_3/2$  ml;  
standardized

$HNO_3$ : conc

HCl: conc

HF: conc

$H_2C_2O_4$ : saturated aqueous solution

NaOH: 10M

$NH_4OH$ : conc

0.5M alpha-HIB (alpha-hydroxyisobutyric acid);  
adjusted to pH 3.29 (52.05 g of alpha-HIB and  
~19 ml conc  $NH_4OH/\ell$ )

Cation-exchange resin: Bio-Rad AG 50W-X4,  
minus 400 mesh ( $NH_4^+$  form)

## 3. Preparation and Standardization of Carrier

Dissolve 12.67 g of  $Y_2O_3$  in a minimum of conc HCl and make the solution up to a volume of 2  $\ell$  with  $H_2O$ .

Transfer 5.0 ml of the carrier solution to a weighed porcelain crucible. Evaporate the solution carefully to dryness and ignite the residue at 1000°C for 1 h. Cool and weigh as  $Y_2O_3$ .

## 4. Procedure

*Step 1.* Add 2.0 ml of standard yttrium carrier to the sample in a 40-ml plastic, tapered centrifuge tube; make the solution 2 to 4M in  $HNO_3$  or HCl and 4M in HF. Centrifuge the  $YF_3$  precipitate and discard the supernate.

*Step 2.* Add 2 ml of 10M NaOH to the precipitate, stir, and heat on a steam bath for ~2 min. Dilute to 20 ml with  $H_2O$  and heat for 2 to 5 min on a steam bath. [This treatment converts  $YF_3$  quantitatively to  $Y(OH)_3$ .] Centrifuge and discard the supernate.

*Step 3.* Dissolve the precipitate in a minimum of  $HNO_3$  and repeat the precipitation of  $YF_3$  and its conversion to hydroxide. Centrifuge and discard the supernate.

*Step 4.* Dissolve the precipitate in a few drops of  $HNO_3$ , dilute with  $H_2O$ , and transfer with the aid of  $H_2O$  to a glass centrifuge tube. The final volume of solution should be ~30 ml. [If there is indication that the  $Y(OH)_3$  has not dissolved completely, add a few drops of  $HNO_3$  and heat.] Precipitate  $Y(OH)_3$  with an excess of conc  $NH_4OH$ , centrifuge, and discard the supernate. Wash the precipitate with 30 ml of  $H_2O$  and discard the wash.

*Step 5.* Add 6 drops of conc  $HNO_3$  to the precipitate and dilute to ~25 ml with  $H_2O$ . Add the equivalent of 1 to 1.5 ml of the cation-exchange resin, stir for ~1 min, centrifuge, and discard the supernate. With the aid of a small amount of  $H_2O$  and a transfer pipette, add the resin to the top of a cation-exchange column that has been prepared as described in THE LANTHANIDES procedure. Connect the top of the column by rubber tubing to a reservoir of 0.5M alpha-HIB, the pH of which has been adjusted to 3.29. Maintain air pressure at 4.5 psi and collect the effluent from the column in 13- by 100-mm glass tubes. The tubes are held in an automatic fraction collector that is set for 18-min change intervals. Under the conditions

described, each tube collects  $\sim 2.5$  ml of effluent. The yttrium appears in tubes numbered 32 through 50, approximately. Determine the exact locations of the element by adding a few drops of saturated  $\text{H}_2\text{C}_2\text{O}_4$ , which precipitates the oxalate. Combine the contents of the  $\sim 18$  yttrium-containing tubes in two 40-ml glass centrifuge tubes, and add an excess of  $\text{H}_2\text{C}_2\text{O}_4$  to precipitate the yttrium quantitatively. Heat the tubes to coagulate the precipitate. Centrifuge one of the tubes and discard the supernate. Pour the contents of the second tube into the first, centrifuge again, and discard the supernate. To the precipitate add 6 to 8 ml of filter paper pulp and a few drops of  $\text{H}_2\text{C}_2\text{O}_4$ . Filter onto filter paper, transfer to a porcelain crucible, and ignite to  $\text{Y}_2\text{O}_3$  at  $1000^\circ\text{C}$  for 10 min. Cool, weigh, mount, and count.

(October 1989)

## YTTRIUM III

R. J. Prestwood

### 1. Introduction

The analytical scheme described here is designed for the separation of yttrium from large samples (5 to 10 g) of underground nuclear debris. It consists primarily of the extraction of the lanthanides and transplutonium actinides from the bulk of the soil sample into tri-*n*-butyl phosphate (TBP) from a highly salted buffered solution. After this task is accomplished, the YTTRIUM II procedure is employed.

### 2. Reagents (in addition to those given in the YTTRIUM II procedure)

Al(NO<sub>3</sub>)<sub>3</sub>: saturated (~2.5M); dissolve 5 lb of Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O in 1050 ml of H<sub>2</sub>O to produce ~2400 ml of solution. Heating speeds up the solution process.

Al(NO<sub>3</sub>)<sub>3</sub>: 1.9M; three parts by volume of saturated Al(NO<sub>3</sub>)<sub>3</sub> and one part of H<sub>2</sub>O  
NH<sub>4</sub>NO<sub>3</sub>-HNO<sub>3</sub>: 10M NH<sub>4</sub>NO<sub>3</sub>-0.2M HNO<sub>3</sub>; dissolve 7 lb of NH<sub>4</sub>NO<sub>3</sub> in H<sub>2</sub>O, add 50 ml of conc HNO<sub>3</sub>, and dilute to 4 l with H<sub>2</sub>O.

LiOH: 4M

Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O: solid

Tri-*n*-butyl phosphate (TBP)

Iron carrier: 10 mg iron/ml, added as Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O in very dilute HNO<sub>3</sub>

Yttrium carrier: 12.67 mg Y<sub>2</sub>O<sub>3</sub>/2 ml; standardized (see YTTRIUM II procedure)

Anion-exchange resin: Dowex AG 1-X8, 50 to 100 mesh

### 3. Procedure

A typical sample consists of ~5 g of debris that has been dissolved by the regular dissolving procedure (see DISSOLUTION OF UNDERGROUND NUCLEAR DEBRIS SAMPLES). A slight modification is employed: the final treatment is dilution to 90 to 100 ml with water rather than with 3M HCl. The analytical procedure can be carried out either with or without yttrium carrier.

*Step 1.* To the solution of the sample (60 to 100 ml), add enough solid Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O and 4M LiOH to make the pH ~0.9 to 1 and the Al(NO<sub>3</sub>)<sub>3</sub> concentration ~1.7M. The final volume of solution is usually 200 to 300 ml.

*Step 2.* Transfer the solution to a 1-l extraction vessel (see E, Fig. 1, in CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM UNDERGROUND NUCLEAR DEBRIS), add 100 ml of TBP, and stir vigorously for ~5 min. Drain the aqueous (lower) phase. To the TBP phase add 200 ml of 1.9M Al(NO<sub>3</sub>)<sub>3</sub>, stir for 2 to 3 min, and discard the aqueous phase. Repeat the wash with Al(NO<sub>3</sub>)<sub>3</sub> solution. To the TBP phase add 100 mg 10M NH<sub>4</sub>NO<sub>3</sub>-0.2M HNO<sub>3</sub>, stir for 2 to 3 min, and discard the aqueous phase. Repeat the wash.

*Step 3.* Add 30 ml of H<sub>2</sub>O, stir for ~2 min, and drain the H<sub>2</sub>O layer into a clean 40-ml glass centrifuge tube. Repeat three times; each time drain the aqueous layer into a clean centrifuge tube. (At least 90% of the yttrium activity is found in the first two tubes.)

If yttrium carrier is used, make each tube alkaline with conc NH<sub>4</sub>OH, heat on a steam bath to coagulate the Y(OH)<sub>3</sub> precipitate, centrifuge, and discard the supernate. Dissolve each precipitate in a few drops of HNO<sub>3</sub> and combine the solutions in a clean 40-ml plastic centrifuge tube. Make the solution ~4M in HNO<sub>3</sub> and 3M in HF, centrifuge, and discard the supernate. Carry out *Step 2* and then *Step 5* of the YTTRIUM II procedure.

In the event that no yttrium carrier was employed, add 3 drops of iron carrier to each tube. Make the first tube alkaline with conc NH<sub>4</sub>OH, heat on a steam bath for a few minutes, centrifuge, and discard the supernate. Successively add the contents of tubes two, three, and four to the first tube; each time repeat the precipitation of Fe(OH)<sub>3</sub> with NH<sub>4</sub>OH and discard the supernate. [The lanthanides and actinides are carried on the Fe(OH)<sub>3</sub>.] Dissolve the Fe(OH)<sub>3</sub> in excess conc

HCl (2 to 3 ml) and pass the solution through an 8-mm by 5-cm Dowex AG 1-X8, 50 to 100 mesh, anion-exchange resin column to remove iron. Wash the column twice with 2- or 3-ml portions of conc HCl and collect the eluates in a 40-ml glass centrifuge tube. Evaporate essentially to dryness and proceed to *Step 5* of the YTTRIUM II procedure. In the absence of yttrium carrier, the yttrium activity in the alpha-HIB elution is confined to three to four tubes, and starts at about tube 30. The exact location (tube numbers) of the yttrium activity is found by radiation monitoring (<sup>91</sup>Y from fission products). After the yttrium in these tubes is combined, carrier may be added to the combined tubes that contain the yttrium activity to precipitate Y<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>, or the alpha-HIB solution may be further processed.

(October 1989)



# CERIUM

D. P. Ames

## 1. Introduction

In the analysis for radiocerium, exchange between carrier and fission-product cerium is effected by a cerium(III)-cerium(IV) oxidation-reduction cycle. Cerium(III) and other lanthanides are separated from other fission products by precipitation as fluorides with HF. Cerium is then oxidized to the +4 state and separated from other lanthanides by precipitation as the iodate,  $\text{Ce}(\text{IO}_3)_4$ . Cerium is converted to the +3 state and zirconium, plutonium(IV), and thallium activities are removed by  $\text{Zr}(\text{IO}_3)_4$  scavenging. Precipitation of  $\text{Ce}(\text{OH})_3$  separates cerium from alkaline earth activities. Cerium is finally precipitated as the oxalate and ignited to the oxide  $\text{CeO}_2$ , in which form it is weighed and counted. The chemical yield is ~75%.

## 2. Reagents

Cerium carrier: 10 mg cerium/ml, added as

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ; standardized

Lanthanum carrier: 10 mg lanthanum/ml, added

as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as

$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

HCl: 6M; conc

$\text{HNO}_3$ : conc

HF: conc; 5M

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{HIO}_3$ : 0.35M

$\text{NH}_4\text{OH}$ : conc

$\text{NaBrO}_3$ : saturated aqueous solution

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ : saturated aqueous solution

$\text{H}_2\text{O}_2$ : 30%

## 3. Preparation and Standardization of Carrier

Dissolve 31.0 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  and dilute to 1 l. [To obtain cerium that is free from other lanthanides, it may be necessary to purify it by two  $\text{Ce}(\text{IO}_3)_4$  precipitations, as in Steps 4 and 5 of the procedure.]

Pipette 5.0 ml of the cerium carrier solution into a 100-ml beaker and dilute to ~20 ml with  $\text{H}_2\text{O}$ . Warm on a steam bath and add ~50 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter through filter paper. Ignite in a porcelain crucible at 800°C for 30 min, cool, and weigh as  $\text{CeO}_2$ .

Four standardizations were carried out; results agreed within 0.5%.

## 4. Procedure

*Step 1.* To a 40-ml glass centrifuge tube, add 2.0 ml of cerium carrier and 5 ml of conc  $\text{HNO}_3$ ; pipette in the sample for analysis. Add 1 ml of saturated  $\text{NaBrO}_3$  solution and heat on a steam bath for 10 min (Note 1).

*Step 2.* Remove the tube from the steam bath and add 30%  $\text{H}_2\text{O}_2$  dropwise while vigorously stirring (Note 2) until the solution has a light reddish-brown color. Heat on the steam bath until the  $\text{Br}_2$  color disappears; add 1 to 2 drops of  $\text{H}_2\text{O}_2$  if necessary.

*Step 3.* Add 2 ml of lanthanum carrier and 2.5 ml of zirconium holdback carrier, and transfer the solution to a 50-ml plastic tube. Add 2 ml of conc HF to precipitate  $\text{CeF}_3$  and  $\text{LaF}_3$ . Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5M HF, centrifuge, and discard the supernate.

*Step 4.* To the precipitate add 1 to 2 ml of saturated  $\text{H}_3\text{BO}_3$  solution and suspend the precipitate by stirring. Then add 4 ml of conc  $\text{HNO}_3$  and stir vigorously until a clear solution is formed. Transfer to a 40-ml glass centrifuge tube and add 4 ml of conc  $\text{HNO}_3$  and 1 ml of saturated  $\text{NaBrO}_3$  solution. Heat on a steam bath for ~10 min.

*Step 5.* Add 20 ml of 0.35M  $\text{HIO}_3$  and stir vigorously. Cool for 5 to 10 min in an ice bath. Centrifuge and discard the supernate; retain the  $\text{Ce}(\text{IO}_3)_4$  precipitate (Note 3).

*Step 6.* Suspend the precipitate in a solution made up by the addition of 8 ml of  $\text{H}_2\text{O}$ , 3 ml of conc  $\text{HNO}_3$ , and 3 ml of 0.35M  $\text{HIO}_3$ . Centrifuge and discard the supernate. Repeat this washing step twice, and suspend the precipitate each time.

*Step 7.* Add 1 ml of lanthanum carrier to the precipitate. Add 4 ml of conc  $\text{HNO}_3$  and 1 to 2 drops of conc  $\text{HCl}$ , and slurry the  $\text{Ce}(\text{IO}_3)_4$  by stirring vigorously. Add 0.2 ml of 30%  $\text{H}_2\text{O}_2$  and stir until dissolution of  $\text{Ce}(\text{IO}_3)_4$  is complete. Add 1 ml of saturated  $\text{NaBrO}_3$  and 4 ml of conc  $\text{HNO}_3$ . Reoxidize cerium(III) to cerium(IV) as in *Step 4*.

*Step 8.* Repeat *Step 5*.

*Step 9.* Repeat *Step 6*, washing the precipitate three times. (All other lanthanides have now been removed from the cerium.)

*Step 10.* Add 1 ml of zirconium carrier to the precipitate from *Step 9*, and dissolve the precipitate as in *Step 7* by using 8 ml of conc  $\text{HNO}_3$ , 0.2 ml of conc  $\text{HCl}$ , and 0.2 to 0.3 ml of 30%  $\text{H}_2\text{O}_2$ . Add 20 ml of 0.35M  $\text{HIO}_3$  to the clear solution to precipitate  $\text{Zr}(\text{IO}_3)_4$  (Note 4). Centrifuge and transfer the supernate to a 50-ml plastic tube; discard the  $\text{Zr}(\text{IO}_3)_4$  precipitate.

*Step 11.* Add 5 ml of conc  $\text{HF}$  to precipitate  $\text{CeF}_3$ . Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5M  $\text{HF}$ . Centrifuge and discard the supernate.

*Step 12.* Dissolve the  $\text{CeF}_3$  by making a slurry in 1 ml of saturated  $\text{H}_3\text{BO}_3$  and adding 2 ml of conc  $\text{HNO}_3$ . Transfer to a 40-ml glass centrifuge tube. Heat on a steam bath for 5 min to ensure complete dissolution.

*Step 13.* Dilute to 10 ml with  $\text{H}_2\text{O}$ , make strongly alkaline with conc  $\text{NH}_4\text{OH}$ , and precipitate  $\text{Ce}(\text{OH})_3$ . Centrifuge and discard the supernate. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$ . Centrifuge and discard the supernate.

*Step 14.* Dissolve the  $\text{Ce}(\text{OH})_3$  in 1 to 2 ml of 6M  $\text{HCl}$ . Heat on the steam bath to ensure complete dissolution.

*Step 15.* Add 25 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to precipitate  $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ . Allow the precipitate to coagulate before removing the tube from the steam bath (3 to 5 min).

*Step 16.* Cool the precipitate for 15 min in an ice bath. Filter on a weighed filter circle.

*Step 17.* Transfer the precipitate to a porcelain crucible and ignite at 800°C for 30 min. Cool for 30 min, weigh as  $\text{CeO}_2$  (Note 5), mount, and count (Note 6).

## Notes

1. In a strongly acidic ( $\text{HNO}_3$ ) solution,  $\text{BrO}_3^-$  ion oxidizes cerium(III) to cerium(IV).

2. Cerium(IV) is reduced by  $\text{H}_2\text{O}_2$  in acid medium. The oxidation-reduction cycle performed in *Steps 1* and *2* promotes exchange between radiocerium and carrier.

3. If the concentration of  $\text{HNO}_3$  is low,  $\text{La}(\text{IO}_3)_3$  will also precipitate at this stage.

4. The  $\text{Zr}(\text{IO}_3)_4$  scavenging step removes any thorium and plutonium isotopes that may be present, as well as active zirconium.

5. The  $\text{CeO}_2$  should be white. If it is not white at this stage, decontamination from other lanthanides is not complete.

6. To obtain the mass 144 chain, count the samples immediately through 217-mg  $\text{Al}/\text{cm}^2$  to cut out the 32.5-d  $^{141}\text{Ce}$  and the 290-d  $^{144}\text{Ce}$  betas. This gives only the activity from the 17.5-min  $^{144}\text{Pr}$ . To eliminate 33-h  $^{143}\text{Ce}$ , allow 20 d from the end of bombardment before beginning the analysis. To determine  $^{141}\text{Ce}$ , it is best to count with no added absorber and use a least squares separation of the  $^{141}\text{Ce}$  and  $^{144}\text{Ce}$ - $^{144}\text{Pr}$  activities.

(October 1989)

## CERIUM-144

J. W. Barnes

### 1. Introduction

The procedure described here has been successfully employed for the analysis of  $^{144}\text{Ce}$ . The major steps include: (a) an oxidation-reduction cycle in the presence of cerium carrier to ensure exchange; (b) two by-product extractions from  $\text{HNO}_3$  solution with dibutyl phosphate (DBP) in  $\text{CCl}_4$  to remove contaminants such as zirconium, neptunium, thorium, plutonium, and uranium; (c) a  $\text{CeF}_3$  precipitation; (d) the extraction of cerium(IV) into hexone; and (e) the final conversion of cerium to the dioxide. The chemical yield is 50 to 60%.

### 2. Reagents

Cerium carrier: 12 mg cerium/ml, added as  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  in 3M  $\text{HNO}_3$ ; standardized  $\text{HNO}_3$ : conc; 9M

HF: conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{NH}_4\text{OH}$ : conc

$\text{NaBrO}_3$ : 2M

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ : saturated aqueous solution

$\text{H}_2\text{O}_2$ : 30%

Dibutyl phosphate (DBP): 5% in carbon tetrachloride

Hexone (4-methyl-2-pentanone)

Ethanol: 95%

### 3. Preparation and Standardization of Carrier

Dissolve 47.8 g of  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  in 190 ml of conc  $\text{HNO}_3$  and dilute to 1 l.

Pipette 5.0 ml of the cerium carrier solution into a 100-ml beaker and dilute to ~20 ml with  $\text{H}_2\text{O}$ . Warm on a steam bath and add ~50 ml of saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter

through filter paper. Ignite in a porcelain crucible at 800°C for 30 min, cool, and weigh as  $\text{CeO}_2$ .

Four standardizations were carried out; results agreed within 0.5%.

### 4. Procedure

*Step 1.* To 2.0 ml of cerium carrier in a 40-ml glass centrifuge tube, add the sample, then 3 to 5 drops of 2M  $\text{NaBrO}_3$  and heat on a steam bath for 10 min. Dilute to 30 ml and add sufficient conc  $\text{NH}_4\text{OH}$  to precipitate  $\text{CeO}_2 \cdot \text{xH}_2\text{O}$ . Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of conc  $\text{HNO}_3$ , and add 3 to 5 drops of 30%  $\text{H}_2\text{O}_2$  and 7 to 8 ml of  $\text{H}_2\text{O}$ .

*Step 2.* Transfer the solution to a 60-ml pear-shaped separatory funnel and shake with ~25 ml of 5% DBP in carbon tetrachloride solution. Permit the layers to separate and drain off the organic (lower) layer. If the original sample contains uranium or plutonium, transfer the organic layer to the appropriate waste bottle. If these elements are absent, discard the organic layer.

*Step 3.* Repeat the extraction with another 25-ml portion of the 5% DBP; treat the organic layer as in *Step 2*.

*Step 4.* Transfer the aqueous layer into a 40-ml plastic centrifuge tube. Dilute to ~20 ml with  $\text{H}_2\text{O}$ , add 3 to 4 ml of conc HF, and stir well to permit the precipitate to coagulate. Centrifuge and discard the supernate. Wash the precipitate with ~20 ml of  $\text{H}_2\text{O}$  and discard the washings.

*Step 5.* Stir the precipitate with 1 ml each of saturated  $\text{H}_3\text{BO}_3$  solution and conc  $\text{HNO}_3$ ; heat if necessary to obtain dissolution. Dilute to 20 to 30 ml with  $\text{H}_2\text{O}$  and add an excess of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 6.* Pretreat 50 ml of hexone with a mixture of 50 ml of 9M  $\text{HNO}_3$  and 2 ml of 2M  $\text{NaBrO}_3$ ; shake for ~1 min and discard the aqueous layer.

Dissolve the precipitate from *Step 5* in 10 ml of 9M HNO<sub>3</sub> and add 2 ml of 2M NaBrO<sub>3</sub>. Transfer to a 125-ml pear-shaped separatory funnel, add 50 ml of hexone, and shake for ~30 s. Discard the aqueous layer. Wash the organic layer twice with 5 ml of 9M HNO<sub>3</sub> that contains 2 to 3 drops of 2M NaBrO<sub>3</sub> and discard the washings. Back-extract the cerium by shaking the hexone solution with 5 ml of H<sub>2</sub>O that contains a few drops of 30% H<sub>2</sub>O<sub>2</sub>. Discard the hexone layer.

*Step 7.* Add conc NH<sub>4</sub>OH to the aqueous layer until an orange precipitate barely persists. Add conc HNO<sub>3</sub> dropwise until the precipitate dissolves, and then add 10 to 15 ml of saturated (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Stir briefly, cool, centrifuge, and discard the supernate. Transfer the precipitate by means of a stream of ethanol onto a weighed filter circle. Transfer the precipitate to a porcelain crucible and ignite at 800°C for 30 min. Cool, weigh as CeO<sub>2</sub>, mount, and beta-count through a 217-mg/cm<sup>2</sup> aluminum absorber (Note).

#### Note

This procedure probably can be used for <sup>143</sup>Ce, but it has not been thoroughly studied for that isotope.

(October 1989)

# THE LANTHANIDES

K. Wolfsberg and D. Handel

## 1. Introduction

After the radiochemical purification of the lanthanides (rare earths) as a group, the individual lanthanides are separated on a cation-exchange column of low cross-linkage and fine particle size at room temperature by elution with alpha-hydroxyisobutyric acid. The separation of many lanthanides, such as yttrium (which behaves as a middle lanthanide), europium, samarium, promethium, neodymium, praseodymium, cerium, and lanthanum, is best achieved in a reasonable length of time by changing the pH of the eluant continuously. Individual or small groups of lanthanides also may be separated by elution at only one pH or by making a step change in concentration or pH of the alpha-hydroxyisobutyric acid.

## 2. Reagents

HClO<sub>4</sub>: conc  
HCl: conc; 6M  
HNO<sub>3</sub>: conc  
H<sub>3</sub>BO<sub>3</sub>: saturated  
H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>: saturated; 0.5%  
HF: conc  
H<sub>3</sub>PO<sub>4</sub>: conc  
H<sub>2</sub>SO<sub>4</sub>: conc  
H<sub>2</sub>O<sub>2</sub>: 30%  
NH<sub>4</sub>OH: conc  
NH<sub>2</sub>OH•HCl: 5M aqueous solution  
Ethanol: 95%  
Zirconium carrier: 10 mg zirconium/ml, added as ZrO(NO<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O in 1M HNO<sub>3</sub>  
Tellurium carrier: 10 mg tellurium/ml, added as Na<sub>2</sub>TeO<sub>3</sub> in H<sub>2</sub>O  
Barium carrier: 10 mg barium/ml, added as Ba(NO<sub>3</sub>)<sub>2</sub> in H<sub>2</sub>O

Alpha-HIB (alpha-hydroxyisobutyric acid) reagent: ~0.5M, adjusted to solutions of desired pH with conc NH<sub>4</sub>OH; stored in 6.5-gal. Nalgene bottles. Solutions of acid concentrations 0.06 and 0.08M made by dilution with H<sub>2</sub>O.

Dowex AG 50W-X4 or AG 50W-X8 cation-exchange resin: minus 400 mesh, NH<sub>4</sub><sup>+</sup> form; also 200 to 400 mesh.

Dowex AG 1-X8 anion-exchange resin: 50 to 100 mesh

Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, thulium, ytterbium, lutetium, and yttrium carriers: 5 mg of oxide/ml; standardized, 99% pure

<sup>145</sup>Pm tracer: produced by <sup>144</sup>Sm(n,γ) <sup>145</sup>Sm → <sup>145</sup>Pm; standardized

0.01M EDTA: 3.743 g of disodium ethylenediamine tetraacetate/l

0.01M La<sup>3+</sup> in 1M HCl: prepared from La<sub>2</sub>O<sub>3</sub>  
NH<sub>4</sub>Cl: 25% wt/vol in H<sub>2</sub>O

pH 10 buffer: 61.5 g of NH<sub>4</sub>Cl dissolved in 400 ml of conc NH<sub>4</sub>OH

Arenazo indicator: 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthylene disulfonic acid trisodium salt: 0.05% in H<sub>2</sub>O

Phenolphthalein: 1% in 50% ethanol

8-quinolinol reagent I: a solution of 0.5 g of 8-quinolinol (8-hydroxyquinoline) and ~100 mg of phenolphthalein in 100 ml of ethanol

8-quinolinol reagent II: a mixture of 10 ml of 8-quinolinol reagent I and 5 ml of conc NH<sub>4</sub>OH diluted to 200 ml with H<sub>2</sub>O

Filter aid: Prepared by disintegrating, in a blender, ten 18.5-cm circles of Whatman No. 42 filter paper in water, diluting to 2 l with H<sub>2</sub>O, and adding 1 ml of conc HCl

HCl rinse solution for anion-exchange resin column: 10 ml of conc HCl and 1 drop of conc HNO<sub>3</sub>; freshly prepared

Ascorbic acid: solid

### 3. Preparation and Standardization of Carriers

Dissolve ~5 g of the desired lanthanide oxide in ~50 ml of 6M HCl. Heat, or add a few drops of conc HNO<sub>3</sub> if dissolution is difficult. Filter and dilute to 1 l; adjust the HCl concentration to 2 to 3M. Any pure soluble cerium(III) salt may be used for cerium carrier.

The lanthanides may be standardized by pipetting 6 ml of carrier solution directly into a weighed porcelain crucible that has been fired for 2 h. Evaporate the solution to dryness. Ignite at 950°C for 2 h and weigh. The lanthanide chloride is converted to the oxide.

For standardization by means of EDTA titration, pipette three 2-ml portions of the carrier into 125-ml erlenmeyer flasks and titrate with EDTA solution, as described in Sec. 9. The titrations should agree within 0.5%.

### 4. Standardization of <sup>145</sup>Pm

The solution should contain 800 to 1200 counts/min of <sup>145</sup>Pm/ml. Pipette 5.0 ml of the solution and ~20 mg of standardized neodymium carrier into each of four centrifuge tubes. Dilute to ~20 ml, heat on a steam bath, and add ~6 ml of conc NH<sub>4</sub>OH. Centrifuge. Dissolve the precipitate in 1 ml of conc HCl, dilute to 20 ml, heat on a steam bath, and add 10 ml of saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Digest the precipitate, centrifuge, filter, ignite to the oxide, and mount as in *Step 10A* of Sec. 10. Count the samples for 3 d on a sodium iodide scintillation counter. The neodymium chemical yield, which corresponds to that of promethium, may be determined in three of the samples by EDTA titration (Sec. 9). The activities, corrected for yield, should agree within 1%. The fourth sample is retained for use as a standard each time yield is determined. The assumed yield of this sample may be calculated.

### 5. Treatment of Resins

Bio-Rad Laboratories will prepare cation-exchange resin according to the following specifications: Dowex AG 50-X4 or X8, "minus 32 wet mesh;" the actual range is 24 to 45 μm. The resin is washed successively with 6M HCl, 1M NH<sub>4</sub>CNS, 6M HCl, 1M NH<sub>4</sub>OH, and H<sub>2</sub>O. The Bio-Rad Dowex AG1 resins need no further purification. Because of the variations among batches of the cation-exchange resin, they should be evaluated before routine use; also, the pH of eluant, eluant concentration, and/or flow rate should be adjusted for the particular separation.

### 6. Preparation of Cation-Exchange Columns

Select a 70-cm length of 8-mm-i.d. Pyrex tubing. Draw one end out to a drop tip (0.8- to 1.2-mm-i.d.), and make a slight constriction 8 mm from the other end for a tubing connection.

To load a column, place a small plug of glass wool in the tip and fill the column with water. Add the cation resin slurry from a plastic wash bottle. The settling rate of the resin may be increased by using air pressure. Resin should be added to a height of ~65 cm. Be sure no part of the resin goes dry. Columns prepared in this manner may be stored by sealing both ends with dropper bulbs or by immersing the columns in a cylinder of water.

### 7. Preparation of Anion-Exchange Columns

Blow out a 15-ml centrifuge tube at the bottom, and attach a 15-cm length of 6-mm-i.d. glass tubing to the column. Draw the end of the glass tubing to a 1-mm-i.d. drip tip. Load the glass tubing part of the column with anion-exchange resin in the same manner as the cation resins were loaded. These columns also may be stored as long as the resin is kept wet. Before using, wash the columns with two 5-ml portions of HCl rinse solution.

## 8. Gradient Elution Equipment

A schematic of the pH gradient elution equipment is shown in Fig. 1. Several columns may be operated from one setup by delivering the eluant from the low-pH flask through "Y" connecting tubes; 500-ml flasks are used for one or two columns, and 1000-ml flasks are used for three or four columns.

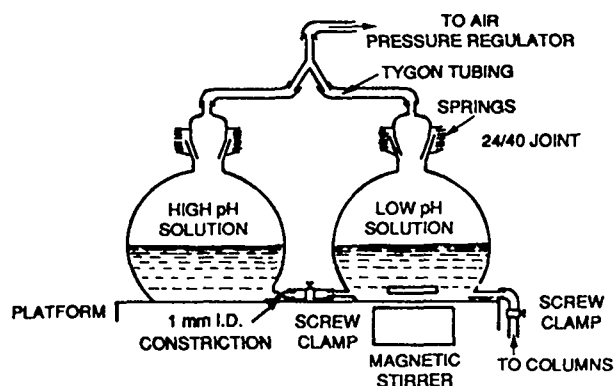


Fig. 1. Gradient elution equipment.

When elution begins, the levels of the two solutions are at the same height. Gravitational leveling causes one-half of the volume removed from the flask containing the solution of low pH to be replaced continuously by solution of high pH. Thus, the pH of the eluant changes continuously from that of the low-pH solution at the beginning of elution to that of the high-pH solution at the end of elution.

For some applications it is desirable to alter the rate of change in pH or the concentration of alpha-hydroxyisobutyric acid during a gradient elution. This can be done by using graduated cylinders instead of flasks (Fig. 1). Glass cylinders of suitable length and diameter are then inserted into the graduated cylinders to give the desired change. For example, a cylinder inserted into the "high-pH" reservoir will decrease the rate of change in pH when the top of the solution reaches the reservoir.

Elution with a single eluant requires only one reservoir. If a stepwise change in eluant is desired, it can be achieved with a manual changeover. If the step change is to occur when the equipment is not

attended, connecting lines from both reservoirs to the column through solenoid valves can be activated by an electric timer. Several plastic solenoid valves are available commercially.

## 9. EDTA Titrations

EDTA titration is a convenient method for chemical yield determination. Titration must be carried out after counting is completed. If the sample cannot be sacrificed or if preliminary answers are required, chemical yield must be determined by weighing the lanthanide oxide.

Dilute the sample to  $\sim 30$  ml in a 125-ml erlenmeyer flask and add an excess of 0.01M EDTA from a 10-ml burette (0.6 to 0.7 ml/mg of lanthanide oxide and  $\sim 0.9$  ml/mg of  $Y_2O_3$ ). Add  $\sim 4$  ml of 25%  $NH_4Cl$  and 1 drop of phenolphthalein. Then add pH 10 buffer until the solution turns pink (the pH will be between 8 and 9). Bring the solution almost to boiling. (The pink color is destroyed.) Add 1 to 2 drops of arsenazo indicator and back-titrate with 0.01 M  $La^{3+}$  solution from another 10-ml burette; the solution turns from salmon to violet or red-violet when  $\sim 0.5$  drop of EDTA is added. More EDTA may be added and another back-titration performed.

The relative strengths of the EDTA and  $La^{3+}$  solution titrants are obtained by starting the back-titration from a solution of  $\sim 6$  ml of  $La^{3+}$  solution and an excess of EDTA. The volume of lanthanum used in any titration is multiplied by the EDTA:  $La^{3+}$  solution ratio. This number is then subtracted from the volume of EDTA delivered to obtain the net volume of EDTA.

The chemical yield of a sample is the net volume of EDTA required to titrate the sample divided by the net volume required to titrate 2.0 ml of carrier. For thickness corrections, the weight of the sample can be calculated from the titration of the sample, the titration of 2.0 ml of carrier, and the gravimetric standardization of the carrier (Sec. 3).



If accurate standardization of the EDTA solution is desired, the solution may be standardized against zinc (using Eriochrome Black T as an indicator) or against a lanthanide oxide that has been ignited at 950°C (Note 1).

## 10. Procedure

In this procedure all precipitates are digested on a steam bath. They may be centrifuged while the solutions are still hot.

*Step 1.* Into a 125-ml erlenmeyer flask, pipette 2 ml of desired carrier and the active sample, 4 ml of conc HClO<sub>4</sub>, and 1 ml of conc HNO<sub>3</sub>; fume to near dryness. Add 3 ml of conc HNO<sub>3</sub> and enough H<sub>2</sub>O to transfer the solution to a 40-ml plastic centrifuge tube. Add H<sub>2</sub>O to bring the volume to ~15 ml, then add 2 to 5 ml of conc HF, digest on a steam bath for 30 min, and centrifuge for 15 min. Decant the supernate and wash the precipitate with ~20 ml of H<sub>2</sub>O that contains a few drops of conc HF. Centrifuge and discard the supernate (Note 2).

*Step 2.* Slurry the precipitate with 2 ml of saturated H<sub>3</sub>BO<sub>3</sub>; add 2 ml of conc HNO<sub>3</sub>, 10 ml of H<sub>2</sub>O, and 2 drops of zirconium carrier. Heat to dissolve any precipitate. Add 2 to 5 ml of conc HF, heat on a steam bath for a few minutes, and centrifuge (Note 3). Wash the precipitate with H<sub>2</sub>O that contains a few drops of HF. Centrifuge and discard the supernate.

*Step 3.* Slurry the precipitate with 2 ml of saturated H<sub>3</sub>BO<sub>3</sub>, add 2 ml of conc HNO<sub>3</sub>, and heat on a steam bath, if necessary, to dissolve the precipitate. Add 15 ml of H<sub>2</sub>O.

*Step 4.* Add 8 ml of conc NH<sub>4</sub>OH, heat for 1 min on a steam bath, digest, and centrifuge. Discard the supernate. (The anion-exchange resin column may be prepared at this time.) Wash the precipitate with 15 ml of H<sub>2</sub>O to which a few drops of conc NH<sub>4</sub>OH has been added. Centrifuge and discard the supernate.

*Step 5.* Dissolve the hydroxide precipitate in 4 ml of conc HCl and 1 drop of conc HNO<sub>3</sub>, and add 2 drops each of zirconium and tellurium carriers. Heat the sample for only 30 s on a steam bath (to promote tellurium exchange but not to reduce the HCl concentration). Pass the solution through an anion-exchange resin column and collect the eluate in a 125-ml erlenmeyer flask. Rinse the column with a 4- and a 6-ml HCl rinse solution (see Sec. 2), and collect the rinsings in the flask.

*Step 6.* Boil out excess HCl by heating the flask over a flame and reduce the volume to 4 to 5 ml. Transfer the solution to a long, tapered centrifuge tube with 15 ml of H<sub>2</sub>O. Add 8 ml of conc NH<sub>4</sub>OH and 3 drops of 5M NH<sub>2</sub>OH•HCl. Heat on a steam bath for ~1 min, digest, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of H<sub>2</sub>O that contains a few drops of NH<sub>4</sub>OH.

*Step 7.* Dissolve the precipitate in 6 drops of conc HCl and dilute the solution to ~30 ml with H<sub>2</sub>O. Add ~30 drops (by transfer pipette) of minus 400 mesh or 200 to 400 mesh cation-exchange resin slurry in H<sub>2</sub>O. Stir or shake for ~5 min and centrifuge for 5 min; let the centrifuge stop without the use of the brake (Note 4). (The centrifuged resin has a volume of ~1 ml.) Discard the supernate.

*Step 8.* Slurry the resin with ~1 ml of H<sub>2</sub>O and, with a transfer pipette, transfer it to the top of a previously prepared cation-exchange resin column. After the resin settles, remove the H<sub>2</sub>O. Rinse the centrifuge tube with 1 to 2 ml of H<sub>2</sub>O, add the rinsings to the column, allow to settle, and remove the H<sub>2</sub>O. (A small piece of glass wool may be put in the top of the column.)

*Step 9.* Connect the column to a delivery tube from the elution equipment. For terbium-europium elution, use a pH gradient setup (see Fig. 1) that has 150 ml of reagent solution of pH 3.73 on the high side. If several columns are operated from one set of flasks, increase the volumes of eluants proportionally. Add a small additional volume of

low-pH solution to the first flask to compensate for the difference in volumes that is caused by the delivery tubing and the stirring bar. Control the rate of elution by the air pressure applied to the reservoirs. Use a fraction collector to collect the eluate in 15-min fractions.

Perform the lutetium-thulium elution in a similar manner, but change the concentration of the alpha-hydroxyisobutyric acid solution rather than the pH (maintain at 5.5). The concentration of the acid solution may be changed by using a gradient setup that has 150 ml of 0.06M acid solution on the low side and 150 ml of 0.08M acid on the high side. Alternatively, the concentration of the acid solution may be changed by using an electric timer to activate the solenoid valves. For this method, connect the column by a Y-tube to two 2-l flasks; one contains 0.06M alpha-hydroxyisobutyric acid solution and the other, 0.08M solution. Turn on the solenoid that regulates delivery of the 0.06M acid first, then set the electric timer to deliver the 0.08M acid solution ~16 h later (Notes 5, 6, and 7).

*Step 10A.* For the light lanthanides and yttrium, add a few drops of saturated  $\text{H}_2\text{C}_2\text{O}_4$  to each fraction to precipitate and locate the individual lanthanides. Promethium is located by measuring the activity in the tubes between samarium and neodymium. Combine the individual lanthanide fractions in centrifuge tubes. To the promethium fraction, add 2 ml of neodymium carrier. Add 5 ml of saturated  $\text{H}_2\text{C}_2\text{O}_4$  acid to the centrifuge tubes and digest the oxalates for 15 min on a steam bath. Centrifuge, suspend the oxalates in ~5 ml of  $\text{H}_2\text{O}$ , and filter on a 2.5-cm filter circle. Ignite the oxalates in a porcelain crucible for ~1 h at 950°C. Oxalates may be mounted directly without weighing if chemical yield is to be determined by EDTA titration (Note 8).

*Step 10B.* For the heavy lanthanides, add ~0.5 ml of 8-quinolinol reagent I to each fraction. Add conc  $\text{NH}_4\text{OH}$  to make each fraction alkaline (red), and combine the fractions that contain an

individual element in a 250-ml beaker. (At least 10 ml of reagent I should be used in the tubes that contain the element.) Add ~1.5 ml of filter aid and digest the mixture on a steam bath for 15 to 30 min. Cool to room temperature and filter on a 4.5-cm circle of paper. Wash with 8-quinolinol reagent II. Ignite the quinolate for 1.5 h at 950°C (Note 8).

*Step 10C.* If a given light lanthanide is to be cycled through a second cation-exchange column (when a separation of  $10^5$  from other lanthanides is required), dissolve and destroy the oxalate by heating it in a centrifuge tube with ~1 ml of conc  $\text{HNO}_3$  that contains ~100 mg of  $\text{KClO}_3$ . For heavy lanthanides, ignite and dissolve the 8-quinolate in ~2 ml of conc  $\text{HCl}$  and 0.5 ml of conc  $\text{HNO}_3$ . Then perform *Step 6* for the hydroxide precipitation before the cation-exchange column step. This usually is done for europium, gadolinium, terbium, lutetium, and thulium, and, when large amounts of americium are present, also for neodymium. (If lutetium is to be recycled, dissolve the oxide formed by ignition of the 8-quinolate in 2 ml of conc  $\text{HCl}$  and 1 drop of conc  $\text{HNO}_3$ . Heat the solution on a steam bath and cool. Then add 6 ml of conc  $\text{HCl}$  and the take up procedure again at *Step 5*.)

*Step 11.* After the crucibles have cooled, add a few drops of ethanol to each sample and grind up the oxides with the fire-polished end of a stirring rod or break them up in an ultrasonic cleaner. Suspend each sample in several milliliters of ethanol and filter onto a circle of paper. Dry the sample for 15 min at 110°C, mount it on an aluminum plate, and cover with Scotch No. 850 Type 2PTA polyester film tape (Note 9).

If chemical yield is to be determined by weight of the oxide, wash, dry, and weigh the circle of paper on which the sample is to be mounted before the mounting operation. The papers and samples should be cooled for 20 min before weighing.

*Step 12.* After sample counting is completed, yield determination by EDTA titration may be

performed. Remove the sample, filter paper, and tape cover from the counting plate by cutting around the outside of the filter paper with a sharp blade. Place this sandwich in a 125-ml erlenmeyer flask. Add 10 ml of H<sub>2</sub>O and 2 ml of conc HCl. Bring to boiling and place the flask on a hot plate; maintain the temperature just below boiling for ~20 min. The filter paper may disintegrate, but this does not interfere. Titrate the sample in the manner described in Sec. 9.

The CeO<sub>2</sub> does not dissolve with the HCl treatment described above. After the sample sandwich is placed in the flask, add ~2 ml of conc H<sub>2</sub>SO<sub>4</sub> and heat the mixture to SO<sub>3</sub> fumes over a flame. Then add a mixture of two parts of conc H<sub>2</sub>SO<sub>4</sub> and one part of 30% H<sub>2</sub>O<sub>2</sub> dropwise to destroy the charred paper and tape. Fume the clear solution down to ~0.25 ml. Dilute to 30 ml, add 0.1 to 0.2 g of ascorbic acid, and proceed with the EDTA titration as described in Sec. 9.

### Notes

1. Consult Refs. 1 and 2 for general information on EDTA titrations; Ref. 3 provides a review of EDTA methods for the lanthanides. This procedure was adapted from Ref. 4.

2. If cerium is to be determined, steps must be taken to promote exchange between radiocerium and carrier. (See Steps 1 and 2 of the CERIUM procedure.)

3. If the sample contains large amounts of elements, such as aluminum, that form amphoteric hydroxides, treatment of the lanthanide fluoride precipitate with an excess of 6M NaOH will precipitate lanthanide hydroxides and dissolve the amphoteric elements. If the amount of fluoride precipitate in Step 1 seems to be too great for the quantity of carrier added, it may be washed with ~10 ml of 6M NaOH and then with H<sub>2</sub>O before carrying out Step 2. The same treatment may be used after Step 2. Precipitation of hydroxides with 6M NaOH may precede or follow Step 3 or may

precede the precipitation with NH<sub>4</sub>OH in Step 6. In these instances, the precipitate is first washed with 10 ml of 6M NaOH and then with H<sub>2</sub>O.

4. The 200 to 400 mesh resin may be centrifuged more easily than the finer resin that is used in the column, and it also settles faster when added to the column. The resin is suspended in water.

5. For the analysis of yttrium, europium, samarium, promethium, praseodymium, cerium, and lanthanum, the initial pH of the eluant (alpha-hydroxyisobutyric acid reagent) is 3.40; the pH is changed at an average rate of ~0.025 pH unit/h. For the operation of one column, this condition is met by starting with 144 ml of 0.394M alpha-hydroxyisobutyric acid, pH 3.40, in the first flask and 144 ml of eluant, pH 4.20, in the second flask. If several columns are operated from one set of flasks, the volumes of eluants are increased proportionally. A small additional volume of low-pH solution is added to the first flask to compensate for the difference in volumes caused by the delivery tubing and the stirring bar. The rate of elution is controlled by the air pressure applied to the reservoirs. The eluant is collected by a fraction collector in 15-min fractions.

When this step is performed, the lanthanides elute in the following manner.

Element	Time that Element Starts Eluting off Column (h)
yttrium	3.1
gadolinium	6.5
europium	8.2
samarium	10.5
promethium	13.2
neodymium	16.5
praseodymium	19.5
cerium	22.5
lanthanum	28.0

Those lanthanides that are present in 6- to 9-mg quantities have elution periods of <2 h. Carrier-free lanthanides elute more sharply; europium, therefore, is not contaminated with gadolinium, which is present carrier-free. Decontamination factors for a particular lanthanide (from other lanthanides) vary from  $3 \times 10^{-5}$  to  $2 \times 10^{-6}$ .

6. For special applications, it may be more convenient to use an eluant at a single pH. For Dowex AG 50W-X8, the following approximate values of pH or alpha-hydroxyisobutyric acid concentration are used to obtain overnight separations: praseodymium, pH 3.98; neodymium, pH 3.82; europium, pH 3.53; terbium, pH 3.34; erbium-holmium, pH 3.21; thulium, 0.08M; and lutetium 0.06M. (For thulium at 0.08M and lutetium at 0.06M, the pH of the eluant is  $\sim 5.5$ .)

7. Some elements elute very closely—scandium-lutetium-ytterbium and americium-neodymium-praseodymium. When contamination from a neighboring element is possible, one or two fractions toward that element should be discarded. It is recommended that  $\sim 10$  mg of praseodymium be added to spread the peak of that element.

8. For the preparation of a sample as a mass separator chlorination source, separation of the desired lanthanide is done without adding the carrier of that element. Usually, 10 mg of a lighter lanthanide carrier are added for hydroxide precipitation before the cation-exchange column separation. The activity peaks are located by gross gamma-counting. Then  $\sim 3$  mg of the appropriate carrier is added to the alpha-hydroxyisobutyrate solution that contains the activity of interest, and the element is precipitated and ignited as in *Step 10*.

After the sample has been ignited, the oxide is transferred into a long, tapered centrifuge tube; 2 ml of conc HCl and 3 to 5 drops of conc HNO<sub>3</sub> are added. The solution is heated gently on a steam bath for 15 min or until the oxide has dissolved and the solution is clear. (A few more drops of

HNO<sub>3</sub> may be necessary to effect solution of the oxide.) The centrifuge tube is placed in an oil bath and evaporated by air jet to a volume of 1 to 2 drops. The drops are transferred in 20-lambda portions to the appropriate end of a quartz vial that contains weighed quartz wool. The vial is dried for  $\sim 8$  min under a heat lamp after each transfer. The centrifuge tube is rinsed with 1 drop of conc HCl and the rinse is transferred to the quartz vial. The vial is heated at 600°C for 20 min, cooled for 20 min, and weighed.

9. The thickness of Scotch polyester film tape (No. 850 Type 2PTA) is uniform along the length of a roll and among most rolls produced from the same batch; its variation is only  $\sim 1.5\%$ . However, there may be a large variation between batches. The tape from two batches examined had thicknesses of 4.9 and 6.3 mg cm<sup>-2</sup>. This variation does not pose a serious problem because several rolls of tape can be obtained from one batch.

## References

1. G. Schwarzenbach, *Complexometric Titrations* (Interscience Publishers, New York, 1955).
2. H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, *Chem. Anal.* **46**, 106 (1958).
3. H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, *Chem. Anal.* **47**, 78 (1959).
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## ADDENDUM I ALTERNATIVE GROUP PURIFICATION

### 1. Introduction

The steps described below are alternatives for *Steps 1* through *7*, Sec. 10 of THE LANTHANIDES procedure. They can be used only for light lanthanides (cerium-terbium) and yttrium. Heavy lanthanides do not back-extract readily from HDEHP (see CONCENTRATION OF TRANS-PLUTONIUM ACTINIDES FROM UNDERGROUND NUCLEAR DEBRIS).

The lanthanides are extracted from a dilute  $\text{HNO}_3$  solution into *n*-heptane that contains di-2-ethylhexyl orthophosphoric acid (HDEHP); the resulting organic phase is scrubbed with dilute  $\text{HNO}_3$ . Under these conditions, the distribution coefficient,  $K(o/a)$ , is  $>96$  for the lanthanides and  $<0.02$  for contaminants in oxidation states of +1 and +2. The lanthanides are back-extracted into a more concentrated  $\text{HNO}_3$ , and the aqueous phase is scrubbed with a solution of HDEHP in trichloroethylene. The  $K(o/a)$  for this extraction is  $<0.02$  for the lanthanides and  $>97$  for contaminants in higher oxidation states. Radioactivities of cesium, barium, cerium, neodymium, europium, yttrium, zirconium, niobium, thorium, and plutonium isotopes were used to obtain the distribution ratios.

### 2. Special Reagents

$\text{HNO}_3$ : 0.05M; 4M

0.5M HDEHP: a solution of di-2-ethylhexyl orthophosphoric acid (mol wt 322.4) in *n*-heptane

0.1M HDEHP: a solution of the acid in trichloroethylene. (If highly purified HDEHP is used, some loss of the lighter lanthanides may occur because the  $K(o/a)$  for extraction from the more dilute nitric acid may be significantly lower.)

### 3. Procedure

*Step 1.* To the active solution in a 125-ml erlenmeyer flask, add 10 mg of carrier of each lanthanide to be determined. For locating purposes,  $\sim 0.3$  mg each of the other lanthanide carriers may be added. If promethium is to be determined, add  $^{145}\text{Pm}$  tracer. (The maximum quantity of carrier that can be used is 60 mg.)

*Step 2.* Add 3 ml of conc  $\text{HClO}_4$ , boil the solution to thick fumes of  $\text{HClO}_4$ , then boil for 1 min. (This step may be omitted if the active solution does not contain species that may prevent exchange of lanthanide activities with the carriers.) Transfer the solution to a 40-ml glass centrifuge tube. Wash the flask with a small amount of  $\text{H}_2\text{O}$  and add washings to the centrifuge tube.

*Step 3.* If the sample does not contain  $\text{HClO}_4$ , evaporate it to dryness under a heat lamp or by boiling gently over a burner; then proceed to *Step 4*. If the sample does contain  $\text{HClO}_4$ , dilute the solution to 20 ml and add 6 to 8 ml of conc  $\text{NH}_4\text{OH}$ . Heat for 2 min on a steam bath, centrifuge, and discard the supernate. Wash the precipitate in 1 to 2 ml of conc  $\text{HNO}_3$  and wash down the sides of the tube with a small volume of  $\text{H}_2\text{O}$ . Evaporate the sample to dryness under a heat lamp or by boiling gently over a burner.

*Step 4.* Dissolve the residue in 10 ml of 0.05M  $\text{HNO}_3$ . Transfer the solution to a 60-ml separatory funnel, add 10 ml of 0.5M HDEHP in *n*-heptane, and shake. (Shake for 1 min if done manually and 2 min if done on a Burrell shaker.) Discard the aqueous (lower) layer.

*Step 5.* Scrub the organic phase with two 10-ml portions of 0.05M  $\text{HNO}_3$  and discard the lower phase after each scrubbing.

*Step 6.* Back-extract the lanthanides by shaking the organic phase with two 5-ml portions of 4M  $\text{HNO}_3$ . After each extraction, drain the

aqueous (lower) phase into the same clean 60-ml separatory funnel. If either yttrium or terbium is to be determined, use four, rather than two, 5-ml portions of 4M HNO<sub>3</sub>. Discard the organic phase.

*Step 7.* Scrub the combined aqueous extracts with two 10-ml portions of 0.1M HDEHP in trichloroethylene. Discard the lower phase after each scrubbing.

*Step 8.* Scrub the aqueous solution once with 10 ml of *n*-heptane to remove most of the dissolved HDEHP. Drain the HNO<sub>3</sub> solution (lower phase) into a 40-ml centrifuge tube and discard the heptane.

*Step 9.* Add 6 to 8 ml of conc NH<sub>4</sub>OH, centrifuge, and discard the supernate. Wash the precipitate with H<sub>2</sub>O and discard the washings.

*Step 10.* Continue with the separation of the individual lanthanides as in *Steps 7 through 11* of THE LANTHANIDES procedure. Addendum II gives alternate methods for sample mounting and yield determination (*Steps 10 and 11*) of THE LANTHANIDES procedure. (Note.)

#### Note

Yttrium can be separated from the lighter lanthanides by slightly modifying the above procedure. Instead of scrubbing with 0.05M HNO<sub>3</sub> in *Step 5*, scrub with four 10-ml portions of 0.75M HNO<sub>3</sub>. With this operation, >99.9% of the neodymium (and lanthanides of lower atomic number) and ~93% of the europium are removed into the aqueous scrubs; 88% of yttrium is retained in the organic phase. Because the remaining europium contamination usually is small relative to the yttrium activity, the yttrium product from *Step 10* may be mounted directly as the oxalate or oxide and counted. [Dissolve the Y(OH)<sub>3</sub> from *Step 9* in ~4 drops of conc HCl, add 20 ml of H<sub>2</sub>O, and proceed as in *Step 10* of THE LANTHANIDES procedure or as in *Alternative Step 10* of Addendum II.]

## ADDENDUM II ALTERNATIVE PROCEDURES FOR SAMPLING, MOUNTING, AND DETERMINING CHEMICAL YIELD

Given below are alternatives to *Steps 10 and 11* for the lighter lanthanides in Sec. 10 of THE LANTHANIDES procedure. If the chemical yield is to be determined by EDTA titration, the time required to prepare a sample for mounting can be shortened by mounting the oxalate rather than the oxide. The oxalate is dissolved for determination of yield. The weight of the oxalate cannot be used for yield determinations.

*Alternative Step 10.* Combine in a centrifuge tube the fractions making up the activity of each lanthanide. Thus, there will be a tube for neodymium activity, one for europium activity, etc. To the tube containing the promethium activity, add 2 ml of neodymium carrier. To each tube, add 5 ml of saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and digest the oxalate precipitates for 15 min on a steam bath. Centrifuge and discard the supernates. Suspend each precipitate in 5 ml of H<sub>2</sub>O, break up the lumps, and filter onto a filter circle. Wash each oxalate with three 5-ml portions of H<sub>2</sub>O, then ethanol, and finally ether. Dry the sample for 10 min at 110°C, mount on an aluminum plate, and cover with Scotch polyester film tape (No. 850 Type 2PTA).

*Alternative Step 11.* After counting has been completed, determine the chemical yield by EDTA titration. Remove the sample, filter paper, and tape cover by cutting down the outside of the filter paper with a sharp blade. Place the sandwich in the titration vessel and add 10 ml of H<sub>2</sub>O and 2 ml of conc HCl. Pipette in an excess of EDTA solution. Heat the solution on a hot plate for ~20 min and adjust the pH to 8 or 9, as described in Sec. 9 of THE LANTHANIDES procedure. Back-titrate the excess EDTA with La<sup>3+</sup> solution (see Note).

## Note

The titration may also be performed with an automatic photoelectric titrator. If done in this manner, Eriochrome Black T is used as the indicator, the wave length is set at 6500 Å, and 0.0125*M* EDTA and 0.025*M* La<sup>3+</sup> solutions are used.

(October 1989)

# SEPARATION OF THE LANTHANIDES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

## 1. Introduction

This procedure was originally developed by David Sisson and Norman Smith of the Lawrence Livermore National Laboratory (LLNL) and is described with their permission. The procedure represents a substantial improvement over previous lanthanide separations, and therefore it is included here.

After the radiochemical purification of the lanthanides as a group, they are placed on a cation-exchange resin of very fine particle size—24 to 43  $\mu\text{m}$ —and then are gradient-eluted with alpha-hydroxyisobutyric acid (alpha-HIB) at pH 5.2 to 5.3 under a pressure of 125 to 175 psi. The acid is run through the exchange columns at a rate of 3 ml/min, and the collection system changes tubes every minute. The very small particle size of the resin permits a rapid separation of the elements.

In the event that only one or two of the lanthanides are to be separated, the appropriate concentrations of alpha-HIB can be used to elute those elements from the column. Also, cation resin of less rigidly defined size, such as minus 400 mesh, may be adequate for these separations.

## 2. Equipment

A diagram of the chromatographic system employed in the separation procedure is shown in Fig. 1. The pieces of equipment are listed here.

- Reservoirs: 4- $\ell$  polypropylene or glass bottles.
- Outlet lines should be fitted with replaceable filters to keep particulates out of the lines and pumps
- Gradient pump: source: Fluid Metering, Inc., Oyster Bay, New York, Model RPG-20-2-CKC;  $\frac{3}{8}$ -in. ceramic piston, plastic cylinder, ceramic cylinder liner

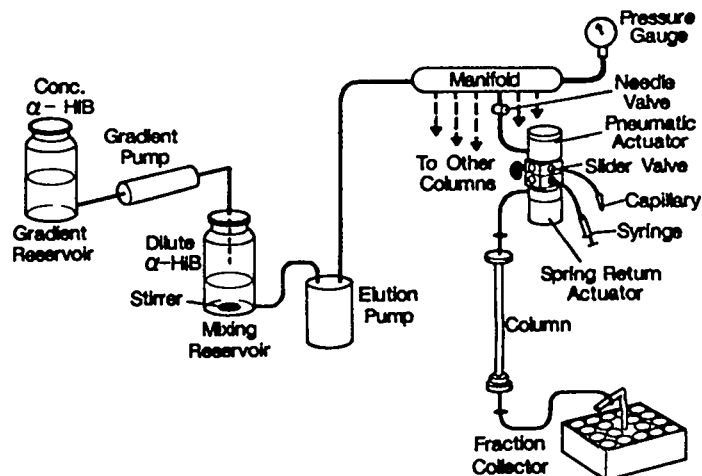


Fig. 1. Chromatographic system.

- Magnetic stirrer: many commercial sources
- Elution pump: source: Eldex Laboratories, Inc., Menlo Park, California; No. B-100-S-4; 32 ml/min.
- Luer 3-way stopcocks: source: Bio-Rad, Richmond, California; attached to elution pump inlet
- TFE tubing:  $\frac{1}{16}$  in., many commercial sources; used for all delivery lines after the pump ( $\sim 200$  ft for six columns)
- FTE Tubing:  $\frac{1}{8}$  in., many commercial sources; used for all delivery lines before pump ( $\sim 30$  ft)
- Two nine-port manifolds: many commercial sources
- Pressure gauge: source: Rainin Instrument Co., Inc., Woburn, Massachusetts, Catalog No. 38-057; 0 to 600 psi
- Needle valve: one for each column; Nupro fine-metering valve SS-1 SG;  $\frac{1}{16}$ -in. Swagelok fittings
- Pneumatic actuator: source: Laboratory Data Control, Riviera Beach, Florida, Catalog No. 42350; one for each column (Fig. 2)
- Four-way slider valve: source: Laboratory Data Control, Riviera Beach, Florida, Catalog No. 42270; two for each column; 0.031-in. bore



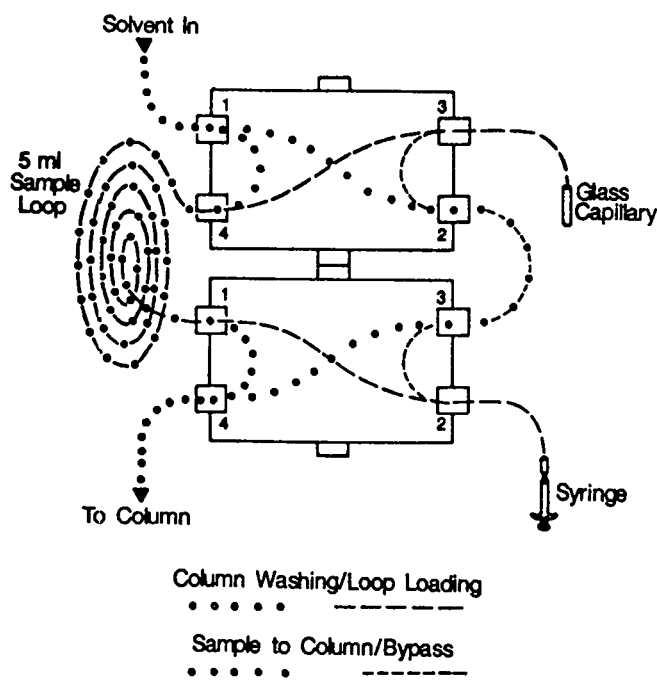


Fig. 2. Injection system.

Sample loop: source: Laboratory Data Control, Riviera Beach, Florida, Catalog No. 43320; 5-ml, one for each column

Plastic syringe: 10 cc, one for each column

Capillary tubes: one for each sample loaded

Spring return actuator: source: Laboratory Data Control, Riviera, Florida, Catalog No. 42370; one for each column

Type LC columns: source: Laboratory Data Control, Riviera, Florida, Catalog No. 40450; 6.3 mm by 33 cm (see Fig. 3)

Collection system: source: Gilson Medical Electronics, Middleton, Wisconsin

(a) Race Track Fractionator: Model FC-220-13; one for every five columns

(b) Set of racks for 13- by 100-mm tubes, Model 22-34-22

(c) Multiple column adaptor; Model 22-17-01

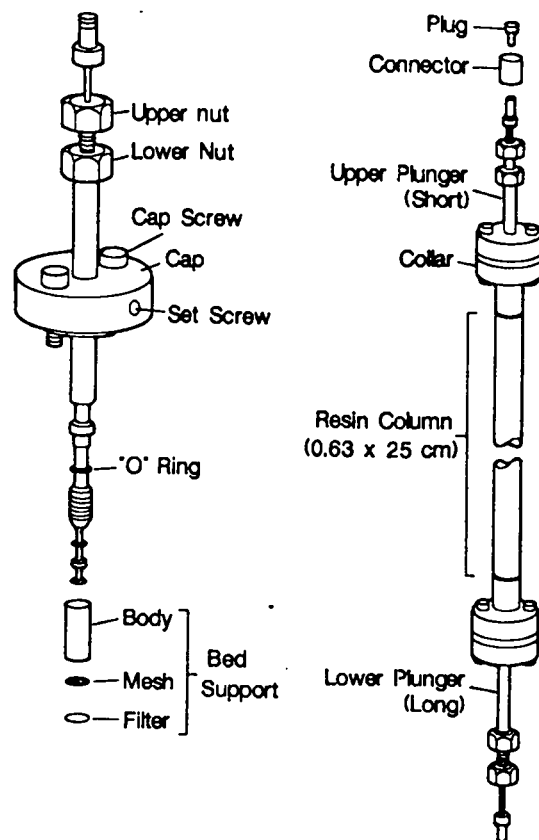


Fig. 3. Type LC columns.

Miscellaneous items: female Luer adapters; male Luer adapters; couplings for  $\frac{1}{16}$ -in. tubing; plugs; tube end fittings for  $\frac{1}{16}$ -in. tubing; replacement LC column tubes; replacement LC column bed supports; replacement diffusing meshes for 6.3-mm bed; replacement 30 frits for 6.3-mm-bore columns; replacement "O" rings for 6.3-mm plungers and bed supports; Teflon tubing and slider valves.

### 3. Reagents

HCl: conc

H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>: saturated aqueous solution

Cation-exchange resin: Dowex AG 50W-X12 (Dowex AG 50W-X8 is also acceptable); particle size, 24- to 43- $\mu$ m (Dowex AG 50W-X12 minus 400 mesh is acceptable for single lanthanide separations)

Alpha-hydroxyisobutyric acid (alpha-HIB): 5M

Alpha-HIB solutions:

<u>Molar conc</u>	<u>5M Alpha-HIB</u>	<u>Conc NH<sub>4</sub>OH</u>
0.05	10 ml/l	2.9 ml/l
0.42	84 ml/l	28 ml/l
1.00	200 ml/l	60 ml/l

8-quinolinol (8-hydroxyquinoline) solution: 6% by weight in absolute ethanol; stored in a dark bottle

8-quinolinol reagent: a mixture of one part by volume of 8-quinolinol solution, one part of absolute ethanol, two parts of conc NH<sub>4</sub>OH, and four parts H<sub>2</sub>O; made up just before use

#### 4. Sample Dissolution and Loading

*Step 1.* Remove the plugs on the delivery lines to be used and close the stainless steel needle valves on those lines that will not be in use.

*Step 2.* Set the elution pump to deliver 3 ml/min/column; pump H<sub>2</sub>O through the delivery system to flush it and to check for free flow in each line. Shut off the pump.

*Step 3.* Remove the plugs from the ends of each column and connect the short (upper) plungers to the delivery lines and the long (lower) plungers to the outlet lines.

*Step 4.* Pump H<sub>2</sub>O through the resin columns for a few minutes to be sure that liquid flows freely through them and that they do not leak.

*Step 5.* Place 0.05M alpha-HIB solution (4000 ml/six columns) in the mixing reservoir; after bleeding air from the line, connect the reservoir to the elution pump.

*Step 6.* Switch the elution pump to the mixing reservoir to precondition the resin columns while the sample loops are being loaded as described in *Step 8.*

*Step 7.* The samples should be in the form of washed hydroxides. To each sample add ~3 drops of conc HCl and stir. Do not add more than 4 to 5 drops of acid. (If the solution is too acidic, the lanthanides will not stick on the resin column.) Wash the tube walls and dilute to 3 ml with H<sub>2</sub>O. Stir and centrifuge. Transfer with a fine-tipped pipette to a 12- or 15-ml graduated centrifuge tube; be careful not to pipette any residue from the bottom of the sample tube.

*Step 8.* Fill each sample loop with 5 ml of H<sub>2</sub>O by either pulling the liquid through the capillary with the syringe or filling the syringe with 5 ml of H<sub>2</sub>O and forcing the liquid through the loop. Care must be taken to avoid air bubbles. Use the syringe to pull the 3 ml of sample solution into the loop and follow with 1 ml of H<sub>2</sub>O. (Be careful to load samples in the proper sequence. Avoid any solids in the cones.) The samples and resin columns are now ready for the elution procedure.

#### 5. Elution Procedure

The collection system should be loaded with tubes and in position, the mixing reservoir should be adjusted to 3750 ml/six columns, and the sample should be loaded.

*Step 1.* Check the system for smooth operation with no leaks. (This is the last opportunity for convenient repairs.) Turn on the control of the collection system, set it to collect at 1 min/tube, and start collecting at tube 1. Actuate the injection valves by pressurizing to 80 to 90 psi. Check for actual injection (valve slide down). A colored band 1 to 3 cm wide should form at the top if neodymium is present.

*Step 2.* After ~10 min, adjust the columns for uniform flow by closing the stainless steel needle valves on columns that are running fast. The pressure should not be >250 psi. It may be necessary to make adjustments during the early part of the elution.

*Step 3.* Turn on the stirring motor to the gradient reservoir and fill the reservoir with ~1000 ml of 0.42M alpha-HIB solution for six columns.

*Step 4.* Add a few drops of precipitating agent—8-quinolinol reagent or saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution—to the collection tubes of every third row. Lutetium, thulium, and scandium are precipitated as 8-quinolates, and yttrium, terbium, europium, and neodymium as oxalates.

The approximate tubes at which the lanthanides are eluted are as follows:

lutetium	25 to 40
thulium	50 to 70
yttrium	108 to 133
terbium	133 to 153
europium	173 to 188
neodymium	193 to 208

(If scandium is to be eluted, start with 0.04M alpha-HIB at pH 5.2. This element should come off the columns at tubes 20 to 30. After scandium comes off, switch to 0.05M alpha-HIB for lutetium, etc.)

*Step 5.* When elution of an element is detected, add the appropriate precipitating agent to the first and last few tubes of the elution band. When elution of the element is complete, combine the tubes containing the heaviest precipitates into a separate, labeled 40-ml glass centrifuge cone for the oxalates or a 150-ml beaker for the 8-quinolates. Label carefully.

*Step 6.* At about tube 32, start the gradient pump, eliminate air from the lines, insert the dripper into the mixing reservoir, and adjust pump settings and mixing reservoir volumes approximately as shown in table at bottom of this page.

*Step 7.* When the last element desired has been eluted, turn off the gradient pump, remove the collection system, switch the elution pump inlet to 1M alpha-HIB solution, and alternately pump alpha-HIB solution and H<sub>2</sub>O three times each for 5 min. Discard effluents.

*Step 8.* Pump H<sub>2</sub>O for 5 to 10 min. Shut off the pump and release injection pressure (injection valves slide up).

*Step 9.* Disconnect the columns from the delivery and outlet lines. Plug the delivery lines and both ends of each column and set the columns aside for regeneration. Open all stainless steel valves.

## 6. Treatment of Eluted Elements

Any lanthanide element that is heavier than yttrium (in terms of its properties, yttrium would occupy a position between dysprosium and holmium in the lanthanide sequence) precipitates more quantitatively as the 8-quinolate than as the oxalate. Every element preceding yttrium in the sequence can best be precipitated with saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution.

Tube No.	Gradient Pump Setting		Reservoir volume (ml)		Notes
	6 Columns	4 Columns	6 Columns	4 Columns	
~30	1.2	0.8	~3000	~2000	During lutetium elution
~80	2.2	1.5	~2000	~1333	After thulium elution
~133	3.1	2.1	~1000	~667	After yttrium elution
~173	6.7	4.5			Start of europium elution

Approximately 2 ml of filter paper pulp is added to each 8-quinolate and oxalate sample, which is then placed in a steam bath for at least 15 min. The 8-quinolates are then cooled for at least 30 min, but the oxalates can be handled while still warm.

The 8-quinolates are filtered through  $\sim 0.5\text{-}\mu\text{m}$  polycarbonate filters, transferred to clean Coors crucibles, and ignited at  $970^\circ\text{C}$  for 30 to 60 min. The samples are then cooled, weighed, and mounted for counting.

The oxalates are centrifuged after removal from the steam bath. The supernate is discarded and the precipitate is suspended in  $\sim 5\text{ ml}$  of  $\text{H}_2\text{O}$ . The oxalate is filtered through Whatman No. 42 filters and is ignited as above. The cooled samples are then weighed and mounted for counting.

## 7. Adaptations of the Procedure for Specific Lanthanides

The following table illustrates roughly the concentrations of alpha-HIB solution at which the various lanthanides (including scandium and yttrium) are eluted at pH 5.2.

Concentration of Alpha-HIB (M)	Lanthanide
0.04	scandium
0.055	ytterbium
0.055-0.065	thulium
$\sim 0.065$	erbium
$\sim 0.075$	holmium
0.075-0.09	yttrium
$\sim 0.09$	dysprosium
0.09-1.05	terbium
0.12-0.14	gadolinium
0.14-0.165	europium
0.17-0.18	samarium
0.17-0.20	promethium
0.21-0.235	neodymium
$\sim 0.235$	praseodymium
0.25-0.28	cerium
0.285-0.31	lanthanum

From this table one can obtain the approximate concentration of alpha-HIB solution required for

the elution of a particular lanthanide. If only one or two elements are to be separated, the appropriate concentrations of alpha-HIB should be used. For example, scandium and yttrium were separated by first employing an acid concentration of  $0.04M$  for scandium and then one of  $0.09M$  for yttrium.

## 8. Regeneration of Resin Columns

Regeneration of the columns serves several purposes: (1) removal of dirty and potentially contaminated filters and resin from columns, (2) replacement of exhausted resin, and (3) replacement of contaminated filters. Refer to Fig. 3 and carry out the following procedure for the regeneration of the columns.

*Step 1.* Remove the plugs and cap screws from the upper and lower plungers. Loosen the lower nuts and withdraw the plungers carefully. Remove and discard the filters.

*Step 2.* Wash the bed supports and force  $\text{H}_2\text{O}$  through each support to check for easy flow (a steady stream).

*Step 3.* Check the diffusing meshes and replace them if necessary. Carefully press a new  $30\text{-}\mu\text{m}$  filter disk into each bed support. (The head of a cap screw works well for this purpose.) Force  $\text{H}_2\text{O}$  through the assembled beds in a small stream or at a fast drip.

*Step 4.* Remove and discard the resin bed. Rinse the empty column and fill it with  $\text{H}_2\text{O}$ .

*Step 5.* Carefully insert an upper plunger into each column, force  $\text{H}_2\text{O}$  through the filter, and adjust the plunger so that the bed support "O" ring is even with the bottom of the collar.

*Step 6.* Tighten both nuts until the bed supports rotate inside the columns without changing the position of the supports. Loosen the two set screws and fasten the caps to the collars

with cap screws. Tighten the set screws and then the lower nuts.

*Step 7.* Hang the columns, fill with slurried resin, and allow the resin to settle.

*Step 8.* Use a H<sub>2</sub>O-filled syringe attached to an empty plunger to pack the settled resin in the columns. (Never allow air to enter the resin bed.) Add fresh resin to the columns and pack until the bed is 5 to 8 mm below the collar; the H<sub>2</sub>O level should be above the bed.

*Step 9.* Insert the lower plungers into the packed columns as the upper plungers were inserted in *Steps 5 and 6.* (Anytime the packed columns are to be left, both plungers must be firmly plugged to exclude air.) The columns are now ready to be flushed.

*Step 10.* Remove the plugs on the delivery lines to be used and close the stainless steel needle valves on those lines that will not be in use. Using the elution pump, force H<sub>2</sub>O through the delivery system to flush the system and check for free flow in each line. Shut off the pump.

*Step 11.* Remove the plugs from both plungers and delivery lines. Set the elution pump to deliver ~3 ml/min/column and pump H<sub>2</sub>O to see that all columns are flowing at about the same rate.

*Step 12.* Pump H<sub>2</sub>O for ~10 min. The pressure should be 75 to 125 psi. Shut off the pump.

*Step 13.* Screw plugs into the lower plungers, disconnect the columns from the delivery lines, and open all the needle valves.

*Step 14.* Loosen the set screws on the upper plungers, press plungers against resin bed, and tighten the set screws. If the "O" ring of the upper bed support is more than a few millimeters from the bottom of the collar, remove the plunger, add more resin, and reseal the plunger. Screw plugs into the plungers, make sure the nuts are tight, and set

aside the columns until needed. Screw plugs into the delivery lines and open all needle valves.

The columns are now ready.

#### Note

Because alpha-HIB will, upon prolonged contact or in high concentration, attack stainless steel, the use of metal should be minimized.

(October 1989)

# A RAPID PROCEDURE FOR THE SEPARATION OF CARRIER-FREE THORIUM FROM URANIUM AND FISSION PRODUCTS

C. J. Orth and W. R. Daniels

## 1. Introduction

This procedure describes the purification of thorium that has been produced by 100-MeV proton irradiation of  $\sim 100$  mg of  $^{238}\text{U}$ . The actual separations are begun at end of bombardment + 20 min, and the procedure requires  $\sim 45$  min. The resin columns are operated under pressure so that effluent flow rates are  $\sim 1$  drop/1 to 2 s from the cation-exchange column and 1 drop/2 to 3 s from the anion-exchange columns.

The separation of thorium requires decontamination from fission products, neptunium, protactinium, and macro uranium. The first decontamination step in the procedure is the adsorption of thorium on a cation resin column from 3M HCl. The element is removed from the column with  $\text{H}_2\text{C}_2\text{O}_4$  and is taken up in conc HCl after the destruction of oxalate. Zirconium is then removed by adsorption on anion resin columns, and the thorium is extracted into 0.5M HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The latter step gives excellent separation from the lanthanides. Finally, the thorium is back-extracted into aqueous HCl-HF and the solution is evaporated on a Teflon foil.

## 2. Reagents

HCl: conc; 6M; 3M; 2M

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc

HF: conc

$\text{H}_2\text{C}_2\text{O}_4$ : 0.5M

$\text{NH}_2\text{OH}\cdot\text{HCl}$ : solid

*n*-heptane

HDEHP solution: 0.5M solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane

AG 50W-X4 cation resin column, 100 to 200 mesh,  $\text{H}^+$  form; stored as a slurry in  $\text{H}_2\text{O}$   
AG 2-X8 anion resin column, 100 to 200 mesh,  $\text{Cl}^-$  form, preequilibrated with conc HCl

## 3. Procedure

*Step 1.* In a 50-ml erlenmeyer flask, dissolve as much as 150 mg of uranium foil in 3 ml of conc HCl and 2 ml of conc  $\text{HNO}_3$ . Add 5 ml of conc  $\text{HClO}_4$ , fume to near dryness, and then add 3 ml of 3M HCl.

*Step 2.* Transfer the solution to the top of a 5-cm by 8-mm AG 50 W-X4 (100 to 200 mesh,  $\text{H}^+$  form) cation resin column. Wash off uranium and other contaminating activities first with 16 ml of 3M HCl and then with 4 ml of conc HCl. Elute the thorium with 10 ml of 0.5M  $\text{H}_2\text{C}_2\text{O}_4$  and collect the eluate in a 50-ml erlenmeyer flask.

*Step 3.* Add 5 ml of conc  $\text{HClO}_4$  and 2 ml of conc  $\text{HNO}_3$ ; evaporate to dryness over a burner. Cool and add 2 ml of conc HCl. Transfer the solution to the top of a 5-cm by 8-mm AG 2-X8 anion resin column. Pass the solution that contains the thorium through two of these columns in succession; follow with 3 ml of conc HCl wash. Collect the effluent in a 50-ml erlenmeyer flask that contains  $\sim 100$  mg  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . (Zirconium and any remaining uranium, neptunium, and protactinium activities remain on the anion resin.) Boil the solution down to  $\sim 2$  ml. (At this point, cerium(IV) has been reduced to the III state.)

*Step 4.* Transfer the solution to a 15-ml tapered glass centrifuge tube and add 2 ml of 0.5M HDEHP solution in *n*-heptane. Shake for 10 s and discard the aqueous (lower) layer, which contains lanthanides. Wash the heptane layer successively with 2 ml each of conc, 6M, and 2M HCl. Each time, shake for 10 s and discard the washes. (At this stage it is possible to gamma-count the thorium in the heptane layer.)

*Step 5.* Add 0.5 ml of conc HF and 1.5 ml of 6M HCl to the heptane solution, shake for 10 s, and discard the heptane (upper) layer. Contact the aqueous layer with 2 ml of *n*-heptane, shake, and discard the heptane layer. Evaporate the aqueous solution to near dryness on an oil bath (an air jet will speed up the evaporation process). Use a finely drawn pipette to place the liquid on a Teflon foil. Rinse the centrifuge tube with a drop of conc HCl and add the rinse to the foil. Evaporate to dryness under a heat lamp.

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# THORIUM

R. J. Prestwood

## 1. Introduction

In the separation of thorium from large amounts of fission products ( $10^{15}$  fissions or more), four principal decontamination steps are employed. (1) The  $\text{Th}(\text{IO}_3)_4$  precipitation gives separation from the lanthanides. (2) The  $\text{Th}(\text{C}_2\text{O}_4)_2$  precipitation effects separation from zirconium. (3) Ion-exchange from a concentrated ( $>12M$ )  $\text{HCl}$  solution on an anion-exchange resin results in the adsorption of zirconium, iron, neptunium, plutonium, and uranium; the thorium passes through the column. (4) Extraction of thorium from an  $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$  solution by means of mesityl oxide gives excellent decontamination from the alkali and alkaline earth metal ions (including radium), lanthanum, and cerium. This extraction is ineffective for the separation of thorium from zirconium, plutonium, and uranium and gives only poor decontamination from neptunium.

Thorium is finally precipitated as the oxalate and ignited to the dioxide, in which form it is mounted and weighed. The yield is 70 to 80%.

## 2. Reagents

Thorium carrier: 10 mg thorium/ml, (see Sec. 3)

Bismuth carrier: 10 mg bismuth/ml, added as  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in dilute  $\text{HNO}_3$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as purified  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : conc; gas

$\text{HNO}_3$ : conc;  $6M$

$\text{H}_2\text{SO}_4$ : conc

$\text{HIO}_3$ :  $1M$  (filtered)

$\text{H}_2\text{C}_2\text{O}_4$ : saturated solution (filtered); 1% solution

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{S}$ : gas

$\text{SO}_2$ : gas

$2.4M$   $\text{Al}(\text{NO}_3)_3$  in  $1.2M$   $\text{HNO}_3$  (filtered)

$\text{KClO}_3$ : solid

Methanol: absolute

Mesityl oxide

Anion-exchange resin column: AG 1-X10, 100 to 200 mesh; stored as a slurry in  $\text{H}_2\text{O}$ .

## 3. Preparation and Standardization of Carrier

If the purity of the thorium is known, the metal may be weighed out directly as a primary standard. It is dissolved on a steam bath in a small excess of conc  $\text{HNO}_3$  in a platinum dish, and there are periodic additions of small amounts of  $0.1M$   $\text{HF}$ . If  $\text{Th}(\text{NO}_3)_4$  is used as carrier, it is dissolved in  $\sim 0.001M$   $\text{HNO}_3$  and filtered. To a  $10.0\text{-ml}$  aliquot (four standardizations are usually carried out) of the carrier, 10 drops of conc  $\text{HCl}$  are added and the solution is boiled over a Fisher burner. Then  $4\text{ ml}$  of saturated  $\text{H}_2\text{C}_2\text{O}_4$  are added and the solution is boiled for 2 min. The  $\text{ThC}_2\text{O}_4$  precipitate is filtered through filter paper and washed with  $\sim 1\%$   $\text{H}_2\text{C}_2\text{O}_4$  solution (the saturated solution is diluted 1:10). The precipitate is transferred to a weighed porcelain crucible and is carefully ignited at  $900^\circ\text{C}$  for 1 h. The carrier is weighed as  $\text{ThO}_2$ .

## 4. Procedure

*Step 1.* Into a  $40\text{-ml}$  short-taper glass centrifuge tube, pipette  $2.0\text{ ml}$  of standard thorium carrier; add the fission-product solution and 5 drops of lanthanum carrier. Precipitate  $\text{Th}(\text{OH})_4$  by means of an excess of conc  $\text{NH}_4\text{OH}$ , centrifuge, and discard the supernate.

*Step 2.* To the precipitate add  $8\text{ ml}$  of conc  $\text{HNO}_3$ ,  $15\text{ ml}$  of  $\text{H}_2\text{O}$ , and  $7\text{ ml}$  of  $1M$   $\text{HIO}_3$ . Centrifuge the  $\text{Th}(\text{IO}_3)_4$  precipitate and discard the supernate. Wash the precipitate with  $15\text{ ml}$  of a solution that is  $4M$  in  $\text{HNO}_3$  and  $0.25M$  in  $\text{HIO}_3$ . Centrifuge and discard the supernate.

*Step 3.* To the precipitate add  $1\text{ ml}$  of conc  $\text{HCl}$  and 5 drops of zirconium holdback carrier.



Heat while stirring over an open flame until the precipitate dissolves and the solution boils. Dilute to 5 ml with H<sub>2</sub>O and bubble in SO<sub>2</sub> gas until the solution becomes essentially colorless. Dilute to 10 ml with H<sub>2</sub>O and boil until the solution is water-white. Add 4 ml of saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution and continue boiling for ~1 min. Centrifuge the oxalate precipitate and discard the supernate.

*Step 4.* To the precipitate add 1 ml of conc HNO<sub>3</sub> and ~100 mg of solid KClO<sub>3</sub>. Heat cautiously to boiling to destroy oxalate. Dilute to 15 ml with H<sub>2</sub>O and use an excess of conc NH<sub>4</sub>OH to precipitate Th(OH)<sub>4</sub>. Centrifuge and discard the supernate.

*Step 5.* Add 10 drops of conc HCl to the precipitate and bubble in HCl gas through a transfer pipette until the solution is saturated. Use a hypodermic syringe and the same pipette to transfer the solution (which has a volume of ~1 ml) onto an AG 1-X10 anion-exchange resin column. (Before use, the resin column is treated with a wash solution made up by adding 1 drop of conc HNO<sub>3</sub> (Note 1) to 20 ml of conc HCl and saturating with HCl gas at room temperature.) Use air pressure to force the sample solution through the column in ~3 min, but do not allow the meniscus to fall below the top of the resin. Collect the effluent in a 40-ml short-taper centrifuge tube. Add 1 ml of the resin wash solution to the original centrifuge tube and use the same pipette to transfer the washings onto the column. Force the washings through the column in the same manner used for the sample solution, and collect them with the sample solution. This wash may be repeated if necessary to obtain the maximum yield of thorium.

*Step 6.* Dilute the collected sample and washes to ~25 ml with H<sub>2</sub>O and make the solution alkaline with conc NH<sub>4</sub>OH. Centrifuge the Th(OH)<sub>4</sub> precipitate and discard the supernate.

*Step 7.* Dissolve the precipitate with 6 drops of 6M HNO<sub>3</sub>. Use 10 ml of 2.4M Al(NO<sub>3</sub>)<sub>3</sub>-1.2M HNO<sub>3</sub> mixture (hereafter called the extraction

mixture) to transfer the sample solution to a 60-ml separatory funnel. Add 10 ml of mesityl oxide to the separatory funnel, shake for 15 to 20 s, and discard the water (lower) layer. Wash the mesityl oxide layer twice with 5-ml portions of extraction mixture and discard each washing. Back-extract the thorium with two 5-ml washes of distilled H<sub>2</sub>O, and collect both H<sub>2</sub>O layers in a 40-ml short-taper centrifuge tube. Dilute to 15 ml and add 8 ml of conc HNO<sub>3</sub> and 7 ml of 1M HIO<sub>3</sub> (Note 2). Centrifuge the Th(IO<sub>3</sub>)<sub>4</sub> precipitate and wash as in *Step 2*.

*Step 8.* Repeat *Steps 3* through *6*.

*Step 9.* To the Th(OH)<sub>4</sub> precipitate, add 5 drops of bismuth carrier and 10 drops of conc H<sub>2</sub>SO<sub>4</sub>. Dilute to 10 ml with H<sub>2</sub>O and saturate the solution with H<sub>2</sub>S. Filter through filter paper and collect the filtrate in a 40-ml short-taper centrifuge tube. Wash the precipitate with a small amount of H<sub>2</sub>O and combine the wash with the filtrate; discard the precipitate. Make the filtrate alkaline with conc NH<sub>4</sub>OH, centrifuge, and discard the supernate.

*Step 10.* Repeat *Step 7*.

*Step 11.* Repeat *Step 3*, but do not add zirconium holdback carrier and do not centrifuge the oxalate precipitate.

*Step 12.* Filter the hot solution that contains the oxalate precipitate onto a filter circle. Wash the precipitate with 1% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution. Use forceps to transfer the filter paper to a porcelain crucible; ignite for 15 to 20 min at 900°C.

*Step 13.* Transfer the ThO<sub>2</sub> to a dry 40-ml long-taper centrifuge tube. (This is done by holding the edge of the crucible with forceps and dumping the contents into the centrifuge tube. Little or no ThO<sub>2</sub> adheres to the crucible.) Grind the ThO<sub>2</sub> with a 5-mm fire-polished glass stirring rod; add 1 ml of absolute methanol and continue grinding until the solid is very fine. Add 10 ml

of methanol and suspend the solid by vigorous swirling. Transfer onto a weighed filter circle. Apply suction until the methanol has passed through the filter circle. Remove the circle, dry in an oven at 115°C for 10 min, place in the balance case for 20 min, weigh, and mount.

### 5. Beta-Counting of Thorium

Whenever thorium beta activities (such as isotopes 231, 233, and 234) are counted and  $^{232}\text{Th}$  is used as carrier, there is a problem with growth of beta activities from the carrier. Examination of the decay chain of  $^{232}\text{Th}$  shows that the amount of beta activity depends upon the quantity of  $^{228}\text{Th}$  present. In the chain, the longest-lived parent of  $^{228}\text{Th}$  (half-life 1.9 yr) is  $^{228}\text{Ra}$  (half-life 6.7 yr). Thus, the amount of  $^{228}\text{Th}$  present in  $^{232}\text{Th}$  depends upon the time at which  $^{228}\text{Ra}$  is separated. The beta-emitters succeeding  $^{228}\text{Th}$  grow in essentially with the half-life of  $^{224}\text{Ra}$  (3.64 d). Therefore, the beta activity that is observed from natural thorium, which has had all of its decay products chemically removed, grows in with a 3.64-d half-life. Thus 1 mg of natural thorium in equilibrium with its decay product has 494 disintegrations/min of beta activity. Because the history of the thorium used as carrier is not usually known, the most convenient way to correct for these counts is the following method.

Pipette out enough carrier solution to give approximately the same weight a true sample would have if carried through the whole separation procedure. Perform *Steps 9* through *13* of the procedure. Note the time of the last mesityl oxide wash in *Step 10*. After the sample is mounted, count it every few hours over a period of several days. If the time of the last mesityl oxide wash is used as  $t_0$ , it is possible to correct for the growth of betas from the carrier.

### 6. Absolute Beta-Counting of Some Thorium Isotopes

The relation between counts and disintegrations for thorium isotopes of mass numbers 231, 233, and 234 can be obtained from  $^{235}\text{U}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$ , respectively. If a weighed quantity of  $^{235}\text{U}$  or  $^{238}\text{U}$  is taken, thorium carrier added, and a chemical separation of thorium made, calculate in each case the number of thorium disintegrations present. By counting the sample and correcting for decay from time of separation, one has a direct relationship between counts and disintegrations. The self-absorption of the sample can be taken into account by this technique on several different weights of thorium carrier with identical specific activity. For example, one adds 100 mg of thorium carrier to a weighed amount of either  $^{235}\text{U}$  or  $^{238}\text{U}$ , mixes the solution thoroughly, takes several aliquots of different sizes, and separates the thorium. In this way, one can plot a curve of sample weight *vs* disintegrations.

In the case of  $^{233}\text{Th}$  the situation is different. The decay product of this isotope is  $^{233}\text{Pa}$ , which is also the immediate decay product of  $^{237}\text{Np}$ . By separating  $^{233}\text{Pa}$  from a known weight of  $^{237}\text{Np}$  and counting the former, one has a direct relationship for  $^{233}\text{Pa}$  of counts *vs* disintegrations. For a sample of  $^{233}\text{Th}$  one takes two known aliquots that differ by a factor of  $\sim 1000$  in activity. (The ratio of  $^{233}\text{Pa}$  to  $^{233}\text{Th}$  half-lives is 1693:5.) The weaker aliquot is counted for  $^{233}\text{Th}$  immediately upon separation of protactinium. The stronger one is permitted to decay until it is all  $^{233}\text{Pa}$  and is then counted. From the previous ( $^{237}\text{Np}$ ) calibration, one then can find the disintegrations of  $^{233}\text{Pa}$  for this sample. The sample is corrected for decay back to the time the weaker sample was counted for  $^{233}\text{Th}$ , thus the number of atoms is obtained for the latter when aliquot correction is made.

## Notes

1. The  $\text{HNO}_3$  is used to maintain an oxidizing medium on the resin to prevent reduction of plutonium.

2. At this point, the solution will be slightly colored from oxidation of dissolved mesityl oxide. This, however, does not affect the results.

(October 1989)

## THORIUM-230

J. W. Barnes and H. A. Potratz

### 1. Introduction

The determination of  $^{230}\text{Th}$  in coral samples involves carrier-free separation of the total thorium content by use of TTA[4,4,4, trifluoro-1-(2-thienyl)-1,3-butanedione]. Thorium is finally adsorbed on a cation-exchange resin column and eluted with  $\text{H}_2\text{C}_2\text{O}_4$ . It is then alpha-counted and pulse-analyzed;  $^{228}\text{Th}$  is employed to determine chemical yield. The chemical yield is 50 to 70%.

#### (A) Determination in Coral Samples

### 2. Reagents

$^{228}\text{Th}$  tracer: known amount; 5 to 100 counts/min  
 $\text{HNO}_3$ : conc  
 $\text{HClO}_4$ : 70%; 3M  
 $\text{HCl}$ : 3M  
 $\text{H}_2\text{C}_2\text{O}_4$ : 0.5M  
 $\text{NH}_4\text{OH}$ : conc; 3M  
TTA[4,4,4, trifluoro-1-(2-thienyl)-1,3-butanedione]  
reagent: 0.5M in benzene  
Dowex AG 50-X4 cation-exchange resin (see Note 2)

### 3. Procedure

*Step 1.* Transfer ~20 g of coral, weighed to the nearest 0.1 g, to a 600-ml beaker. Add  $^{228}\text{Th}$  tracer in known amount (5 to 100 counts/min) and wash down the sides of the beaker with  $\text{H}_2\text{O}$ .

*Step 2.* With a watch glass in place on top of the beaker, gradually add 75 ml of conc  $\text{HNO}_3$ , dropwise at first to prevent excessive foaming. Place the covered beaker on a hot plate and allow the solution to boil until the vegetable fibers present in most samples have disintegrated and brown fumes are no longer evolved. Cool to room temperature and cautiously add 70%  $\text{HClO}_4$ . (During this and subsequent steps that involve fuming with  $\text{HClO}_4$ , the operator should wear a

face shield and rubber gloves.) Evaporate to dense white fumes and continue heating for at least an additional 5 min. Cool to room temperature and dilute to ~200 ml with  $\text{H}_2\text{O}$ .

*Step 3.* Add conc  $\text{NH}_4\text{OH}$  until the solution is barely acid and then use 3M  $\text{NH}_4\text{OH}$  and 3M  $\text{HClO}_4$  to adjust the pH to 2.0 to 2.5.

*Step 4.* To a separatory funnel add the solution from Step 3 and 150 ml of 0.5M TTA in benzene. Stir for at least 1.5 h with an electric stirrer. Permit the layers to separate, draw off the aqueous layer, and discard (Note 1).

*Step 5.* Wash the benzene layer that contains the thorium complexed with TTA for ~30 s by stirring with 100 ml of  $\text{H}_2\text{O}$ . Discard the washings. Wash again with 50 ml of  $\text{H}_2\text{O}$  and discard the washings.

*Step 6.* Extract the thorium from the benzene by stirring for 3 min with 100 ml of 3M  $\text{HCl}$ .

*Step 7.* Transfer the aqueous phase to a beaker and evaporate with an air jet on a steam bath until the volume has been reduced to 20 to 30 ml. Transfer the solution to a 40-ml glass centrifuge tube and continue evaporation to a volume of 1 to 2 ml.

*Step 8.* Add 1 ml of conc  $\text{HNO}_3$  and boil over a flame until brown fumes no longer evolve. Cool to room temperature, then add 0.3 to 0.4 ml of 70%  $\text{HClO}_4$ , and boil until white fumes appear. Cool to room temperature and dilute to ~3.5 ml with  $\text{H}_2\text{O}$ .

*Step 9.* Transfer the solution to the top of an AG 50-X4 cation-exchange column (Note 2); rinse the centrifuge tube with 0.5 ml of  $\text{H}_2\text{O}$  and add the rinsings to the column. (If air bubbles are present in the column, they should be removed by stirring with platinum wire.) Force the solution through the column under 2 lbs. of air pressure and then wash the column with 3 to 4 ml of 3M  $\text{HCl}$  under

the same pressure. Discard the first effluent and the wash.

*Step 10.* Pour 2 ml of 0.5M  $H_2C_2O_4$  onto the column and allow the solution to run through under atmospheric pressure. Collect the drops from the column on 1-in.-square (1- to 3-mil) platinum plates, which are placed just far enough below the column so that drops separate from the tip before hitting the plate. Collect 9 drops of eluate on each of four plates. Dry the plates under a heat lamp; then ignite over an open flame.

*Step 11.* Alpha-count the individual plates and then pulse-analyze those plates that carry the activity.

## (B) Determination in Old Fission-Product Material

### 1. Introduction

The method described for the determination of  $^{230}Th$  in coral samples is not satisfactory for fission-product solutions inasmuch as the plutonium present in the latter comes through the separation procedure and seriously interferes in pulse analyses. To overcome this difficulty, plutonium is removed on an anion-exchange column from concentrated hydrochloric acid medium immediately before thorium is adsorbed on the cation-exchange column.

### 2. Reagents

$^{228}Th$  tracer: known amount; 5 to 100 counts/min  
 $HNO_3$ : conc  
 $HClO_4$ : 70%; 3M  
 $HCl$ : 3M  
 $H_2C_2O_4$ : 0.5M  
 $NH_4OH$ : conc; 3M  
TTA[4,4,4, trifluoro-1-(2-thienyl)-1,3-butanedione]  
reagent: 0.5M in benzene  
Dowex AG 50-X4 cation-exchange resin (see Note 2)

Solution A: 0.1 ml of conc  $HNO_3$  for every 15 ml of conc  $HCl$

Dowex A1-X2 anion-exchange resin (Note 3)

### 3. Procedure

*Step 1.* To an aliquot of the sample in a 150-ml beaker, add  $^{228}Th$  tracer in known amount (5 to 100 counts/min) and then boil until white fumes appear. Dilute to 40 ml with  $H_2O$ .

*Step 2.* Repeat Steps 3 through 7 of Procedure A, except cut down amount of all reagents by a factor of 5.

*Step 3.* Add 0.3 to 0.4 ml of 70%  $HClO_4$  and boil until white fumes appear. Cool to room temperature and dilute to ~4 ml with Solution A. (Solution A consists of conc  $HNO_3$  mixed with conc  $HCl$  in the ratio of 0.1 ml  $HNO_3$  to 15 ml of  $HCl$ .)

*Step 4.* Transfer the solution to the top of a 5-cm by 2-mm Dowex A1-X2 anion-exchange column (Note 3) and rinse the centrifuge tube with ~0.5 ml of Solution A, adding the rinsings to the column. (Observe the usual precautions to avoid introduction of air bubbles.) Force the solution through the column under 1 to 2 lb of air pressure and collect the effluent in a 40-ml test tube. Rinse the column with 3 ml of Solution A under the same pressure and collect the effluent in the same test tube. Plutonium is retained on the column, and thorium comes through in the effluent.

*Step 5.* The effluent is evaporated with an air jet to ~1 ml on a steam bath.

*Step 6.* Add 1 ml of conc  $HNO_3$  and boil over a flame until brown fumes are no longer evolved. Cool to room temperature and add 1 ml of 70%  $HClO_4$ . Boil until white fumes appear, then cool to room temperature and dilute with  $H_2O$  to ~3.5 ml.

*Step 7.* Repeat Steps 9 through 11 of Procedure A.

## Notes

1. The chemical yield may be increased slightly by taking the aqueous layer through an additional extraction.

2. The tube used to support the resin column is shown in Fig. 1. It is constructed by blowing out the end of a 15-ml centrifuge tube and then sealing on a length of 3- to 4-mm-i.d. tubing. The AG 50-X4 resin is water-graded, and the fraction that settles at the rate of 2 to 5 cm/min is selected for use. This is washed several times with conc HCl and then with H<sub>2</sub>O. To support the resin column, a layer of HCl-washed sand ~5 mm thick is placed in the tip of the column tube. A slurry of graded HCl-washed resin is then added by means of a syringe pipette; the resin slurry is introduced into the tube near the bottom to eliminate air bubbles. The amount of slurry added should be sufficient to produce a column 7 to 9 cm in length after settling. Resin settling may be hastened by applying up to 10 lbs. of air pressure to the top of the column. To control pressure, the air line is connected to the top of the column through a reducing valve. Slurry liquid is allowed to flow through the column until the liquid level reaches the top of the resin; the stopper is then removed from the top of the column tube. Air must not be permitted to enter the resin column. If air does enter, the resin is reslurried to remove air bubbles. The cation-exchange column prepared as described above is washed with 2 to 3 ml of 3M HClO<sub>4</sub> and is then ready for use.

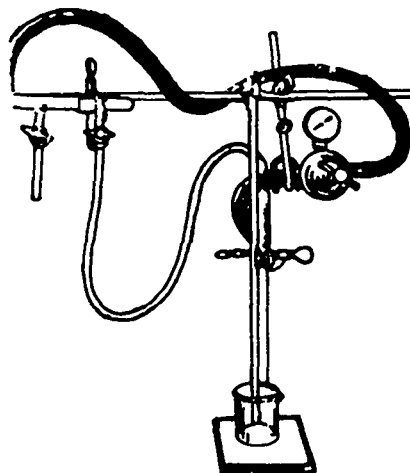


Fig. 1. Resin column.

3. The anion-exchange column is prepared in essentially the same manner as the cation column (see Note 2). The resin used is a 0.5- to 2-cm/min fraction of Dowex Al-X2. The resin is prepared for use by washing with Solution A.

(October 1989)

# PREPARATION OF CARRIER-FREE <sup>234</sup>Th TRACER

G. A. Cowan

## 1. Introduction

In the separation of <sup>234</sup>Th from uranium, the latter, originally present in the form of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, is converted to a soluble carbonate complex. At pH 8.0 to 8.5, the cupferrate of <sup>234</sup>Th is made and separated from the uranium by extraction into CHCl<sub>3</sub>. The thorium is back-extracted into dilute HNO<sub>3</sub> that contains Br<sub>2</sub>, which decomposes the cupferrate and allows extraction of all the organic material and excess Br<sub>2</sub> into the organic phase.

## 2. Reagents

UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>: 1 g uranium/10 ml, added as U<sub>3</sub>O<sub>8</sub>  
or UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O in dilute HNO<sub>3</sub>

HNO<sub>3</sub>: 3M

(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>: saturated aqueous solution

Br<sub>2</sub> water: saturated solution

Cupferron: 6% aqueous solution (freshly prepared  
and kept in the refrigerator)

CHCl<sub>3</sub>

Hydrion paper (short range)

## 3. Procedure

*Step 1.* Pipette 10 ml of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution into a 250-ml beaker; treat with saturated (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution and H<sub>2</sub>O until the yellow precipitate that first forms has dissolved. Add sufficient (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to make the final pH of the solution 8.0 to 8.5 (Note).

*Step 2.* Transfer the solution to a 250-ml separatory funnel; add 1 to 2 ml of 6% aqueous cupferron reagent and 10 ml of CHCl<sub>3</sub>. Shake well and transfer the CHCl<sub>3</sub> layer that contains the <sup>234</sup>Th to a clean separatory funnel. Repeat the CHCl<sub>3</sub> extraction and combine the extracts.

*Step 3.* Wash the CHCl<sub>3</sub> extracts with 20 ml of H<sub>2</sub>O to which has been added 1 ml of cupferron

reagent and sufficient (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution to make the pH 8.0 to 8.5. Transfer the CHCl<sub>3</sub> phase to a clean separatory funnel.

*Step 4.* To the CHCl<sub>3</sub> phase add 10 ml of 3M HNO<sub>3</sub> and a few milliliters of saturated Br<sub>2</sub> water and shake. Discard the CHCl<sub>3</sub> phase and wash the aqueous phase twice with CHCl<sub>3</sub>; discard the washings. Transfer to a 250-ml beaker and boil for a minute to remove the last traces of CHCl<sub>3</sub>. Transfer the solution to a volumetric flask of the appropriate size and make up to volume with H<sub>2</sub>O.

*Step 5.* Pipette aliquots of solution to 1-in. cover glasses and evaporate to dryness under a heat lamp. Count.

## Note

A pH of 8.0 to 8.5 appears to be optimum for the preparation and extraction of the <sup>234</sup>Th cupferrate; however, a pH in the range 7 to 8.5 is suitable.

(October 1989)

# TRACER METHODS FOR ANALYSIS OF THORIUM ISOTOPES

J. W. Barnes

## 1. Introduction

The principal purification step in tracer work with thorium isotopes depends on the fact that the relatively small, highly charged thorium(IV) ion is more tightly bound to a cation-exchange resin such as Dowex 50-X4 than are the ions of most other elements. Thorium is adsorbed on the resin bed and washed with dilute HCl solutions to remove most impurities; it is then eluted from the column in a very narrow band with  $\text{H}_2\text{C}_2\text{O}_4$ . Because  $\text{Th}(\text{C}_2\text{O}_4)_2$  is insoluble, macro quantities cannot be eluted from the column in this way. The Dowex 50-X4 resin with 4% divinyl benzene in the original polystyrene bead is more satisfactory for this separation than resins of any of the other cross-linkages. For example, Dowex 50-X2 does not adsorb thorium strongly enough under the experimental conditions to be useful; the higher cross-linkages in Dowex 50-X8 or -X12 do not allow impurities to be removed at a reasonable rate and also cause so much tailing in the elution that the thorium is not concentrated in the small volume desired. In tracer work with thorium, it is well to avoid solutions containing  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , or  $\text{PO}_4^{3-}$ , because they cause considerable losses in the steps that involve anion- and cation-exchange columns.

During analysis for any thorium isotope in a solution that contains organic matter (such as incompletely decomposed filter paper), it is a necessary first step, after addition of a suitable tracer, to boil to dense fumes with  $\text{HClO}_4$ . Even though thorium has only one stable valence state in solution, there is strong evidence for lack of exchange between added tracer and the radioisotope already in the solution when a hydroxide precipitation is performed without fuming. It is difficult to determine whether this apparent lack of complete exchange results from complexing of thorium by organic molecules that

survived the initial solution of the sample in  $\text{HNO}_3$  and  $\text{HClO}_4$ , or from the existence of thorium in the solution as some polymeric ion. Routine fuming of this type of sample improves the precision of the analysis. If the analysis is performed on solutions that contain macro quantities of calcium, two precipitations of thorium on a carrier hydroxide such as iron or a lanthanide are necessary to remove most of the calcium. Because most of the analyses were done on solutions that contained a very large excess of fission products (Sec. 5), two Dowex 50-X4 columns were used.

Some of the zirconium and probably a few other unknown contaminants are eliminated when they are adsorbed from conc HCl solution onto a relatively highly cross-linked, strong-base anion-exchange resin such as Dowex 1-X8 or -X10. Two of these columns are used, one after the other, if one of the beta-emitting thorium isotopes is being separated. If an alpha-emitting thorium isotope is being purified, one anion column may be sufficient. If the sample contains fission products several days old and does not have excessive amounts of plutonium and neptunium, two cation columns provide sufficient decontamination.

Tracer amounts of thorium can be separated from uranium in quantities up to  $\sim 1$  g with one Dowex 50-X4 column. Up to  $\sim 10$  g of uranium can be adsorbed on a 150- to 200-ml bed of Dowex 1-X8 from conc HCl; thorium is left in the effluent. A carrier-free source of  $^{231}\text{Th}$  was prepared from 2 kg of oralloy during several ether extractions. Finally, a cation column was employed to concentrate the activity in 1 to 2 drops of  $\text{H}_2\text{C}_2\text{O}_4$  (Sec. 7).

Section 6 describes the application of the above principles of separation to the specific analysis of thorium in coral or limestone samples, as developed by W. M. Sackett.



## 2. Reagents

Iron carrier: 10 mg iron/ml, added as 72.3 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /l of aqueous solution

HF: conc

$\text{HClO}_4$ : conc; 3M

HCl: conc; gas; 6M; 3M

$\text{HNO}_3$ : conc

$\text{NH}_4\text{OH}$ : conc

$\text{H}_2\text{C}_2\text{O}_4$ : 0.5M

$\text{NaBrO}_3$ : 0.5M

Anion-exchange resin: AG 1-X8, 100 to 200 mesh; stored in conc HCl

Anion-exchange resin: AG 1-X10, 100 to 200 mesh

Cation-exchange resin: AG 50-X4, 50 to 100 mesh

Cation-exchange resin: AG 50-X4, 100 to 200 mesh

Cation-exchange resin: AG 50-X4, 200 to 400 mesh

Both of the cation resins are stored in 3M HCl. It may not be necessary to purify the resins further if they are obtained from Bio-Rad Laboratories. However, if the decontamination or chemical yields are not satisfactory, it may be necessary to treat the resins as described here. A quantity of the resin is placed in a large fritted-disk funnel of medium or coarse porosity. (The treatments described below are speeded considerably by draining reagents into a large (2- to 4-l) suction flask under vacuum to promote complete removal of a reagent before the next one is added. When adding a reagent to the partially dried resin, it is helpful to stir with a heavy porcelain spatula and then let the reagent settle and flow by gravity to prolong the treatment time before suction is applied and the reagent is removed.) The reagents used successively for treating the resin are (1) an organic solvent such as acetone or alcohol, which removes short-chain organic polymers that are not firmly anchored in the resin matrix, (2) water to rinse out the organic solvents, and (3) conc HCl that contains  $\sim 1$  ml of 2M  $\text{NaBrO}_3$ /100 ml to dissolve extraneous inorganic matter. This solution is removed with water or dilute HCl in an amount equal to 10

to 20 times the volume of resin being purified. (At this point, the resin may be washed with 3M  $\text{NH}_4\text{OH}$  and then with water, but it probably is not necessary.) The resin should now be washed with 5 to 10 times its own volume of whatever solution it will be stored in. Undesirable fine particles can be removed by running distilled water upward through the fritted disk to float the particles over the top; the bulk of the resin will be left in the tube.

## 3. Special Equipment

Resin columns: four per sample: three 0.6-cm i.d. and 7-cm length; one 0.35-cm i.d. and 7-cm length. The glass container for the column of resin is most conveniently made by sealing a piece of tubing (either 0.6-cm i.d. by 7 cm or 0.35-cm i.d. by 7 cm) to the bottom of a tapered 15-ml centrifuge tube. If glass wool is to support the resin, the size of the opening in the tip at the bottom of the column is not critical; 0.3 to 2 mm is satisfactory. A glass-wool column plug is made by cutting off a short piece of fiber, wetting and rolling it into a ball, and using a rod to push it to the bottom of the column. The hole size for a sand support should not be much larger than 0.3 to 0.5 mm; first put in a layer of coarse sand and then cover it with a layer of finer material. The sand should be boiled and leached with HCl. The choice between sand and glass wool as a column support is a matter of personal preference.

Pressure regulator: The pressure of air used to push solutions through columns is regulated by a diaphragm reducing valve that has a scale reading from 0 to 100 lb; the first mark at  $\sim 4$  to 5 lb. If an ordinary on-off valve is used in place of the diaphragm valve, light pressure may be obtained in several ways. (1) Carefully hold one outlet from the manifold to an ear and turn the valve until air can barely be felt or heard. (2) Insert a T tube between the reducing valve and the manifold and lead a plastic or rubber tube below the surface of a column of water in some conveniently sized

tube (such as a liter graduate). Open the valve and pass just enough pressure to cause bubbles to rise in the tube.

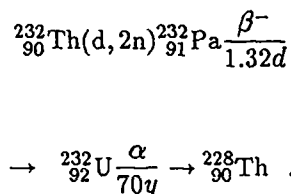
#### 4. Preparation and Standardization of Tracers and the Calculations Involved in Their Use

In analyses for the beta-emitters  $^{231}\text{Th}$  and  $^{234}\text{Th}$ , the best tracer is  $^{230}\text{Th}$  because no daughter products grow into it within a time that could affect the analysis. To obtain good statistics with a single alpha-counting for determining chemical yield, it is desirable to use  $\sim 10\,000$  counts/min of  $^{230}\text{Th}$  tracer. It is helpful to have on hand several standards that are made with the amount of tracer being used in the analysis. The chemical yield is determined by a ratio of sample-to-standard; these two are counted very close together to eliminate any small error caused by change in response of the alpha counter.

The beta-counting efficiencies for  $^{231}\text{Th}$  and  $^{234}\text{Th}$  are determined by mixing a known amount of  $^{230}\text{Th}$  tracer with a known quantity of the appropriate uranium parent—either  $^{235}\text{U}$  or  $^{238}\text{U}$ . After a  $\text{HClO}_4$  fuming to ensure exchange and to eliminate nitrate that may be present, the solution is diluted to 2 to 3M in  $\text{H}^+$  ion concentration. An AG 50-X4 column step is performed as in Step 9, Sec. 5 of the fission-product decontamination, except that 1 to 2 drops of 0.5M  $\text{NaBrO}_3$  are added to the initial solution and to the wash to ensure that the uranium will be present as U(VI). Uranium(IV) behaves like thorium(IV) on this column and will leave enough deposit on the plate to cause errors in the alpha counting. The directions for obtaining large quantities of  $^{231}\text{Th}$  or  $^{234}\text{Th}$  for use as tracers are given in Sec. 7.

The best tracer to use in analysis for  $^{230}\text{Th}$  is  $^{228}\text{Th}$ , which should be as free from  $^{229}\text{Th}$  as possible. Because  $^{230}\text{Th}$  and  $^{228}\text{Th}$  are both alpha emitters, the final plate is pulse-analyzed to find the ratio of the two. The alpha energy of  $^{229}\text{Th}$  (compared to that of  $^{228}\text{Th}$ ) is so much closer to

the alpha energy of  $^{230}\text{Th}$  that tail corrections are much larger and more subject to error when  $^{229}\text{Th}$  is present in the  $^{228}\text{Th}$  tracer. This tracer is made by the (d, 2n) reaction on  $^{232}\text{Th}$ .



It is possible to standardize a solution of  $^{228}\text{Th}$  by allowing it to decay until all its daughters are at equilibrium, then alpha-counting it and subtracting the contribution of the rest of the decay chain. It is, however, quicker and more reliable to mix accurately measured quantities of  $^{228}\text{Th}$  and a known  $^{230}\text{Th}$  solution, fume with  $\text{HClO}_4$ , and then separate from daughter activities with an AG 50-X4 column as in Step 9 of Sec. 5. The resultant plate is pulse-analyzed to get the ratio of  $^{228}\text{Th}$  to  $^{230}\text{Th}$  (which, when multiplied by the alpha count of  $^{230}\text{Th}$ , gives the correct alpha-count rate for  $^{228}\text{Th}$ ).

If  $^{228}\text{Th}$  tracer is to be used for an appreciable length of time, a decay correction for its 1.9-yr half-life must be made.

A correction must be made in pulse analyses involving  $^{228}\text{Th}$ . The energy from 4.6% of the alphas of the  $^{224}\text{Ra}$  daughter of  $^{228}\text{Th}$  coincides with the alpha peak of  $^{228}\text{Th}$ . The time of last separation of the daughter is noted when the  $\text{HCl}$  wash comes off the last AG 50-X4 column. This parent-daughter relationship falls into the classification of transient equilibrium, where the equation of radioactive decay is simplified to

$$N_2(t) = \frac{N_1^0 \lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t}) ,$$

where the subscript 2 refers to  $^{224}\text{Ra}$  and the subscript 1 refers to  $^{228}\text{Th}$ . Because  $N_1^0$  is constant

for the times involved, it is convenient to prepare a plot of  $N_2/N_1^\circ$  against time by using the above equation. The elapsed time from the end of the HCl wash on the last cation-exchange column to the midpoint of the pulse analysis is noted on the curve; the fraction  $N_2/N_1^\circ$  is read from the graph, multiplied by 0.046, and subtracted from the counts under the  $^{228}\text{Th}$  peak.

To get the counting rate of  $^{230}\text{Th}$  in a sample with  $^{228}\text{Th}$  tracer, the ratio of the  $^{230}\text{Th}/^{228}\text{Th}$  peaks is multiplied by the alpha-counting rate of  $^{228}\text{Th}$ , as obtained above.

## 5. Procedure for Thorium Isotopes in a Solution of Fission Products

*Step 1.* Pipette the tracer into an erlenmeyer flask of the proper size: a 50-ml flask for a sample-plus-tracer volume <10 to 15 ml and a 125-ml flask for 12 to 50 ml. Pipette the sample into the flask; use a clean pipette for each sample so that the solution will not become contaminated with the tracer. Add a few drops of iron carrier and ~1 ml of conc  $\text{HClO}_4$ . Evaporate to dense white fumes, and continue heating for at least 2 min after their first appearance. This evaporation is most rapidly done over a Fisher burner, but if there is no hurry, use an air jet, hot plate, or oil bath. Cool and add 10 to 15 ml of  $\text{H}_2\text{O}$  and transfer to a short-taper 40-ml glass centrifuge tube. There may be a fine-grained residue of  $\text{SiO}_2$  in the flask, but thorium loss at this point is not very great.

*Step 2.* Add an excess of conc  $\text{NH}_4\text{OH}$ , mix well, centrifuge, and discard the supernate.

*Step 3.* Dissolve the precipitate from *Step 2* in 1 ml of 3M HCl, and dilute with  $\text{H}_2\text{O}$  to half the volume of the tube. Add conc  $\text{NH}_4\text{OH}$  to precipitate the hydroxide, centrifuge, and discard the supernate.

*Step 4.* Dissolve the precipitate from *Step 3* in ~5 ml of 3M HCl. If there is a very heavy precipitate of  $\text{Fe}(\text{OH})_3$ , it may be necessary to add

more 3M HCl to obtain complete solution. (Again, ignore a small residue of  $\text{SiO}_2$  if it is present.) Prepare a 0.6-cm-diam by ~7-cm-length column filled with AG 50-X4, 50 to 100 mesh resin. Pour the HCl solution onto the top of the resin and allow it to run through by gravity. Wash the column with 10 ml of 3M HCl and discard both the wash and the first effluent. Put a 50-ml erlenmeyer flask that contains 1 ml each of conc  $\text{HClO}_4$  and  $\text{HNO}_3$  under the column; add 3.5 ml of 0.5M  $\text{H}_2\text{C}_2\text{O}_4$  to the top and allow it to pass through by gravity.

*Step 5.* Evaporate the solution from *Step 4* to dense white fumes and continue heating for ~1 min.

*Step 6.* Transfer the solution to a 40-ml long-taper centrifuge tube and rinse the contents of the flask into it with 2 ml of conc HCl. Add 2 to 3 drops of 0.5M  $\text{NaBrO}_3$  and saturate with HCl gas while the tube is surrounded by water at room temperature. Prepare a wash solution by adding a few drops of  $\text{NaBrO}_3$  to conc HCl, and saturate it with gaseous HCl at the same time.

*Step 7.* Prepare two 0.6-cm-diam anion-exchange resin columns for each sample. Fill each to a height of ~7 cm with AG 1-X8 or AG 1-X10, 100 to 200 mesh resin. Add the solution from *Step 6* to the top of one of the columns and collect the effluent in a dry centrifuge tube. Rinse the original tube and column with 1.0 to 1.5 ml of the wash solution prepared in *Step 6*. Combine this wash with the effluent and pass through the second column. Rinse the second column in the same manner as the first, and collect the combined effluents in a 50-ml erlenmeyer flask. It may be desirable to use very light air pressure to push the solution through these two columns.

*Step 8.* Evaporate the solution from *Step 7* to 2 to 3 ml. Add 1 ml of conc  $\text{HNO}_3$  and 0.5 ml of conc  $\text{HClO}_4$ , and continue heating until dense white fumes have been evolved for ~1 min. Cool and add 2 ml of water.

*Step 9.* Prepare a cation-exchange resin column, 0.35 cm by ~7 cm, filled with 100 to 200 mesh AG 50-X4 resin. Pour the solution from *Step 8* on the top of the column and force it through with light air pressure (2 to 3 lb). Wash the column with 4.5 ml of 6M HCl; discard this wash and the first effluent. Add 0.3 to 0.4 ml of 0.5M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and push down the column with very light air pressure. Be sure that the leading edge of the H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> band does not reach the bottom of the resin and get discarded with the other effluent. Add 0.7 ml of 0.5M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to the top of the column and collect the sample on a 5-mil platinum plate. For alpha-counting only, use a 1.75- to 2-in.-diam plate; if beta-counting is also to be performed, collect the sample on a 1-in.-diam plate. Dry the samples under heat lamps; leave them there until most of the H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> has sublimed and then heat them to red heat in a flame.

## 6. Thorium Procedure for Coral or Limestone Samples

*Step 1.* Dissolve 100 to 125 g of coral (accurately weighed) in 250 ml of conc HNO<sub>3</sub> and make up to 500 ml with H<sub>2</sub>O. This provides a solution that contains ~0.2 g of coral/ml.

*Step 2.* Add a 50-ml aliquot of the well-mixed solution to a 90-ml glass centrifuge tube with 1 ml of <sup>234</sup>Th tracer solution (see Sec. 7) and 1 ml of iron carrier. Stir, heat in a hot water bath for 1 h, then cool (Note 1).

*Step 3.* Add conc NH<sub>4</sub>OH slowly while stirring until Fe(OH)<sub>3</sub> precipitates and then centrifuge for 5 min (Note 2).

*Step 4.* Decant and dissolve the precipitate in 5 ml of conc HNO<sub>3</sub>, dilute with H<sub>2</sub>O, and again precipitate Fe(OH)<sub>3</sub> with conc NH<sub>4</sub>OH.

*Step 5.* Centrifuge, decant, and dissolve the precipitate in 5 ml of conc HNO<sub>3</sub>; use H<sub>2</sub>O to wash the solution into a platinum dish. Add 10 ml of conc HClO<sub>4</sub> and 5 ml of conc HF.

*Step 6.* Take to fumes of HClO<sub>4</sub> three times; wash the sides of the dish with water after each fuming (Note 3).

*Step 7.* Dilute the HClO<sub>4</sub> solution to ~25 ml with H<sub>2</sub>O.

*Step 8.* Fill a cation-exchange column (4 by 150 mm) that has a 40-ml reservoir with an AG 50-X4, 200 to 400 mesh, resin-water mixture and pack to ~120 mm. Wash the resin with 3M HClO<sub>4</sub> and add the solution from *Step 7*. Allow the solution to flow at atmospheric pressure or adjust the air pressure to give a flow of 1 drop/30 s.

*Step 9.* When the solution reaches the top of the resin, add 3M HCl acid in several 1-ml portions; wash down the sides of the column each time. Continue washing until the ferric chloride color disappears.

*Step 10.* Elute the thorium with 2 to 3 ml of 0.5M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and catch the eluate in a centrifuge tube. Add 5 ml of conc HNO<sub>3</sub> and 5 ml of conc HClO<sub>4</sub>; take to fumes of HClO<sub>4</sub> three times. Wash the breaker down with H<sub>2</sub>O after each fuming.

*Step 11.* Add the solution, which is diluted with H<sub>2</sub>O to 12 ml, to a second column (2 by 150 mm) that has a 15-ml reservoir; pack to a height of 120 mm with the same resin and treat as in *Step 8*. Adjust the flow rate as in *Step 8*.

*Step 12.* When the solution reaches the level of the resin, wash with five 1-ml portions of 3M HCl; rinse the sides of the centrifuge tube with each portion.

*Step 13.* Elute the thorium with 0.5M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and collect the first 12 drops of eluate on a platinum plate. Evaporate to dryness under a heat lamp, and flame.

*Step 14.* Count <sup>234</sup>Th to determine the yield; pulse-analyze the alpha radiation (Notes 4 and 5).

## 7. Isolation of Thorium Decay Products from Large Quantities of Uranium Parent

Thorium-231 is isolated from a solution of oralloy ( $\sim 93.5\%$   $^{235}\text{U}$ ) and  $^{234}\text{Th}$  is obtained from normal uranium after the  $^{231}\text{Th}$  present is allowed to decay. For preparation of tracer using either of these thorium isotopes, the final step is an AG 50-X4 cation-exchange column step, as in the determination of counting efficiency of  $^{231}\text{Th}$  or  $^{234}\text{Th}$  (see Sec. 4); however, the final  $\text{H}_2\text{C}_2\text{O}_4$  effluent is fumed nearly to dryness with 1 ml each of conc  $\text{HNO}_3$  and  $\text{HClO}_4$ . If an amount of uranium up to  $\sim 1$  g is sufficient to supply the amount of tracer needed, the AG 50-X4 column can be used as described in Sec. 4. Sources of  $^{231}\text{Th}$  or  $^{234}\text{Th}$  can be milked from a "cow" of the appropriate uranium isotope that is adsorbed on an AG 1-X8 column. The uranium is dissolved in conc  $\text{HCl}$ , and some oxidizing agent such as  $\text{BrO}_3^-$  ion,  $\text{Br}_2$  water, or  $\text{Cl}_2$  gas is used to oxidize the uranium to uranium(VI). The solution is then saturated with  $\text{HCl}$  gas at room temperature and uranium is adsorbed on an AG 1-X8 column.

For 10 g of uranium, a column  $\sim 25$ -mm diam that holds 150 to 200 ml of resin bed is satisfactory. The resin is prewashed with conc  $\text{HCl}$  that contains  $\sim 0.5$  ml of  $2M$   $\text{NaBrO}_3/100$  ml of acid. The uranium solution is passed through the column and then recycled two or three times so that more of it is adsorbed. Then the column is washed with  $\sim$  twice the resin bed volume of conc  $\text{HCl}$  that contains 1 to 2 drops of the bromate solution. After a suitable growth time for the thorium daughter, the column is treated with conc  $\text{HCl}$  as above. The solution is evaporated to a small volume, fumed with 1 ml each of conc  $\text{HNO}_3$  and  $\text{HClO}_4$ , and treated with the AG 50-X4 column step as described in Sec. 4.

A  $^{231}\text{Th}$  source reading  $>1$  r was prepared from 2 kg of oralloy. The uranium metal was dissolved in an excess of conc  $\text{HNO}_3$ , and this solution was evaporated until the temperature became constant at  $\sim 118^\circ\text{C}$ . [This is the boiling point of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .] This solution, which

freezes at  $\sim 60^\circ\text{C}$ , is cooled to 70 to  $80^\circ\text{C}$ ; the molten hexahydrate is poured into a 5-l separatory funnel that contains 3 to 4 l of diethyl ether that is being rapidly stirred with an air-driven stirrer. This step must be done in a hood with explosion-proof fixtures or outdoors. If the molten hexahydrate is added in a slow stream to the ether while being stirred well, the operation is perfectly safe. The ether losses are not large because the vapor pressure of the ether decreases rapidly as the uranium is dissolved. It is more rapid and easier to add the molten hexahydrate than to crystallize it and add the crystals. The final solution in ether from the 2 kg of oralloy should have a volume of  $\sim 4$  l. An aqueous layer of  $\sim 600$  ml is withdrawn. The ether solution is scrubbed with three 3-ml portions of  $\text{H}_2\text{O}$  to ensure complete removal of any thorium that might be present. Thorium-231 is allowed to grow for 1 to 2 d and then is removed with three 3-ml portions of  $\text{H}_2\text{O}$ . This aqueous layer is shaken with two 200-ml portions of ether to remove more of the uranium. The residual water layer is first evaporated on a steam bath to remove ether, and then is fumed with 1 ml each of conc  $\text{HNO}_3$  and  $\text{HClO}_4$ . The AG 50-X4 column is used as in Sec. 5 except that the column dimensions are 0.2 cm by 5 cm. The bulk of the  $^{231}\text{Th}$  can be followed down the column with a beta-gamma survey meter;  $>80\%$  of it is usually concentrated in 2 to 3 drops. The  $\text{H}_2\text{C}_2\text{O}_4$  acid eluate is placed in small drops on a 10-mil platinum wire  $\sim 1.5$  in. long, and the wire is gradually heated to red heat by applying a current that is controlled by a Variac. In this way, the  $\text{H}_2\text{C}_2\text{O}_4$  is completely volatilized and leaves a nearly mass-free deposit of  $^{231}\text{Th}$ . The ether "cow" of uranium can be kept for several weeks and used to prepare a number of samples.

### Notes

1. The high acid concentration and the phosphate, chloride, and other impurities in the coral seem to take the thorium into a completely exchangeable form.

2. Large quantities of phosphate increase the formation of  $\text{Ca}_3(\text{PO}_4)_2$ , which coprecipitates with  $\text{Fe}(\text{OH})_3$ , and also lead to a decrease in yield as a result of the formation of phosphate complexes of thorium.

3. The solution is fumed three times to ensure that no fluoride or oxalate remains to interfere in the separation.

4. The isotopic thorium composition is calculated from the growth and decay of alpha activity.

5. The yield for this procedure varies from 50 to 90%.

(October 1989)

## PROTACTINIUM

H. A. Potratz and N. A. Bonner

### 1. Introduction

In the determination of  $^{233}\text{Pa}$  in the presence of fission-product material,  $\text{LaF}_3$  scavenging is followed by the carrying of protactinium on  $\text{Ba}[\text{ZrF}_6]$ . The fluorozirconate is then converted to an iodate of undetermined composition. This iodate is dissolved in  $\text{HCl}$  and the protactinium is extracted into diisopropyl carbinol; the zirconium remains in the aqueous phase. The protactinium is back-extracted with  $\text{HF}$  and mounted carrier-free for counting. Protactinium-231 is used as a tracer to determine chemical yield.

The procedure was tested on a fission-product mixture from  $3.2 \times 10^{14}$  fissions 3 d after the end of bombardment. Final activity was  $8 \pm 5$  counts/min and the yield was 76%.

### 2. Reagents

$^{231}\text{Pa}$  tracer

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Barium carrier: 30 mg barium/ml, added as  $\text{BaCl}_2$  in  $\text{H}_2\text{O}$

$\text{HCl}$ : 6M; conc

$\text{HNO}_3$ : conc

$\text{HF}$ : conc

$\text{HIO}_3$ : 1M

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

Diisopropyl carbinol

### 3. Procedure

*Step 1.* To the fission-product mixture in  $\sim 2M$   $\text{HCl}$  in a 50-ml plastic centrifuge tube, add 3 ml of conc  $\text{HNO}_3$ , 2 ml of zirconium carrier, 2 ml of conc  $\text{HF}$ , and  $^{231}\text{Pa}$  tracer in known amount (Note 1).

*Step 2.* Dilute to 20 ml and add 1 to 2 ml of lanthanum carrier. Centrifuge and transfer

the supernate to a clean plastic tube. Wash the precipitate with  $\text{H}_2\text{O}$  and combine the supernate with the previous one; discard the precipitate.

*Step 3.* Add 3 ml of barium carrier and allow the mixture to stand for 2 to 3 min. Centrifuge and wash the precipitate with  $\text{H}_2\text{O}$ ; discard both the supernate and the washings. Dissolve the  $\text{Ba}[\text{ZrF}_6]$  precipitate by treating with 3 ml of saturated  $\text{H}_3\text{BO}_3$ , 1 ml of conc  $\text{HNO}_3$ , and 2 ml of  $\text{H}_2\text{O}$ .

*Step 4.* Heat the mixture on a steam bath until the precipitate dissolves completely. Add 15 ml of 1M  $\text{HIO}_3$  and allow to stand for 5 to 10 min. Centrifuge (Note 2), wash with  $\text{H}_2\text{O}$ , and discard the supernate.

*Step 5.* Add 5 ml of conc  $\text{HCl}$  to the iodate precipitate and heat on the steam bath for  $\sim 2$  min. Add 2 ml of  $\text{H}_2\text{O}$  and continue heating until the precipitate is entirely dissolved. Transfer the solution to a 125-ml separatory funnel. Complete the transfer with 30 ml of 6M  $\text{HCl}$ . Add 35 ml of redistilled diisopropyl carbinol and shake thoroughly. (If the activity level is high, agitate the mixture with a stream of air.) Draw off and discard the aqueous phase. (This contains most of the zirconium.) Wash the carbinol phase with two 25-ml portions of 6M  $\text{HCl}$  and discard the washings. Treat the carbinol phase with two 10-ml portions of a solution that is made by diluting a mixture of 3 ml of conc  $\text{HNO}_3$  and 0.5 ml of conc  $\text{HF}$  to 20 ml. Transfer the aqueous extracts to a clean plastic tube and discard the carbinol phase. To the combined aqueous extracts add 2 ml of conc  $\text{HF}$  and 2 ml of zirconium carrier.

*Step 6.* Repeat Steps 2 through 5, and then Steps 2 through 4.

*Step 7.* Dissolve the iodate precipitate in 5 ml of conc  $\text{HCl}$ . Heat and add 2 ml of  $\text{H}_2\text{O}$ . Transfer the solution to a 60-ml separatory funnel. Complete the transfer with 10 ml of 6M  $\text{HCl}$ . Shake the solution with 10 ml of diisopropyl carbinol. Wash the carbinol phase with two 10-ml portions of 6M

HCl and discard the aqueous phases. Transfer the carbinol phase to a plastic centrifuge tube. Add 0.8 ml of H<sub>2</sub>O and 0.2 ml of conc HF and agitate thoroughly. Centrifuge. Use a drawn-out dropper tube to draw off and discard as much of the carbinol phase as possible. Add 5 ml of carbinol, shake, centrifuge, and discard the carbinol phase. Repeat the carbinol wash and draw off. Again, use a drawn-out dropper to transfer the aqueous phase onto a platinum disk of 1-in. diam. Evaporate under a heat lamp. Alpha-count for <sup>231</sup>Pa. Count betas of <sup>233</sup>Pa under a 10 mg/cm<sup>2</sup> aluminum absorber.

### Notes

1. Only a small amount of <sup>231</sup>Pa tracer should be used. The gamma radiation gives ~0.02 count/min on the beta counter for 1 count/min on the alpha counter.

2. This precipitate is not a simple zirconium iodate. It may be BaZr(IO<sub>3</sub>)<sub>6</sub>.

(October 1989)



## URANIUM-232 AND URANIUM-233

D. W. Efurud and F. R. Roensch

### 1. Introduction

The following procedure was devised to provide samples suitable for measuring the  $^{232}\text{U}$  and  $^{233}\text{U}$  alpha activity in underground nuclear debris. The uranium is initially separated from 0.3 to 1.5 g of debris by the procedure noted in *Step 1*. The residual quantities of thorium and plutonium in the samples are removed by a series of anion-exchange steps.

### 2. Reagents

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc

HBr: 47% ultrapure; nonstabilized

$\text{CH}_3\text{OH-HNO}_3$ : 90% by volume of methanol and 10% 5M  $\text{HNO}_3$

Type 1 reagent-grade  $\text{H}_2\text{O}$

Anion-exchange resin: Bio-Rad macroporous resin AG MP-1, 50 to 100 mesh; washed 20 times with Type 1 reagent-grade  $\text{H}_2\text{O}$  and stored as an aqueous slurry

### 3. Procedure

*Step 1.* Place the 40-ml centrifuge tube that contains the uranium isolated by the SEPARATION OF URANIUM AND PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS procedure in a heating block at  $95^\circ\text{C}$  and evaporate to dryness. Add 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  and heat at  $130^\circ\text{C}$  for 1 h. Evaporate to dryness at a temperature  $>180^\circ\text{C}$ . Cool the sample to room temperature and add 3 ml of  $\text{CH}_3\text{OH-HNO}_3$  mixture.

*Step 2.* Pass the solution through an anion-exchange column (Note) that has been preconditioned with three 1-ml aliquots of the  $\text{CH}_3\text{OH-HNO}_3$  mixture. Collect the eluate in a 40-ml glass centrifuge tube. Elute the remaining

uranium from the column with three 1-ml  $\text{H}_2\text{O}$  washes and collect the washes in the same centrifuge tube. Evaporate the solution to dryness. Add 0.5 ml of conc  $\text{HClO}_4$  and evaporate to dryness.

*Step 3.* Dissolve the residue in 1 ml of 47% HBr and pass the solution through an anion-exchange column that has been preconditioned with three 1-ml aliquots of conc HBr. Rinse the column with three 1-ml aliquots of HBr. Elute the uranium from the column into a 40-ml glass centrifuge tube with three 1-ml aliquots of  $\text{H}_2\text{O}$ . Place the sample on a heating block and evaporate to dryness. Add 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$ ; fume to dryness.

*Step 4.* Repeat *Step 3*. The sample is now ready to be electrodeposited on a platinum disk for alpha-analysis.

### Note

The resin column is prepared in a disposable automatic pipettor tip 7-cm length and 5-mm i.d. A plug of prewashed quartz wool is placed in the tip and resin is added to a depth of 2 cm.

(October 1989)

# URANIUM-235 I

W. G. Warren

## 1. Introduction

The procedure described below is a carrier-free method for the determination of  $^{235}\text{U}$  that employs  $^{232}\text{U}$  as a tracer. Decontamination from neptunium and plutonium is excellent. Removal of plutonium is in part effected by conversion to the tetrapositive state, formation of the cupferron complex, and extraction of the complex into  $\text{CHCl}_3$ . Separation of lanthanides, partial removal of neptunium, and further decontamination from plutonium is obtained by adsorption of uranium from conc  $\text{HCl}$  solution onto a Dowex A2 anion-exchange resin column. Washing of the column with  $10M$  and then with  $5M$   $\text{HCl}$  removes adsorbed plutonium and neptunium, respectively. Uranium is eluted from the column by means of  $0.1M$   $\text{HNO}_3$  and then is electroplated on platinum. The chemical yield, determined by alpha-counting the  $^{232}\text{U}$  tracer, is 50 to 90%. The  $^{235}\text{U}$  is fission-counted.

## 2. Reagents

$^{232}\text{U}$  tracer: amount to be added is determined by the alpha-counting technique employed

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Iron carrier: 10 mg iron/ml, added as  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

$\text{HCl}$ :  $5M$ ;  $10M$ ; conc

$\text{HNO}_3$ :  $0.1M$ ;  $6M$

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_2\text{OH} \cdot \text{HCl}$ :  $5M$

$(\text{NH}_4)_2\text{C}_2\text{O}_4$  in  $\text{H}_2\text{O}$ : 4%

Aqueous cupferron reagent: 6%

Methyl red indicator solution: 0.1% in 90% ethanol

Methanol: anhydrous

$\text{CHCl}_3$

$\text{NH}_3$ : gas

Dowex A2-X8 anion-exchange resin, 400 mesh

## 3. Special Equipment

Plating assembly (see Fig. 1): one cell per aliquot of sample

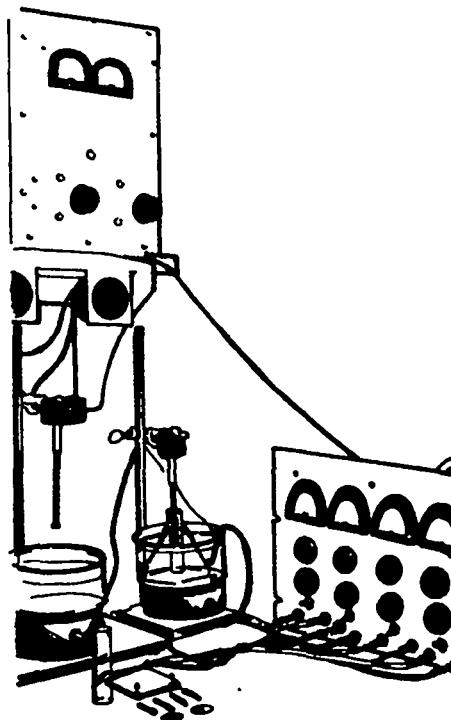


Fig. 1. Plating assembly.

Source of current: Fisher Powerhouse (dc); variable resistance in series with cell

Cell (see Fig. 2): brass base (3 in. by 3 in.) for holding platinum cathode; 5-mil platinum circular 1-in. disk (cathode); gasket to seal cathode and chimney; glass chimney,  $\frac{7}{8}$ -in. i.d., 4-in. height, and four ears at height of 3 in.;  $1\frac{1}{4}$ -in. steel springs for holding chimney to base; rotating platinum anode. The cell is heated for 1 h at  $105^\circ\text{C}$  after assembly to ensure formation of seal between glass and platinum.

Water bath for cell (see Fig. 1): Autemp heater; 6-in. crystallizing dish (for water bath); rubber pad for holding cell.

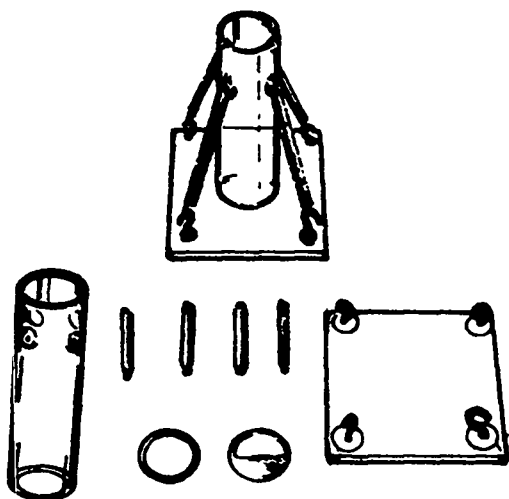


Fig. 2. Parts of plating cell.

#### 4. Procedure

*Step 1.* To an aliquot of sample <20 ml (Note 1) in a 40-ml centrifuge tube, add 1 ml of  $^{232}\text{U}$  tracer and 3 drops of lanthanum carrier; bubble in  $\text{NH}_3$  gas until the precipitate that forms coagulates. Digest for 15 min on a steam bath, centrifuge, and discard the supernate.

*Step 2.* Dissolve the precipitate in 0.6 ml of conc HCl and dilute to 10 ml with  $\text{H}_2\text{O}$ . Add 5 drops of 5M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (Note 2) and 2 drops of iron carrier (if this element is not already present), and allow to stand for 10 min. Add 4 ml of  $\text{CHCl}_3$  and 6 ml of 6% cupferron. Extract the plutonium(IV)-cupferron complex by stirring for 2 min. Use a transfer pipette to remove and discard the  $\text{CHCl}_3$  layer. Extract the aqueous phase three additional times with  $\text{CHCl}_3$ . To the aqueous layer add 3 drops of lanthanum carrier and bubble in  $\text{NH}_3$  gas until the precipitate formed coagulates. Digest for 15 min on a steam bath, centrifuge, and discard the supernate.

*Step 3.* Dissolve the precipitate in 1 ml of conc HCl; transfer the solution with three additional 1-ml HCl rinses to the 3-mm by 5-cm Dowex A2 resin column, which has been washed twice with 2.5-ml portions of conc HCl. Force the solution through the column under pressure. Wash the column twice with 2.5-ml portions of 5M HCl and discard the washings.

*Step 4.* Elute the uranium from the column into the plating cell with two 2.5-ml portions of 0.1M  $\text{HNO}_3$ .

*Step 5.* Add 5 ml of 4%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 3 drops of methyl red indicator solution; make alkaline by the dropwise addition of conc  $\text{NH}_4\text{OH}$ . Make the solution barely red to the indicator by the dropwise addition of 6M  $\text{HNO}_3$ , and add 3 drops in excess.

*Step 6.* Plate at 1.1 A and 8 V for 1.5 h at 80°C in a hot water bath. At the end of the first 10 min, add 3 drops of methyl red indicator solution and make acid with 6M  $\text{HNO}_3$ . Check acidity at two additional 10-min intervals; at the end of 40 min add 3 drops of conc  $\text{NH}_4\text{OH}$ . At 10-min intervals thereafter ensure that the plating solution is barely alkaline to the indicator.

*Step 7.* Remove the cell from the water bath, wash three times with methanol, and dismantle the cell, carefully keeping the platinum disk flat. Flame the disk over a burner, alpha-count, and then mount for fission-counting against standard  $^{235}\text{U}$  foils.

#### Notes

1. The aliquot of sample taken must have a  $^{235}\text{U}$  content similar to those of the  $^{235}\text{U}$  standard foils against which it is to be compared.

2. The  $\text{NH}_2\text{OH}\cdot\text{HCl}$  reduces the plutonium to the +4 state, in which form it is complexed by the cupferron.

(October 1989)

## URANIUM-235 II

G. W. Knobeloch

Bio-Rad AG 1-X8 anion-exchange resin, 100 to 200 mesh; water slurry

### 1. Introduction

In the carrier-free method described below for the determination of uranium in underground nuclear debris, it is not necessary to obtain complete decontamination from fission products because the uranium is finally fission-counted. The chemical yield is determined by alpha-counting the  $^{232}\text{U}$  used as tracer. The uranium is first adsorbed on an anion-exchange resin column from a solution at least  $10M$  in  $\text{HCl}$ . The bulk of the fission products is removed from the uranium by elution with  $8M$   $\text{HNO}_3$ , and then some decontamination from neptunium and plutonium is accomplished by column washes with  $3M$   $\text{HCl}$ . The uranium is eluted from the column by water and is placed on a fresh anion-exchange column. Decontamination from plutonium is completed by elution with an  $\text{HI-HCl}$  mixture. Then the resin is treated with  $\text{H}_2\text{O}_2$  to oxidize the uranium to the +6 state, and neptunium is removed with  $3M$   $\text{HCl}$ . The uranium is finally eluted with water and is electroplated onto platinum. The procedure given below is suitable for samples that have plutonium activity of  $<10^5$  alpha counts/min. Note 2 explains how the procedure may be modified for decontamination from plutonium of greater activity.

### 2. Reagents

$^{232}\text{U}$  tracer: amount to be added is determined by the alpha-counting technique employed

$\text{HCl}$ :  $2M$ ;  $3M$ ; conc

$\text{HNO}_3$ :  $8M$

$\text{HI-HCl}$  mixture: 1:9 by volume of 47%  $\text{HI}$  and conc  $\text{HCl}$

$\text{H}_2\text{O}_2\text{-HCl}$  reagent: one part by volume of 30%  $\text{H}_2\text{O}_2$  to 40 parts of  $9M$   $\text{HCl}$

$\text{NH}_4\text{OH}$ : conc

$\text{NH}_4\text{Cl}$ : solid

Ethanol: absolute

Methyl red indicator solution: 0.5% in ethanol

### 3. Procedure

*Step 1.* Place an aliquot of sample solution ( $<50$  ml) in a 125-ml erlenmeyer flask; add 1 ml of  $^{232}\text{U}$  tracer and 20 ml of conc  $\text{HCl}$ ; and evaporate the solution to dryness. Repeat twice the addition of  $\text{HCl}$  and evaporation. Take up the residue in 10 to 20 ml of conc  $\text{HCl}$ ; heat if necessary to effect solution.

*Step 2.* Add the solution to an AG 1-X8 anion-exchange resin column (prewashed with conc  $\text{HCl}$ ) (Note 1), and allow it to flow through the column under gravity. (Uranium is adsorbed on the column.) Wash the erlenmeyer flask with conc  $\text{HCl}$  and pass the wash through the resin column. Discard the effluents.

*Step 3.* Wash the column twice with  $8M$   $\text{HNO}_3$  (Note 2) and twice with  $3M$   $\text{HCl}$ . Discard the effluents. Elute the uranium with two 6-ml portions of  $\text{H}_2\text{O}$  into a clean 125-ml erlenmeyer flask.

*Step 4.* Evaporate the solution to dryness and take up the residue in 10 to 20 ml of conc  $\text{HCl}$ . Place the solution on another AG 1-X8 resin column and allow it to flow through under gravity. Wash the erlenmeyer flask with conc  $\text{HCl}$  and pass the wash through the resin column. Discard the effluents.

*Step 5.* Wash the column (a) twice with  $8M$   $\text{HNO}_3$ , (b) twice with conc  $\text{HCl}$ , (c) twice with  $\text{HI-HCl}$  mixture, (d) once with conc  $\text{HCl}$ , (e) twice with  $\text{H}_2\text{O}_2\text{-HCl}$  reagent, (f) and then twice with  $3M$   $\text{HCl}$ . Discard all effluents. Elute the uranium with two 6-ml portions of  $\text{H}_2\text{O}$  into a clean 125-ml erlenmeyer flask.

*Step 6.* Evaporate to dryness the solution that contains the uranium. Destroy the  $\text{HI}$  by heating to dryness twice after adding 1-ml portions of conc

HNO<sub>3</sub>. Convert to the chloride by two successive evaporations to dryness after adding 1 ml of conc HCl.

*Step 7.* Dissolve the residue in 1 ml of conc HCl. Use 5 ml of H<sub>2</sub>O to transfer the solution to an electroplating cell. Rinse the erlenmeyer flask with 5 ml of H<sub>2</sub>O and add the rinse to the plating cell.

*Step 8.* To the cell add ~0.5 g of NH<sub>4</sub>Cl and 3 drops of methyl red indicator solution. Make the solution alkaline with conc NH<sub>4</sub>OH and then barely acidic with 2M HCl. Electroplate the uranium onto a 1-in. platinum disk at 2 A for 15 min. One minute before completion of the plating, add 1 ml of conc NH<sub>4</sub>OH to the cell. Discard the cell solution and rinse the cell with three 5- to 10-ml portions of absolute ethanol. Disassemble the cell, flame the platinum disk, and mount it for counting.

1-ml portions of conc HNO<sub>3</sub>. Convert to the chloride by two successive evaporations to dryness after adding 1 ml of conc HCl. Carry out *Steps 4* through *6* as described. Dissolve the residue in 1 ml of conc HCl and place on a third AG 1-X8 resin column. Wash twice with 8M HNO<sub>3</sub>, twice with conc HCl, twice with 3M HCl; elute the uranium with two 6-ml portions of H<sub>2</sub>O into an electroplating cell. Plate as in *Step 8*.

(October 1989)

## Notes

1. The choices of anion resin column size and volume of washes are functions of plutonium activity and size of the underground debris sample. The following table shows these relationships.

Size of Debris Sample (g)	Plutonium Limit (count/min)	Resin Dimensions (cm)	Wash Volumes (ml)
<0.0375	<10 <sup>3</sup>	1 by 5	4
0.0375 to 0.075	10 <sup>3</sup> -3 × 10 <sup>4</sup>	1 by 7	6
0.075 to 1.50	3 × 10 <sup>4</sup> -3 × 10 <sup>6</sup>	1 by 15	10
1.50 to 4.50	3 × 10 <sup>6</sup> -10 <sup>7</sup>	1 by 20	15
>4.5	>10 <sup>7</sup>	1 by 30	25

2. For samples that have plutonium levels >10<sup>5</sup> cpm, the procedure is modified, beginning with *Step 3*. Wash the column twice with 8M HNO<sub>3</sub>, twice with conc HCl, twice with HI-HCl mixture, once again with conc HCl, and twice with 3M HCl. Discard the effluents. Elute the uranium with two 6-ml portions of H<sub>2</sub>O into a clean 125-ml erlenmeyer flask. Evaporate to dryness and destroy the HI by heating to dryness twice after adding

# URANIUM-237

W. G. Warren

## 1. Introduction

In this carrier-free procedure for the determination of  $^{237}\text{U}$ , the element is first adsorbed on an anion-exchange resin column from a solution at least  $10M$  in  $\text{HCl}$ . The bulk of the fission products is removed from the uranium by elution with  $8M$   $\text{HNO}_3$ ; the plutonium is removed by elution with a mixture of conc  $\text{HI}$  and  $\text{HCl}$ . The resin is then treated with  $\text{H}_2\text{O}_2$  to ensure oxidation of uranium to the +6 state, and the neptunium is removed from the column by means of  $3M$   $\text{HCl}$ . The uranium is eluted with  $\text{H}_2\text{O}$  and placed on another anion resin column from conc  $\text{HCl}$  solution. Further decontamination of the element is accomplished by column washings with  $8M$   $\text{HNO}_3$ ,  $10M$   $\text{HCl}$ , and  $3M$   $\text{HCl}$ . Following elution of uranium with  $\text{H}_2\text{O}$ , the element is placed on a cation-exchange resin column, which is then washed with  $0.1M$   $\text{HCl}$ —a treatment that presumably removes traces of tellurium and iodine. The uranium is eluted with  $3M$   $\text{HCl}$  and is electroplated onto platinum.

The procedure is carried out in the presence of  $^{233}\text{U}$  tracer, and yield is determined by alpha-counting this isotope. Uranium-237 is determined by beta-counting.

## 2. Reagents

$^{233}\text{U}$  tracer: amount to be added is determined by the alpha-counting technique employed  
 $\text{HCl}$ :  $0.1M$ ;  $2M$ ;  $3M$ ;  $10M$ ; conc  
 $\text{HNO}_3$ :  $8M$   
 $\text{HI-HCl}$  mixture: 1:9 by volume of 47%  $\text{HI}$  and conc  $\text{HCl}$   
 $\text{NH}_4\text{OH}$ : conc  
 $\text{NH}_4\text{Cl}$ : solid  
Ethanol: absolute  
Methyl red indicator solution: 0.5% solution of the indicator in ethanol

$\text{H}_2\text{O}_2$  reagent: 0.5 ml of 30%  $\text{H}_2\text{O}_2$  to 40 ml of  $9M$   $\text{HCl}$

Bio-Rad AG 1-X8 anion-exchange resin: 100 to 200 mesh; water slurry

Bio-Rad AG 50W-X8 cation-exchange resin: 100 to 200 mesh; water slurry

## 3. Procedure

*Step 1.* To an aliquot of sample (<50 ml) in a 125-ml erlenmeyer flask, add 1 ml of  $^{233}\text{U}$  tracer and 20 ml of conc  $\text{HCl}$ ; evaporate the solution to dryness. Repeat twice the addition of  $\text{HCl}$  and evaporation. Take up the residue in 10 to 20 ml of conc  $\text{HCl}$ ; heat if necessary to ensure solution.

*Step 2.* Add the solution to a 1- by 5-cm AG 1-X8 anion-exchange resin column that has been prewashed with conc  $\text{HCl}$ , and allow it to flow through the column under gravity. (Uranium is adsorbed on the column.) Wash the erlenmeyer flask with 4 ml of conc  $\text{HCl}$  and pass the wash through the resin column. Discard the effluents.

*Step 3.* Carry out the following sequence of column washes: (a) twice with 4-ml portions of  $8M$   $\text{HNO}_3$ , (b) twice with 4 ml of conc  $\text{HCl}$ , (c) once with 6.5 ml and then 2 ml of  $\text{HI-HCl}$  mixture, (d) again with 4 ml of conc  $\text{HCl}$ , (e) twice with 4-ml portions of  $\text{H}_2\text{O}_2$  reagent ( $\text{I}_2$  is removed and the resin column is decolorized), and (f) twice with 4-ml portions of  $3M$   $\text{HCl}$ . Discard all effluents. Elute the uranium with two 4-ml portions of  $\text{H}_2\text{O}$  and collect the eluate in a clean 125-ml erlenmeyer flask.

*Step 4.* Evaporate the solution to dryness and take up the residue in 10 ml of conc  $\text{HCl}$ . Place the solution on another AG 1-X8 resin column and allow it to flow through under gravity. Wash the erlenmeyer flask with 4 ml of conc  $\text{HCl}$  and pass the wash through the resin column. Discard the effluents.

*Step 5.* Wash the column twice with 4 ml of 8M HNO<sub>3</sub>, 4 ml of 10M HCl, and 4 ml of 3M HCl. Discard all effluents. Elute the uranium with two 4-ml portions of H<sub>2</sub>O, and collect the eluate in a clean 40-ml graduated long-taper glass centrifuge tube. Dilute the eluate to 10 to 15 ml.

*Step 6.* Place the solution on an AG 50W-X8 cation resin column, 4 mm by 6 cm, and allow it to pass through under slight air pressure. (The optimum flow rate through the column is 1 drop/6 s.) Discard the effluent.

*Step 7.* Wash the column with two 2.5-ml portions of 0.1M HCl and discard the washings. Use two 2.5-ml portions of 3M HCl to elute the uranium from the resin column into an electroplating cell.

*Step 8.* To the cell add ~0.5 g of NH<sub>4</sub>Cl and 3 drops of methyl red indicator solution. Make the solution alkaline with conc NH<sub>4</sub>OH and then barely acidic with 2M HCl. Electroplate the uranium onto a 1-in. platinum disk at 2 A for 15 min; 1 min before completion of the plating, add 1 ml of conc NH<sub>4</sub>OH to the cell. Discard the cell solution and rinse the cell with three 5- to 10-ml portions of absolute ethanol. Disassemble the cell, flame the platinum disk, and mount it for counting.

(October 1989)

# TOTAL URANIUM I

E. J. Lang

## 1. Introduction

For its determination in material that contains fission products, uranium is first converted to uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2$ . The nitrate is then extracted into ether. After removal of the ether, the uranium is finally incorporated into NaF pellets and determined fluorimetrically.

## 2. Reagents

Uranium standard: 0.2  $\mu\text{g}$  uranium/50  $\lambda$  of solution; made up by dissolving normal uranium in  $\text{HNO}_3$ ; the final acid concentration is  $\sim 3M$ .

HCl: conc

$\text{HNO}_3$ : 3M; conc

$\text{Al}(\text{NO}_3)_3$  reagent: 700 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\ell \text{H}_2\text{O}$ .

Before use, this reagent is treated in the following manner: 35 ml of conc  $\text{HNO}_3$  and 100 ml of anhydrous ethyl ether are added to 500 ml of the  $\text{Al}(\text{NO}_3)_3$  solution in a 1-l separatory funnel. The resulting mixture is shaken for 5 min and then allowed to stand for 5 min. The  $\text{Al}(\text{NO}_3)_3$  layer is then transferred to a 1-l separatory funnel that has been cleaned with distilled  $\text{H}_2\text{O}$ . The process is repeated until a total of five extractions have been made.

NaF: solid

LiF: solid

NaF flux: a solid mixture of NaF-LiF that contains 2% by weight of LiF.

Ethyl ether: anhydrous

Acetone: reagent grade

## 3. Procedure

*Step 1.* Pipette an aliquot of the sample (containing  $\sim 1 \mu\text{g}$  of uranium) into a 50-ml beaker and evaporate to dryness under a heat lamp. Add 2 to 3 ml of conc  $\text{HNO}_3$  and 1 ml of  $\text{H}_2\text{O}$ ; again evaporate to dryness. Repeat the additions and the evaporation twice.

*Step 2.* To the residue, add 1 ml of  $\text{H}_2\text{O}$  and 5 ml of conc  $\text{HNO}_3$ . Transfer the solution to the sample holder of an ether extraction apparatus that contains 60 ml of  $\text{Al}(\text{NO}_3)_3$  reagent. Rinse the beaker three times with 2-ml portions of  $\text{H}_2\text{O}$ , and add the washings to the sample holder. Add ether up to the arm of the sample holder, add 8 ml of  $\text{H}_2\text{O}$  and 50 ml of ether to the receiver, and assemble the extraction apparatus. Extract for 1.75 h. The uranium is now in the receiving flask.

*Step 3.* Remove the receiving flask and use a stream of  $\text{N}_2$  to take off the ether completely.

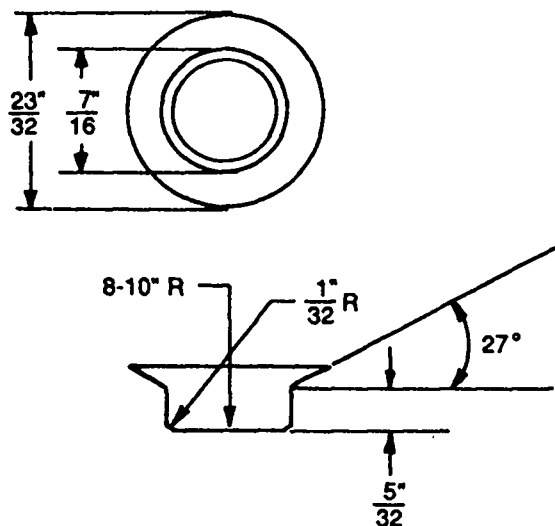
*Step 4.* With three  $\text{H}_2\text{O}$  rinses (5 ml each), transfer the material remaining in the receiver to a 50-ml reinforced platinum dish. Evaporate to 1 to 2 drops under a heat lamp and use a micropipette to transfer to a 2-ml volumetric flask. Add 3 drops of 3M  $\text{HNO}_3$  to the dish, swirl, and transfer the rinsings to the volumetric flask. Repeat the  $\text{HNO}_3$  rinse.

*Step 5.* Rinse the sides of the platinum dish with 5 ml of  $\text{H}_2\text{O}$ , add 0.5 ml of conc  $\text{HNO}_3$ , evaporate the solution to 1 to 2 drops, and transfer to the 2-ml volumetric flask. Add 3 drops of 3M  $\text{HNO}_3$  to the dish, swirl, and transfer to the volumetric flask. Repeat the addition of 3M  $\text{HNO}_3$  and repeat the entire step twice.

*Step 6.* Make the solution up to volume with 3M  $\text{HNO}_3$  and shake well. In a porcelain spot plate, place six numbered and weighed special platinum dishes (Fig. 1). To each of nine spots on a paraffin-coated microscope slide, add 1 drop of 3M  $\text{HNO}_3$ . Use a micropipette, coated on the outside with paraffin up to the first bulb, to withdraw a 50- $\lambda$  aliquot from the 2-ml volumetric flask; transfer to a special platinum dish. Rinse the pipette by dipping the tip into one of the drops of 3M  $\text{HNO}_3$  on the microscope slide and drawing the liquid to above the mark. Add the rinsing to the special platinum dish that contains the sample. Dip the pipette tip into the same drop of 3M  $\text{HNO}_3$  and draw the liquid about half way up the first bulb. Withdraw



the pipette tip from the drop and draw the liquid into the second bulb. Force the liquid back and forth between the two pipette bulbs several times and transfer the liquid to the platinum dish. Fill five other special platinum dishes in the manner described above.



PT. DISHES 20 MIL. PT

FIRST OPERATION	BLANKING
SECOND OPERATION	ANNEALING
THIRD OPERATION	FORMING

Fig. 1. Specifications for Pt dishes.

*Step 7.* Evaporate the solutions in the special platinum dishes under a heat lamp for  $\sim 15$  min.

*Step 8.* To three of the six dishes add  $50 \lambda$  ( $0.2 \mu\text{g}$ ) of the uranium standard in the manner described in *Step 6*, including the  $\text{HNO}_3$  rinsings.

*Step 9.* Evaporate the contents of all the platinum dishes to dryness under a heat lamp.

*Step 10.* Use a pelletizer made of a 10-ml graduated pipette, the ends of which are cut and to which the tubing is fitted with a solid glass plunger, to introduce  $\sim 300$  mg of NaF flux into each platinum dish. Crush the pellets with a platinum spatula (made by flattening one end of a 75-mil

platinum rod). On an analytical balance, adjust the weight of the flux in each dish to  $300 \pm 0.2$  mg.

*Step 11.* Fuse the contents of one platinum dish in the fusion apparatus (Fig. 2) for exactly 10 min (Note 1). At 10 s before the end of the 10-min fusion period, heat a pair of platinum-tipped tweezers in the flame; at the conclusion of fusion, remove the dish from the flame with the tweezers. Hold the dish at the end of the iron ring for 20 s and then replace it in the porcelain spot plate. Repeat the fusion procedure with each platinum dish.

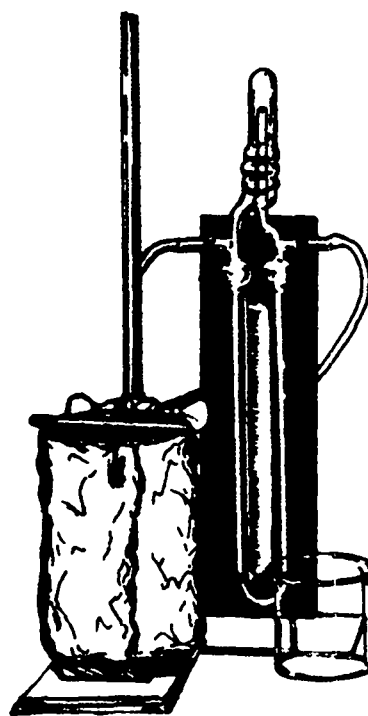


Fig. 2. Fusion apparatus.

*Step 12.* Allow the platinum dishes to cool for 2 to 3 h. Tap out each of the fused fluxes into an individual hole in the porcelain spot plate. The samples are now ready for fluorimetric analysis.

*Step 13.* Into each hole in the sample holder of the D.C. Fluorophotometer (Figs. 3 and 4), place a fused flux, bottom side up, and determine the quantity of fluorescence (Notes 2 and 3).

*Step 14.* After the analysis, the special platinum dishes are cleaned in the following manner. Place the dishes that contained only aliquots of the sample in a 1-l erlenmeyer flask with 200 ml of conc HCl, and reflux the solution for ~8 h. Pour off the acid and rinse the flask and dishes several times with distilled H<sub>2</sub>O. Then add 200 ml of conc HNO<sub>3</sub> to the flux and reflux this solution overnight. Pour off the acid and rinse the flask and dishes several times with distilled H<sub>2</sub>O. Place the platinum dishes on a clean towel by inverting the flask. Flame them by gentle heating in an open flame, and while they are still hot, immerse them in distilled H<sub>2</sub>O. Store in Petri dishes. Clean the platinum dishes that contained the standard uranium in a separate flask.

AMMETER FOR ULTRAVIOLET LIGHT SOURCE

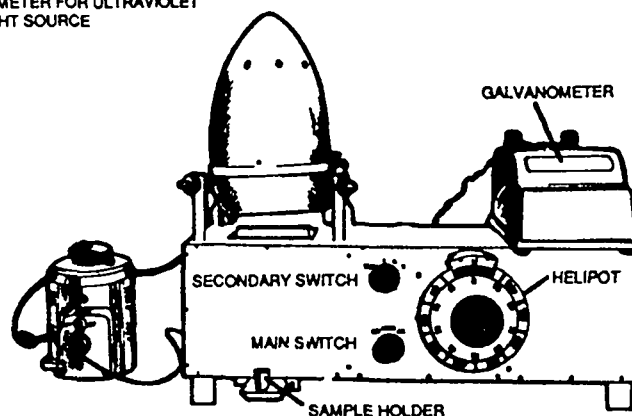


Fig. 4. D. C. Fluorophotometer.

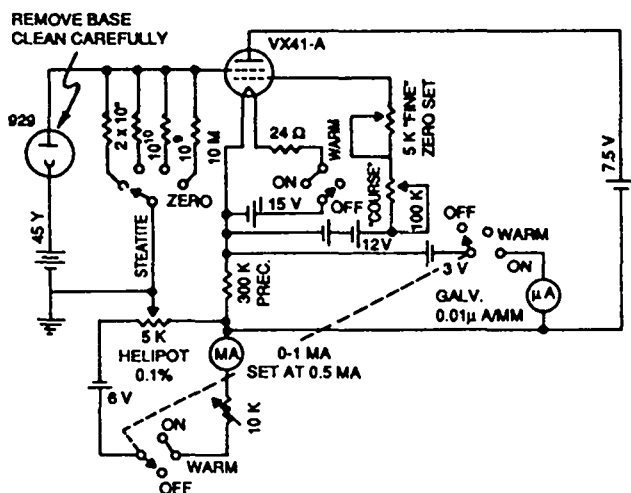


Fig. 3. D. C. Fluorophotometer schematic.

### Notes

1. Methane is burned in the Fisher burner of the fusion apparatus; temperatures are controlled by the rate of gas flow. It is important that the temperature be sufficiently high to melt the flux but not so high as to cause the flux to attack the platinum dish. If the cooled flux is yellow, the temperature of fusion has been too high and the platinum dish has been attacked. (The determination of the optimum conditions for fusion is at best an art and the technique must be worked out by each analyst.)

2. The D.C. Fluorophotometer (Figs. 3 and 4, designed by R. J. Watts, LANL) is operated in the following manner. The instrument is permitted to warm up for ~2 h before use by turning the secondary switch to *zero*, the main switch from *off* to *warm*, and the ultraviolet light source from *off* to *on*. The ultraviolet light source and the main switch may also be controlled by means of a No. 1191W Tork clock. The current through the ultraviolet light source should be adjusted to 0.9 A by a Type 216 Powerstat. After the instrument has warmed up, the main switch is turned to *on* and the helipot is to 0. The secondary switch is now adjusted to the proper range (1, 2, or 3, depending upon the uranium concentration of the sample), and the galvanometer is "zeroed" by the zero set. A sample is then positioned in the light path by the sample holder; the holder is adjusted forward and back until the maximum deflection is obtained on the galvanometer. The helipot is adjusted to *zero* the galvanometer and the helipot reading is taken.

3. Calculation of the average uranium content in a 50- $\lambda$  aliquot sample:

A = average of the helipot readings when the 50- $\lambda$  aliquots contain no added standard uranium.

B = average of the helipot readings when the 50- $\lambda$  aliquots contain added standard uranium.

D = uranium content in 1  $\mu\text{g}$  of the standard in the 50- $\lambda$  aliquots.

$(\frac{A}{B-A}) D = \mu\text{g}$  of uranium in 50- $\lambda$  aliquot sample + NaF flux.

The value obtained by the above calculation is corrected for the uranium in the NaF flux, which is determined in the same manner as that for the sample. The uranium value is then adjusted to take into account the chemical yield of the analytical procedure. When original aliquots of sample contain  $\sim 1 \mu\text{g}$  of the metal, no correction is necessary for the uranium in reagents other than NaF.

(October 1989)

# TOTAL URANIUM II

W. G. Warren

## 1. Introduction

This procedure is appropriate for samples that contain 300 to 500 mg of uranium.

Uranium(VI) is reduced to a mixture of uranium(III) and uranium(IV) by means of zinc amalgam in a Jones reductor. All the uranium is then converted to the +4 state by atmospheric oxidation, and the uranium(IV) is determined by titration with standard  $\text{Ce}(\text{SO}_4)_2$  in the presence of ferroin as indicator. The running of appropriate blanks is essential. The chief interferences in the determination are iron, molybdenum, tungsten, vanadium, and  $\text{NO}_3^-$  ion.

## 2. Reagents

$\text{H}_2\text{SO}_4$ : 5% by volume (5 ml of conc  $\text{H}_2\text{SO}_4$  to 95 ml of  $\text{H}_2\text{O}$ )

$\text{H}_2\text{SO}_4$ : conc

$\text{HClO}_4$ : conc

$\text{HCl}$ : conc

$\text{HNO}_3$ : conc; 2.5M

$\text{H}_2\text{O}_2$ : 30% solution

Uranium metal: pure

Ferric ammonium sulfate:  $\sim 0.1M$

Ceric sulfate: standardized. Make up an aqueous solution  $\sim 0.01M$  and standardize against pure uranium in the following manner. Weigh out to the nearest 0.1  $\sim 1$  g of pure uranium and dissolve the metal in conc  $\text{HCl}$ ; add a few drops of conc  $\text{HNO}_3$  if necessary. Make the solution up to exactly 100 ml by the addition of 2.5M  $\text{HNO}_3$ . Analyze aliquots of the uranium solution as described in Sec. 3. The solution should be standardized once a month while it is in use.

Jones reductor: for preparation, see a reference book on quantitative analysis.

Ferroin indicator: 0.025M (in  $\text{H}_2\text{O}$ )

## 3. Procedure

*Step 1.* Place the weighed or pipetted sample in a 250-ml beaker. If the sample is in metallic form, bring it into solution with conc  $\text{HCl}$  and 30%  $\text{H}_2\text{O}_2$ ; proceed to *Step 2*. If the sample is an oxide, dissolve it in a minimum of conc  $\text{HClO}_4$ , add 100 ml of 5%  $\text{H}_2\text{SO}_4$ , and proceed to *Step 3*. If the sample is in liquid form, start with *Step 2*.

*Step 2.* Add 5 ml of conc  $\text{H}_2\text{SO}_4$ , cover the beaker with a Speedyvap, and take the solution to dryness to remove nitrate and organic matter. Repeat the process three times, washing down the Speedyvap and the walls of the beaker each time. If more than trace quantities of nitrate or organic matter are present, a few drops of conc  $\text{HClO}_4$  are added before the second and third evaporation. After the final evaporation, add 100 ml of 5%  $\text{H}_2\text{SO}_4$ .

*Step 3.* Activate a Jones reductor by passing through it 100 ml of 5%  $\text{H}_2\text{SO}_4$ ; discard the effluent. Pass the solution that contains the sample through the reductor and collect it in a 500-ml erlenmeyer flask. Pass three 50-ml portions of 5%  $\text{H}_2\text{SO}_4$  through the reductor, and in each case collect the effluent in the same erlenmeyer flask.

*Step 4.* Aerate the solution in the flask for  $\sim 5$  min with a stream of air from a glass gas dispersion tube. The bubbles must be active enough to stir the solution. Withdraw the aerating tube and rinse it; collect the rinsings in the erlenmeyer flask.

*Step 5.* Add 3 drops of the ferroin indicator and titrate with standard ceric sulfate until the orange color just begins to fade. At this point add 3 ml of 0.1M ferric ammonium sulfate solution to restore the orange color, and proceed cautiously with the addition of ceric sulfate until the color of the solution changes to blue-green. This is the endpoint of the titration.

*Step 6.* Run two blanks and average their titration values.

*Step 7.* Subtract the average blank titration from the volume of ceric sulfate found in *Step 5*. Calculate the amount of uranium in the sample by one of the following formulas:

% uranium in weighed sample =

$$\frac{\text{ml Ce(SO}_4)_2 \times N \times F \times 100}{\text{g of sample}}$$

or grams total uranium in liquid sample =

$$\text{ml Ce(SO}_4)_2 \times N \times F \times \frac{\text{total vol of sample}}{\text{aliquot vol of sample}}$$

N = normality of Ce(SO<sub>4</sub>)<sub>2</sub>. The factor F in these calculations is the milliequivalent weight of the uranium with suitable corrections for the isotopic composition:

Depleted uranium	0.11900
Normal uranium	0.11904
93% <sup>235</sup> U	0.11760
98% <sup>233</sup> U	0.11650

(October 1989)

# PURIFICATION OF HIGHLY IRRADIATED URANIUM

K. Wolfsberg

## 1. Introduction

This procedure describes the purification of uranium that has been irradiated for several weeks. The initial experiment was performed to produce  $^{237}\text{U}$ , which was to be separated from other uranium isotopes in a mass separator. To facilitate heat transfer during the irradiation process, the uranium (in the form of  $\text{U}_3\text{O}_8$  highly enriched in  $^{236}\text{U}$ ) was intimately mixed with the rabbit material, aluminum.

Separation of the uranium requires decontamination from fission products, neptunium isotopes, macro amounts of aluminum,  $^{24}\text{Na}$  formed from the aluminum by the  $(n,\alpha)$  reaction, and other induced activities such as  $^{51}\text{Cr}$ . The major steps include (a) adsorption of the uranium from solution in a large volume of  $\text{HCl}$  (8 to 9M) onto an anion-exchange resin, (b) extraction into ethyl acetate from a  $\text{HNO}_3\text{-Al}(\text{NO}_3)_3$  solution, and (c) a second adsorption onto an anion-exchange resin. The chemical yield is  $\sim 90\%$ .

## 2. Reagents

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 6M  $\text{HCl}$

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$  in 3M  $\text{HCl}$

$\text{HNO}_3$ : conc

$\text{HCl}$ : conc; 9M; 8M

$\text{HCl-HNO}_3$ : 9:1 by volume of the conc acids (prepared just before use)

$\text{HCl-Br}_2$ : 9M  $\text{HCl}$ , saturated with  $\text{Br}_2$

$\text{HCl-HI}$ : 9:1 by volume of conc  $\text{HCl}$  and 47%  $\text{HI}$  (prepared just before use)

5M  $\text{HCl}$ -0.3M  $\text{HF}$

0.1M  $\text{HCl}$ -0.06M  $\text{HF}$

$\text{NH}_4\text{OH}$ : conc; 6M

$\text{Al}(\text{NO}_3)_3$ : saturated aqueous solution ( $\sim 2.5\text{M}$ )

Ethanol: absolute

Ethyl acetate

Anion-exchange resin: Bio-Rad AG 2-X8, 100 to 200 mesh

## 3. Procedure

*Step 1.* Cut off that section of the rabbit that holds the irradiated sample. (This section will contain  $\sim 5$  g of aluminum.) Heat and dissolve the sample with the cut-off section of the rabbit in a mixture of 190 ml of conc  $\text{HCl}$  and 10 ml of conc  $\text{HNO}_3$ . Dissolution takes  $\sim 40$  min and the volume of liquid is reduced to  $\sim 140$  ml. Add two 10-ml portions of the  $\text{HCl-Br}_2$  mixture (Note 1). Cool and dilute the solution to 300 ml with 9M  $\text{HCl}$  (Note 2) that contains 1 drop each of zirconium, tellurium(IV), and tellurium(VI) carriers. Filter the solution through filter paper to remove the small quantity of flocculent solid ( $\text{Al}_2\text{O}_3$ ?) that generally persists after the dissolution process.

*Step 2.* Fill an 8-mm-i.d. glass column with anion-exchange resin to a height of 3 in. Preequilibrate the resin with 8M  $\text{HCl}$ . Use air pressure to pass the solution from *Step 1* through the column at the rate of 10 drops/7 to 8 s. (All other column operations in this step and all in *Step 6* are carried out at the rate of  $\sim 10$  drops/20 s.) Wash the column first with 5 ml of 8M  $\text{HCl}$  and then with 5 ml of the conc acid; discard the washings. Elute the uranium into a 40-ml glass centrifuge tube with two 5-ml portions of  $\text{H}_2\text{O}$  and then with one 10-ml portion of  $\text{H}_2\text{O}$  (Note 3).

*Step 3.* Make the solution alkaline with 4 ml of conc  $\text{NH}_4\text{OH}$  (or 10 ml of 6M  $\text{NH}_4\text{OH}$ ). Centrifuge and discard the supernate (Note 4). Dissolve the precipitate in 1 ml of conc  $\text{HNO}_3$  and add 10 ml of saturated  $\text{Al}(\text{NO}_3)_3$ .

*Step 4.* Transfer the solution to a 40-ml extraction vessel that contains 10 ml of ethyl acetate. Stir or shake for 1 min and then discard

the lower (aqueous) phase. Scrub the organic phase twice with 10-ml portions of saturated  $\text{Al}(\text{NO}_3)_3$  and discard the washings. Back-extract the uranium with two 10-ml portions of  $\text{H}_2\text{O}$  and collect the extracts in a 40-ml centrifuge tube. Discard the organic phase (Note 5).

*Step 5.* Make the solution alkaline with 4 ml of conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate. Dissolve the precipitate in 10 ml of conc  $\text{HCl}$ .

*Step 6.* Prepare another resin column as in *Step 2*. Because  $\text{HF}$  will be employed in one of the column steps, plug the tip of the column with polypropylene felt. Preequilibrate the resin with conc  $\text{HCl}$ . Successively, pass the following solutions through the column and discard all effluents: (a) the solution from *Step 5*, (b) two 5-ml portions of conc  $\text{HCl}$ , (c) two 5-ml portions of  $\text{HCl-HI}$ , (d) two 5-ml portions of  $\text{HCl-HNO}_3$  (the column will bubble), (e) five 5-ml portions of 5M  $\text{HCl-0.3M HF}$  (after the last addition, blow the column dry), and (f) 5 ml of absolute ethanol. Use two 5-ml portions of 0.1M  $\text{HCl-0.06M HF}$  to elute the uranium into a 40-ml centrifuge tube (Note 6):

### Notes

1. The addition of  $\text{Br}_2$  ensures that no reducing substances are present; failure to take this step may result in a 5% loss of uranium in *Step 2*.

2. Higher  $\text{HCl}$  concentrations, or higher aluminum concentrations, can cause the anion-exchange resin to become clogged during *Step 2*.

3. Less than 1% of the uranium is lost in this step. Further column operations, such as those in *Step 6*, result in additional losses of uranium. The column step decontaminates the uranium from all of the aluminum,  $^{24}\text{Na}$ , and fission products in the (I), (II), and (III) oxidation states. The gamma activity from fresh fission products is reduced to a factor of one-third. At this stage, the main contaminants of the uranium are molybdenum,

tellurium, zirconium, niobium, neptunium, and plutonium.

4. The supernate contains most of the  $^{99}\text{Mo}$ .

5. About 3% of the uranium is lost in this step. Neptunium and plutonium follow uranium in the extraction. The extraction step separates uranium from most of the fission products; it is a particularly good step for removal of tellurium. Zirconium is retained in the organic phase. The uranium removed from this step invariably contains some aluminum from the  $\text{Al}(\text{NO}_3)_3$  reagent. This fact should be kept in mind if the extraction step is used in some other procedure.

6. Overall decontamination factors from neptunium and plutonium are  $\sim 10^3$ . Most of the plutonium (>99%) and  $\sim 1.5\%$  of the neptunium are eluted in the  $\text{HCl-HI}$  washes. In six 5M  $\text{HCl-0.3M HF}$  washes, neptunium is eluted 60, 31, 6.2, 1.1, 0.3, and 0.7%, respectively. For uranium, the losses with the same reagent are 0.01, 0.03, 0.2, 0.7, 1.5, and 2%. A sixth wash is, therefore, not prescribed. If the  $\text{HCl-HNO}_3$  washes are omitted, a neptunium decontamination of  $\sim 10^4$  is obtained with the 5M  $\text{HCl-0.3M HF}$  washes. In the first two washes with 5M  $\text{HCl-0.3M HF}$ ,  $\sim 15\%$  of a 25-mg sample of uranium is lost; with a tracer uranium sample, the loss is  $\sim 5\%$ . Any zirconium and niobium present are eluted in the 5M  $\text{HCl-0.3M HF}$  washes. Any molybdenum still present remains on the column; molybdenum has its lowest  $K_d$  at  $\sim 2\text{M HCl}$ . Any tellurium still present follows the uranium.

(October 1989)

# SEPARATION OF URANIUM AND PLUTONIUM FROM LARGE SAMPLES OF UNDERGROUND DEBRIS

H. L. Smith and G. W. Knobloch

## 1. Introduction

This procedure was devised for the separation of uranium and plutonium from solutions of high ionic strength, which were obtained by dissolving underground nuclear debris. In the separation, these elements are oxidized to the +6 state and extracted into diethyl ether from a solution saturated with  $\text{NH}_4\text{NO}_3$  and  $\sim 2M$  in  $\text{HNO}_3$ . The extraction is an excellent decontamination step because very little else is taken into the ether. The uranium and plutonium are back-extracted into water and the aqueous solution is evaporated to dryness. Then the procedure for the SEPARATION OF URANIUM AND PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS is performed.

## 2. Reagents

$\text{HNO}_3$ : fuming  
 $\text{HClO}_4$ : conc  
 $\text{NH}_4\text{NO}_3$ : solid  
Diethyl ether

## 3. Procedure

*Step 1.* Transfer the sample in  $\text{HCl}$  and  $\text{HClO}_4$  to an erlenmeyer flask of suitable size. Add a volume of fuming  $\text{HNO}_3$  that is equivalent to  $\sim 10\%$  of the sample volume; heat carefully on a hot plate for several hours, and boil to dryness to drive off all the  $\text{HClO}_4$ .

*Step 2.* Add  $\sim 50$  ml of fuming  $\text{HNO}_3$  and evaporate to dryness again. Heat the sides of the flask to expel any residual  $\text{HClO}_4$ .

*Step 3.* Dissolve the residue in  $\sim 40$  ml of fuming  $\text{HNO}_3$ ; warm if necessary. Transfer the solution to 40-ml glass centrifuge tubes and centrifuge out any insoluble residue (Note 1).

*Step 4.* Transfer the supernate to a 1-l beaker, dilute with  $\text{H}_2\text{O}$  to make the solution  $\sim 2M$  in  $\text{HNO}_3$ , and add solid  $\text{NH}_4\text{NO}_3$  until the solution is saturated with that reagent. Transfer to a separatory funnel and extract twice with equal volume portions of diethyl ether (Note 2). Combine the ether phases in a clean separatory funnel.

*Step 5.* Back-extract with three portions of  $\text{H}_2\text{O}$ , each equivalent in volume to  $\sim 10\%$  of the combined ether phases. Combine the aqueous extracts and begin with *Step 1* of the procedure for the SEPARATION OF URANIUM AND PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS.

## Notes

1. If the residue shows no activity, it may be discarded. If, however, it contains a substantial fraction of the total activity in the sample, an attempt should be made to bring the active substances into solution. Heating with  $6M$   $\text{NaOH}$ , followed by acidification with  $\text{HNO}_3$ , will usually remove most of the activity from the precipitate.

2. Isopropyl ether is not satisfactory as an extractant.

(October 1989)



# NEPTUNIUM I

H. L. Smith

## 1. Introduction

This procedure for the determination of  $^{239}\text{Np}$  affords excellent decontamination from milligram quantities of uranium, the fission products obtained from  $10^{13}$  fissions, and plutonium. The decontamination factor for plutonium is  $\sim 10^4$ .

An initial fuming with  $\text{H}_2\text{SO}_4$  is recommended both to ensure exchange between the  $^{237}\text{Np}$  tracer and  $^{239}\text{Np}$ , and to complex uranium(VI). If the sample is a dissolved uranium foil,  $\text{HNO}_3$  must be added before the fuming step to convert uranium to the +6 state. Neptunium(IV) and (V) are carried down by  $\text{LaF}_3$  precipitations in the presence of zirconium and strontium holdback carriers. These precipitations provide decontamination from the activities of zirconium and strontium as well as from uranium. Lanthanum fluoride scavenging with neptunium in the hexapositive state decontaminates from the lanthanides and partially from plutonium.

## 2. Reagents

Lanthanum carrier: 5 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Strontium carrier: 10 mg strontium/ml, added as  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrOCl}_2$  in  $\text{H}_2\text{O}$

$^{237}\text{Np}$  standard solution: 5000 to 10 000 counts/min/ml in 2 to 4M HCl or  $\text{HNO}_3$

HCl: 0.1M; 1M; 2M; conc

$\text{H}_2\text{SO}_4$ : conc

$\text{HNO}_3$ : conc

$\text{H}_3\text{BO}_3$ : saturated solution

HF: 1:1  $\text{H}_2\text{O}$  and conc HF

HI-HCl: 1 ml 55 to 57% HI + 9 ml conc HCl (This mixture should be saved if kept refrigerated but should be discarded when it becomes very dark brown)

HF- $\text{HNO}_3$ : equal parts by volume of 2M solutions

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : 5M (or saturated)

$\text{KMnO}_4$ : 10% solution

$\text{NH}_4\text{OH}$ : conc; dilute

Methyl red indicator solution: 0.5% in 90% ethanol

Dowex 1-X10 anion-exchange resin: 100 to 200 or 200 to 400 mesh; slurry in  $\text{H}_2\text{O}$

## 3. Standardization of Tracer

The usual technique for standardizing alpha-emitting tracers consists of the evaporation of a measured volume of solution on a platinum plate and alpha-counting it. This technique does not work very well in the case of  $^{237}\text{Np}$  because of the relatively low specific activity of the isotope, which is  $\sim 800$  counts/min/ $\mu\text{g}$ ; stippling produces a rather massive deposit. A preferable technique is described here. Prepare a solution of pure  $^{239}\text{Np}$  from pile-irradiated  $^{238}\text{U}$  that contains  $\sim 10^4$  counts/min/100  $\mu\text{l}$ . Weigh an aliquot of this solution onto a platinum plate and add another weighed aliquot to 1 ml of tracer. The  $^{239}\text{Np}$  can now be used as a beta-emitting tracer to determine the absolute amount of  $^{237}\text{Np}$ .

Evaporate the  $^{239}\text{Np} + ^{237}\text{Np}$  sample to dryness with  $\text{HNO}_3$ , take into solution with 1 ml of conc HCl, pass the solution through an anion column as described in Step 11, and then elute the neptunium with 0.1M HCl. Electroplate as described in Step 12. Alpha- and beta-count the sample; beta-count the pure  $^{239}\text{Np}$  aliquot. Use the known specific beta activity of the  $^{239}\text{Np}$ , to calculate the activity of  $^{237}\text{Np}$ /ml of solution.

## 4. Procedure

*Step 1.* Pipette 1 ml of  $^{237}\text{Np}$  standard into a clean 125-ml erlenmeyer flask and then pipette in the sample. Wash down the sides of the flask with a little  $\text{H}_2\text{O}$ , add 10 drops of conc  $\text{H}_2\text{SO}_4$  (Note 1), and evaporate nearly to dryness on a hot plate. (No harm is done if the solution is permitted to evaporate to hard dryness.)

*Step 2.* Dissolve the residue by boiling briefly in a minimum of 2M HCl. Transfer the solution to a clean 40-ml Pyrex centrifuge tube, wash the flask once with H<sub>2</sub>O, and transfer the washings to the tube. The volume of solution should be 5 to 10 ml. (Ignore any small residue.)

*Step 3.* Add 5 drops of lanthanum carrier and 3 drops of zirconium holdback carrier. Add 2 drops of NH<sub>2</sub>OH•HCl/ml of solution, stir, and let stand for a few minutes. Add HF dropwise until the yellow color of the solution disappears and the solution becomes cloudy (LaF<sub>3</sub>). Centrifuge. Remove and discard the supernate. Wash the precipitate with 1 to 5 ml of HF-HNO<sub>3</sub>.

*Step 4.* Dissolve the precipitate by slurring with 3 drops of saturated H<sub>3</sub>BO<sub>3</sub> and adding 3 drops of conc HCl. (Ignore any small residue.) Add 3 ml of 2M HCl and precipitate La(OH)<sub>3</sub> by adding ~1 ml of conc NH<sub>4</sub>OH. Centrifuge and discard the supernate. Wash the precipitate by boiling it briefly with several milliliters of H<sub>2</sub>O.

*Step 5.* Dissolve the precipitate in ~5 ml of 2M HCl. Reprecipitate LaF<sub>3</sub> by adding 10 drops of NH<sub>2</sub>OH•HCl and 10 drops of HF; centrifuge and discard the supernate. Wash the precipitate with 1 ml of HF-HNO<sub>3</sub>. If the precipitate volume is >0.2 ml, repeat the hydroxide and fluoride precipitations until the volume of LaF<sub>3</sub> precipitate is <0.2 ml.

*Step 6.* Dissolve the fluoride precipitate in 1 drop each of saturated H<sub>3</sub>BO<sub>3</sub> and conc HNO<sub>3</sub>. Add 10 drops of KMnO<sub>4</sub> and allow to stand for 5 min. Add 2 drops of HF and allow the solution to stand for a few minutes. Centrifuge and transfer the supernate to a clean centrifuge tube. Wash the precipitate with 0.5 to 1 ml of HF-HNO<sub>3</sub>, centrifuge, and add the supernate to the previous one. Discard the precipitate.

*Step 7.* Add 2 drops of lanthanum carrier to the solution, stir, centrifuge, and transfer the supernate to a clean centrifuge tube. Wash the precipitate

with 0.5 to 1 ml HF-HNO<sub>3</sub>, add the washings to the previous supernate, and discard the precipitate.

*Step 8.* Add 5 drops of NH<sub>2</sub>OH•HCl and 2 drops of zirconium carrier; let stand for a few minutes. Add 2 drops of lanthanum carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml of HF-HNO<sub>3</sub>, centrifuge, and discard the supernate.

*Step 9.* Repeat Steps 6 and 7.

*Step 10.* Add 5 drops of NH<sub>2</sub>OH•HCl and 2 drops of strontium holdback carrier; let stand for a few minutes. Add 2 drops of lanthanum carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml of HF-HNO<sub>3</sub>, centrifuge, and discard the supernate.

*Step 11.* Dissolve the precipitate with 1 drop of saturated H<sub>3</sub>BO<sub>3</sub> and 10 drops of conc HCl. Pass the solution through a Dowex 1-X10 anion-exchange column, 3 cm by 3 mm, and wash the column with 1 ml of conc HCl. The neptunium is now in the +4 oxidation state and is adsorbed on the column. If necessary, remove plutonium from the column with HI-HCl. (Note 2). Elute the neptunium with 0.5 ml of 0.1M HCl. If a plutonium removal step has been done, the solution should be taken to dryness before electroplating; otherwise the eluate can be received directly into the electroplating cell (cathode: 1-cm-diam platinum disk).

*Step 12.* Adjust the acidity to obtain 1 to 2 ml of a solution that is ~6M in HCl. Add 1 drop methyl red indicator, make alkaline with conc NH<sub>4</sub>OH, and then make barely acidic with 1M HCl. Electroplate for 20 min at 0.5 A. Make alkaline with dilute NH<sub>4</sub>OH for the last minute of plating. (A minor explosion occurred when conc NH<sub>4</sub>OH was used.) Decant the plating solution; rinse the cell with H<sub>2</sub>O and alcohol. Dismantle the cell and ignite the platinum cathode to red heat in a burner. Mount, alpha-count to determine the chemical yield, and beta-count on 3 consecutive days.

## Notes

1. If the sample has been obtained from more than the equivalent of 50 mg of underground nuclear debris, do not add any  $\text{H}_2\text{SO}_4$  because  $\text{CaSO}_4$  will precipitate and carry neptunium to some extent. Repeated fuming with  $\text{HNO}_3$  will probably promote exchange.

2. The procedure should remove 95% of the plutonium initially present in the sample. If, at this point, enough plutonium remains to interfere with the determination of the neptunium yield (that is, >1% of the neptunium tracer), plutonium may be removed more efficiently by the following method. Allow 1 ml of HI-HCl solution to drip through the column under no added pressure. Wash the column with several milliliters of conc HCl and discard the effluent, which contains the plutonium in the +3 state; proceed with the rest of *Step 11*. This one elution step removes 99.5% of the plutonium.

(October 1989)

# NEPTUNIUM II

D. W. Efurud and Joy Drake

## 1. Introduction

The following procedure was devised to separate trace quantities of neptunium-236, 237, 238 and 239 from up to 100 g of debris from underground detonations. The neptunium is separated from the other actinides and fission products by a thenoyltrifluoroacetone (TTA) extraction. Final purification of the neptunium is accomplished on two anion-exchange resin columns. It is strongly recommended that the purification procedure be performed in a Class 100 clean area and that HCl, HNO<sub>3</sub>, and HClO<sub>4</sub> acids be prepared by subboiling distillation. All glassware, Teflon, and quartz should be leached in aqua regia and rinsed in Type 1 reagent-grade water.

Samples prepared by this procedure are suitable for analysis by alpha, beta, gamma-ray, and mass spectrometric measurement techniques. Typical chemical yields for the purification procedure are 50 to 80%.

## 2. Reagents

<sup>236</sup>Np tracer: 10<sup>10</sup> atoms

HClO<sub>4</sub>: conc

HF: conc

HNO<sub>3</sub>: conc; 8M

HCl: conc HCl saturated with anhydrous HCl gas;  
5M; 3M; 1M

HCl-HF: 3M HCl-3M HF; 6.5M HCl-0.004M HF;  
conc HCl saturated with anhydrous HCl gas  
and made 0.06M in HF

HI-HCl: 1:9 mixture of ultrapure, nonstabilized  
48% HI in HCl saturated with anhydrous HCl  
gas

HBr: 47% ultrapure, nonstabilized HBr

TTA reagent: 0.5M thenoyltrifluoroacetone in  
o-xylene

NH<sub>2</sub>OH•HCl: solid

FeCl<sub>2</sub>•4H<sub>2</sub>O

Anion-exchange resin: Bio-Rad macroporous  
anion-exchange resin AG MP-1, 50 to 100  
mesh

Type 1 reagent-grade water

## 3. Procedure

*Step 1.* Place an aliquot of the sample in a Vycor beaker and add <sup>236</sup>Np tracer. To equilibrate the sample and tracer, add 10 ml of HClO<sub>4</sub> and fume over a burner at 180°C or higher. The HClO<sub>4</sub> equilibration step is omitted for untraced samples.

*Step 2.* Cool the contents of the beaker. Add 100 ml of 1M HCl and warm slightly to dissolve solids. Make the solution 1M in NH<sub>2</sub>OH•HCl and 0.25M in FeCl<sub>2</sub>. Mix the solution and, after a 5-min reduction period, extract the neptunium with an equal volume of 0.5M TTA-xylene for 10 min. When the two phases have separated, draw off the aqueous phase and discard. Wash the organic phase by shaking with an equal volume of 1M HCl for 3 min. Discard the aqueous layer. Repeat the wash two more times. Strip the neptunium from the organic phase by shaking with 30 ml of 8M HNO<sub>3</sub> for 2 min. Discard the organic layer. Wash the 8M HNO<sub>3</sub> with an equal volume of 0.5M TTA-xylene for 5 min. Discard the organic layer.

*Step 3.* Prepare the sample for loading on an anion-exchange column by adding 1 ml of conc HClO<sub>4</sub> and evaporating to dryness. Cool the beaker and add 2 ml of conc HCl saturated with anhydrous HCl gas (saturated HCl). Load the saturated HCl that contains the neptunium onto an anion column that has been conditioned by three 1-ml washes with Type 1 reagent-grade water and 1-ml of saturated HCl. (Note 1). Wash the beaker that contained the neptunium with 1 ml of the saturated HCl solution and add the wash to the resin column. Discard the effluent. Wash the column with 5 ml of saturated HCl that contains 0.06M HF. Rinse the column with three successive additions of 9 drops of HI-HCl reagent (Note 2). Elute the neptunium into a 30-ml Teflon beaker with 3 ml of 6.5M HCl-0.004M HF. Evaporate the solution to dryness.

*Step 4.* Use a second macroporous anion-exchange resin column to achieve the level of purity required for mass spectrometry. Dissolve the sample in 1 ml of saturated HCl. Prepare this column as described in *Step 3*. Load the neptunium solution on the anion column. Wash with 1 ml of saturated HCl. Elute the neptunium with 5 ml of ultrapure, nonstabilized 47% HBr into a clean quartz test tube (Note 2).

*Step 5.* Evaporate the HBr solution to dryness in a heating block. Destroy the traces of HBr and organic material eluted from the resin by adding 3 drops of conc HNO<sub>3</sub> and 3 drops of conc HClO<sub>4</sub>. Heat at 130°C for 1 h. Raise the temperature of the heating block to 180°C and evaporate the sample to dryness.

#### Notes

1. The Bio-Rad macroporous anion-exchange resin AG MP-1, 50 to 100 mesh, was prepared by warming it overnight in 5M HCl. It was washed 20 times with Type 1 reagent-grade water. The resin column was prepared in a 7-cm-length by 5-mm-i.d. disposable automatic pipettor tip. These tips were leached in dilute HNO<sub>3</sub> and soaked in Type 1 reagent-grade water. A plug of prewashed quartz wool was placed in the tip and resin was added to a depth of 2 cm. Quartz wool must be used because glass wool contains too many leachable impurities.

2. Ultrapure, nonstabilized HI and HBr must be used; the H<sub>3</sub>PO<sub>2</sub> stabilizer and impurities in reagent-grade HI and HBr will contaminate the samples so that they cannot be analyzed by mass spectrometry.

(October 1989)

# PLUTONIUM

D. C. Hoffman

## 1. Introduction

This procedure for plutonium depends upon the almost-quantitative carrying of plutonium(IV) on  $\text{LaF}_3$  and the great difference between adsorption of plutonium(III) and that of plutonium(IV) in 12M HCl medium on a Dowex A-1 anion-exchange resin. One cycle of the procedure serves to separate plutonium from other alpha-emitters; two cycles usually give complete decontamination from beta-emitting fission products.

The initial  $\text{LaF}_3$  precipitation, carried out in the presence of  $\text{NH}_2\text{OH}$ , is an excellent volume-reducing step and also eliminates many elements (notably iron) that may interfere in the subsequent adsorption of plutonium on the resin column. After dissolution of the  $\text{LaF}_3$  precipitate in 12M HCl, neptunium, plutonium, and any traces of iron and uranium are adsorbed on the anion resin column, whereas the lanthanides, americium, and curium pass through the column. Plutonium is eluted from the column after reduction to plutonium(III) with HI; neptunium is not reduced to the +3 state and remains behind. (A solution that contained 15  $\mu\text{g}$  of  $^{235}\text{U}$  was run through the procedure, and no fission counts above the usual background of 0.1 to 0.2 ng could be detected.)

The plutonium is collected directly from the resin column on 1  $\frac{7}{8}$ -in. platinum disks that are flamed, alpha-counted, and, if necessary, pulse-analyzed. The plates are usually very clean and may be alpha-pulse-analyzed with a resolution of 1 to 1.5%.

Samples may be run in quadruplicate and yields are usually determined in one of two ways. Enough  $^{236}\text{Pu}$  tracer to equal 25 to 50% of the total plutonium alpha-activity expected may be added to one or two of the original aliquots. On completion of the analysis, the fraction of  $^{236}\text{Pu}$  in the sample is determined by pulse analysis, and the yield is

calculated. Yields may also be determined by spiking two of the four samples with a standardized solution of plutonium activity that is at least five times as active as the aliquot to be analyzed. The average number of counts per minute in the two unspiked samples is subtracted from the average in the two spiked samples. The resulting value, divided by the number of counts per minute in the spike, gives the yield. The chemical yield is usually  $\sim 97\%$ ; for a set of four aliquots analyzed simultaneously, this value is constant to within  $\pm 1\%$ . In analysis of solutions of very high ionic strength, the yields are somewhat lower (90 to 97%), probably because under these conditions the  $\text{LaF}_3$ -carrying step is less efficient.

## 2. Reagents

Lanthanum carrier: 5 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$^{236}\text{Pu}$ : standardized solution in 3M HCl; or standardized spike solution (any mixture of plutonium isotopes in 3M HCl)

HCl: conc; 3M

HF: conc

HF-HNO<sub>3</sub>: equal volumes of 2M solutions

HNO<sub>3</sub>: conc

H<sub>3</sub>BO<sub>3</sub>: saturated aqueous solution

NH<sub>2</sub>OH·HCl: 35% by weight in H<sub>2</sub>O; solid

Solution I: 0.1 ml conc HNO<sub>3</sub>/15 ml conc HCl

Anion-exchange resin: AG 1-X10, 200 to 400 mesh; slurry in H<sub>2</sub>O

HI stock solution: Distill HI (Mallinckrodt analytical reagent-grade, 5.5M in HI, 1.5% H<sub>3</sub>PO<sub>2</sub> preservative) under nitrogen. The HI cannot be used without distillation because H<sub>3</sub>PO<sub>2</sub> preservation apparently causes the eluted drops to attack the platinum collection disks and make the samples unsuitable for pulse analysis. Commercial preparations of HI without preservative usually contain so much free iodine that they are unsuitable. Even after being stored under nitrogen, distilled HI is slowly oxidized. Oxidation is inhibited by the addition of sufficient hydrazine (up to 20% by volume of 64 to 84% N<sub>2</sub>H<sub>4</sub> in H<sub>2</sub>O) to

decolorize the HI solution. The final solution is  $\sim 4.4M$  in HI.

HI-HCl eluant: 1 ml of HI stock solution is added to 7 ml of conc HCl to give a solution  $\sim 0.44M$  in HI. The precipitate that results from the hydrazine present is removed by centrifugation; the supernate is saturated with gaseous HCl. The solution is permitted to come to equilibrium at room temperature before use; because the solution is readily oxidized, fresh reagent is required every few days.

### 3. Procedure

*Step 1.* Pipette 1 ml of tracer or spike solution into 40-ml long-taper, glass centrifuge tubes that will hold samples on which yield is determined. Pipette sample (3M in HCl) into each centrifuge tube; use 1-ml aliquots if possible, although aliquots as large as 25 ml can be used if necessary. Bring all solutions to the same volume by adding to those that do not contain tracer (or spike) acid of the same concentration as that in the tracer (or spike).

*Step 2.* To each tube add 1 to 2 drops of lanthanum carrier/ml of solution and then stir. Add 4 to 5 drops of  $N_2HOH \cdot HCl$ /ml of solution and stir. Add 3 drops of conc HF/ml of solution (Note 1), stir, and let stand for 5 min (Note 2).

*Step 3.* Centrifuge and discard the supernate.

*Step 4.* Wash the precipitate with 10 drops of 2M HF-2M  $HNO_3$ . Stir, centrifuge, and discard the supernate.

*Step 5.* Dissolve the  $LaF_3$  precipitate by adding 2 to 3 drops of saturated  $H_3BO_3$  solution, stirring, and then adding 0.5 ml of conc HCl while stirring. If the solution is clear and colorless, continue adding conc HCl until the volume of solution is 2 ml. Add 1 drop of conc  $HNO_3$  and heat gently. The solution is now ready for *Step 6*. If, after treatment with

conc HCl, the solution is yellow—even faintly so—dilute to 2 ml with  $H_2O$ ; omitting the addition of lanthanum carrier, repeat *Steps 2* through *5*.

*Step 6.* Transfer the solution to a 3- to 5-cm by 4-mm Dowex AG-1 resin column that has been washed with  $\sim 1$  ml of Solution I (Note 3). (This wash may be driven through the column with air pressure.) By means of air pressure, push the solution that contains the sample through the column. Wash the centrifuge tube with two 1-ml portions of Solution I and discard the washes.

*Step 7.* Wash the sides of the centrifuge tube with 1.5 ml of conc HCl, stir with a stirring rod, and remove the rod. Centrifuge the HCl wash and pass the solution through the resin column under pressure.

*Step 8.* Add a few crystals of  $N_2HOH \cdot HCl$  directly to the top of the resin column. Wash the centrifuge tube with 1 ml of conc HCl, transfer the wash to the top of the column and push it through with pressure. Do not let the column run dry under pressure because air bubbles will be forced into the column and will cause channeling and erratic elution of activity.

*Step 9.* Transfer  $\sim 1$  ml of HI-HCl eluant to the top of the column, but apply no pressure during elution. The dark band of the eluant may be seen migrating down the column. Start collecting the drops around the edge of  $1 \frac{7}{8}$ -in. platinum disk when the band is halfway down the column. After the band reaches the bottom of the column, collect 15 drops of eluant, and place as many of them as possible in the center of the disk. If necessary, collect the rest on top of the drops already around the edge of the disk.

*Step 10.* Place the disk on a hot plate (setting  $\sim 400$ ) under a heat lamp and allow the drops to evaporate. Heat the disk to red heat in an open flame and then cool. Alpha-count if the original aliquot was spiked; pulse-analyze and alpha-count if  $^{236}Pu$  tracer was used. (Notes 4 and 5).

## Notes

1. When an appreciable quantity of iron is present, sufficient HF must be added not only to complex this element (thus decolorizing the solution) but also to precipitate lanthanum carrier.

2. When the plutonium sample is from underground nuclear debris and is to be subjected to mass spectrometric analysis as well as the regular procedure, aluminum must be removed before *Step 2* of the procedure is performed.

Add the recommended amount of lanthanum carrier, and then add several drops of thymolphthalein indicator solution to the sample, which is 3M in HCl. Place the sample in an ice bath and add enough 50% NaOH to turn the indicator blue. Stir, centrifuge, and discard the supernate. Wash the precipitate with a small amount of H<sub>2</sub>O, stir, centrifuge, and discard the supernate. Dissolve the precipitate in 1 to 2 drops of conc HCl and dilute to 2 to 3 ml with 3M HCl. Continue with *Step 2* of the procedure, but omit the addition of lanthanum carrier.

3. The presence of conc HNO<sub>3</sub> in Solution I is necessary to destroy the reducing properties of the original resin and thus avoid premature reduction of plutonium(IV) to the tripositive state.

4. To fission-count the plutonium, plates may be prepared by taking the activity directly from the column. However, if any drops are permitted to run together (producing an extreme "bathtub effect"), the fission-counting results are invariably too low. To avoid such effects that are attributable to sample thickness, the samples should be electroplated as described in the procedure for ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING.

5. The neptunium activity that remains on the column after elution of plutonium may be removed in the following manner:

(a) Use pressure to force concentrated HCl that contains several drops of HNO<sub>3</sub>/ml through the column until the dark color has been removed. Discard the effluent. (During this process the column may separate as a result of bubbling, etc., but can be resettled by applying pressure.)

(b) Wash the resin with conc HCl and pressure; permit the column to rebed itself.

(c) Elute the neptunium with 0.1M HCl. The yield may be very low after only one elution with 0.1M HCl; use about three cycles of elution alternately with 0.1M HCl and conc HCl to produce yields up to 85%.

(October 1989)



# ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING

D. C. Hoffman

## 1. Reagents

HCl: conc; 1M  
HNO<sub>3</sub>: conc  
NH<sub>4</sub>OH: conc  
Ethanol: absolute  
NH<sub>4</sub>Cl: solid  
Methyl red indicator solution

## 2. Procedure

*Step 1.* In a graduated centrifuge tube, collect the eluate from *Step 9* of the PLUTONIUM procedure. (Collect the same amount of eluate that would normally be collected on the platinum disk for pulse analysis). To the eluate add 2 to 3 drops of conc HNO<sub>3</sub> and place the tube in an oil bath that is maintained at ~100°C. Use an air jet to evaporate the solution to dryness. Add 3 drops of conc HCl and take the resulting solution to dryness. Repeat the HCl treatment four times.

*Step 2.* After the final evaporation, take the residue up in 0.5 ml of conc HCl and transfer to an electroplating cell that is equipped with a 1-in. platinum plating disk, a thin-walled chimney, and a plastic gasket (Note). Wash the centrifuge tube with two 0.5-ml portions of distilled H<sub>2</sub>O, and transfer the washings to the plating cell (~1.5-ml volume). Add two small spatulas of NH<sub>4</sub>Cl and 2 drops of methyl red indicator solution. Make the solution alkaline with conc NH<sub>4</sub>OH and then add 1M HCl dropwise until the solution is barely acidic.

*Step 3.* Electroplate at 2 A and ~6.8 V for 15 min while stirring the solution with a graphite rod. Just before plating is completed, add 0.5 ml of conc NH<sub>4</sub>OH. Immediately turn off the stirrer and the current and pour the plating liquid back into the centrifuge tube. Remove the chimney and wash the platinum disk with H<sub>2</sub>O and then with ethanol. Flame the plate and count for 1 min on an alpha counter.

*Step 4.* Use Duco cement to mount the platinum plate on a standard fission mount.

## Note

The electroplating setup is the same as that used in the (Plutonium) URANIUM-235 I procedure.

(October 1989)

# REMOVAL OF $^{239}\text{Pu}$ FROM LANTHANIDES, CESIUM, AND ZIRCONIUM

B. E. Cushing

## 1. Introduction

Plutonium(IV) can be quantitatively removed from the lanthanides, cesium, and zirconium by extraction with triisooctylamine. The separation is not satisfactory if the plutonium is in any other oxidation state than +4. The extraction is carried out in the presence of the appropriate carrier or carriers; for example, if the solution, after removal of plutonium, is to be used for analysis of zirconium, this element is employed as carrier.

## 2. Reagents

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Cesium carrier: 10 mg cesium/ml, added as CsCl in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

HCl: 5M; conc

$\text{H}_2\text{SO}_4$ : conc

$\text{NaNO}_2$ : 0.1M

Triisooctylamine: 20% by volume in *n*-heptane

## 3. Procedure

All operations are performed in a glove box.

*Step 1.* Pipette an aliquot of the sample into a 50-ml erlenmeyer flask and add 1 ml each of the desired carriers. Add 10 to 20 drops of conc  $\text{H}_2\text{SO}_4$  and heat to fumes of  $\text{SO}_3$ .

*Step 2.* Cool the solution and transfer to a 40-ml glass centrifuge tube with 5 to 10 ml of 5M HCl. Add ~10 drops of 0.1M  $\text{NaNO}_2$  and heat in a boiling water bath for 5 min.

*Step 3.* Transfer the solution to a 125-ml separatory funnel and rinse the centrifuge tube with

a minimum amount of 5M HCl; add the rinsings to the separatory funnel. Add an equal volume of 20% (by volume) triisooctylamine in *n*-heptane and shake well.

*Step 4.* Allow the phases to separate and draw off the aqueous phase into a clean 40-ml centrifuge tube.

*Step 5.* To the aqueous extract add 10 drops of 0.1M  $\text{NaNO}_2$  and heat in a boiling water bath for 5 min.

*Step 6.* Repeat *Step 3* (Notes 1 and 2).

## Notes

1. The extraction is repeated if necessary. In one experiment, three extractions were sufficient to completely remove 47 mg of plutonium.

2. This procedure does not remove  $^{241}\text{Am}$  activity. Americium activity may be separated from the plutonium-free aqueous solution by following the additional steps below.

(a) Use ammonia gas to precipitate hydroxides. Centrifuge, discard the supernate, and wash the precipitate with  $\text{H}_2\text{O}$ . Centrifuge and discard the supernate.

(b) Dissolve the precipitate in 1 to 2 drops of conc HCl and add 1 ml of 5M  $\text{NH}_4\text{CNS}$  buffered at pH 1.2. Put the solution on an AG 1-X8 anion-exchange resin column (100 to 200 mesh; 1 cm by 6 cm), which has been equilibrated with 5M  $\text{NH}_4\text{CNS}$  solution.

(c) Elute with 10 ml of the cold 5M  $\text{NH}_4\text{CNS}$  solution. This procedure gives a decontamination factor of  $\sim 5 \times 10^3$  and should be repeated to ensure removal of americium.

(October 1989)

# HDEHP SEPARATION OF PLUTONIUM FROM UNDER- GROUND NUCLEAR DEBRIS

D. C. Hoffman and F. O. Lawrence

## 1. Introduction

In this procedure, plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl phosphoric acid) in *n*-heptane from 4M HNO<sub>3</sub> solutions of the fluoride-soluble fractions obtained from underground nuclear debris. The method is convenient for isolating plutonium from large volumes of solutions of high ionic strength—solutions for which the element does not carry well on a fluoride precipitate. The plutonium is predominantly in the (VI) oxidation state in the samples. The element is recovered from the organic phase by reduction to the (III) state and back-extraction with NH<sub>4</sub>I-HCl solution. This step accomplishes extensive decontamination because most of the species that extract into HDEHP from 4M HNO<sub>3</sub> are not back-extracted by the NH<sub>4</sub>I-HCl solution. Further purification of the plutonium can be accomplished by the usual LaF<sub>3</sub> precipitations and elution from an anion-exchange resin column with HI-HCl solution, as described in the PLUTONIUM procedure.

Plutonium(IV) is also extracted quantitatively by HDEHP in *n*-heptane, but it appears that in this oxidation state the element is so tightly held in the organic phase that it is not effectively reduced and back-extracted.

## 2. Reagents

HDEHP solution: 0.5M solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane (43 ml—or ~40.25 g—of the acid in 250 ml of solution).

HCl: 9M

HNO<sub>3</sub>: 4M; conc

NH<sub>4</sub>I: saturated aqueous solution

NH<sub>4</sub>I-HCl solution: one volume of the saturated

NH<sub>4</sub>I solution to 8 of 9M HCl

NH<sub>2</sub>OH•HCl: solid

## 3. Procedure

*Step 1.* Pre-equilibrate the 0.5M HDEHP with an equal volume of 4M HNO<sub>3</sub>. To an aliquot of the sample (~4M in HNO<sub>3</sub>) in either a narrow-necked 40-ml conical centrifuge tube or a 60-ml separatory funnel, add one-half to one-third its volume of the pre-equilibrated HDEHP. Shake for 1 min and allow the phases to separate; centrifuge if necessary. Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 4M HNO<sub>3</sub>, and discard the wash.

*Step 2.* To the organic phase, add ~50 mg of solid NH<sub>2</sub>OH•HCl and then one-half volume of NH<sub>4</sub>I-HCl solution. Shake for 2 min and drain the aqueous (bottom) layer into a clean 40-ml centrifuge tube. Discard the organic layer.

*Step 3.* If the final volume of the aqueous layer is <10 ml, dilute with H<sub>2</sub>O to about three times the volume and proceed to *Step 2* of the PLUTONIUM procedure. If the volume is >10 ml, transfer the solution to a 125-ml erlenmeyer flask and evaporate to the desired volume over a burner. Then proceed to *Step 2* of the PLUTONIUM procedure. Be sure to oxidize the plutonium(III) by adding 1 drop of conc HNO<sub>3</sub> to the HCl solution and warming just before passing it through the anion resin column.

(October 1989)

# THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION I

D. C. Hoffman and F. O. Lawrence

## 1. Introduction

The basic principle in the separation of plutonium from large volumes of solution is the same as that used in the procedure for HDEHP SEPARATION OF PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS, in which plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane from acidic solution. In the procedure described below, the plutonium is extracted into HDEHP-*n*-heptane that has been impregnated on an inert support (a fluorohalocarbon resin). Extraction on such a column is much more convenient than one in which the plutonium-containing solution is extracted with a large volume of HDEHP solution. Moreover, the back-extraction of plutonium from the column is more efficient than from HDEHP solution. With the use of the column, the separation of phases is clean—which is not always true in ordinary liquid-liquid extraction.

## 2. Reagents

$^{238}\text{Pu}$  standardized tracer solution, in 3M HCl  
HCl: 9M; 4M  
CrO<sub>3</sub>: solid  
NH<sub>4</sub>I: saturated aqueous solution  
NH<sub>4</sub>I-HCl: one volume of saturated NH<sub>4</sub>I solution  
to eight volumes of 9M HCl  
NH<sub>2</sub>OH•HCl: solid  
CTFE-2300 (fluorohalocarbon resin) powder:  
source: Allied Chemical Corporation,  
Morristown, New Jersey  
HDEHP: di-2-ethylhexyl orthophosphoric acid:  
purified according to the directions in the  
Reference.  
*n*-heptane

## 3. Procedure

*Step 1.* Pipette the tracer plutonium and the sample in 4M HCl into an erlenmeyer flask and add a few crystals of CrO<sub>3</sub>. Heat to boiling and then let cool to room temperature.

*Step 2.* To the CTFE-2300 (1 g/50 ml of sample solution) (Note), add enough of a mixture of equal volumes of purified HDEHP and *n*-heptane to make a slurry. Allow to equilibrate for 5 min. Stir well; pour the resulting mixture into a glass column (i.d. ~1 cm), the tip of which has been plugged with glass wool. Wash the column with 2 ml of 4M HCl.

*Step 3.* Pour the cooled, sample-containing mixture onto the column and allow it to pass through either under gravity or with the application of a slight air pressure. Discard the effluent.

*Step 4.* Wash the (resin) column with 2 ml of 4M HCl and then with 2 ml of 9M HCl. Discard the washings. Add a few crystals of NH<sub>2</sub>OH•HCl to the top of the column.

*Step 5.* Add 2 ml of NH<sub>4</sub>I-HCl solution to the column to elute the plutonium, and collect the eluate in a 40-ml glass centrifuge tube.

*Step 6.* Dilute the eluate to 3M in HCl by addition of the appropriate quantity of H<sub>2</sub>O. Perform *Steps 2* through *10* of the PLUTONIUM procedure.

### Note

Different batches of CTFE vary somewhat in their properties, so different support-to-sample ratios may be necessary.

### Reference

K. Wolfsberg, Ph.D. Thesis, Washington University, St. Louis, Missouri (1959), p. 60.

(October 1989)

# THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION II

F. O. Lawrence and D. C. Hoffman

## 1. Introduction

In this procedure, DBHQ, (2,5-di-tertiary butylhydroquinone) in 2-ethyl-1-hexanol solution is used for the back-extraction of plutonium(IV) from solutions of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane.

Treatment with DBHQ reagent, followed by contact with 6M HCl, will back-extract both plutonium(IV) and (VI) quantitatively from HDEHP-*n*-heptane solutions. Plutonium(IV), once extracted into HDEHP solutions, is apparently so tightly complexed that previous attempts to back-extract it quantitatively with other reagents, even with those which should reduce the element to the tripositive state, have been unsuccessful. Presumably, in the back-extraction with the DBHQ solution, the plutonium is reduced to the +3 state and then strongly complexed by the DBHQ.

The extraction coefficients (for transfer from aqueous media to HDEHP solution) for plutonium(IV) are very much higher than for plutonium(VI). The volume of HDEHP extractant for the former species can be as little as one-fifth the volume of the sample. The procedure can be adapted readily to a mixture of the two plutonium species by increasing the volume of HDEHP extractant to one-third of the sample volume.

To determine the element quantitatively,  $^{236}\text{Pu}$  tracer is added;  $\text{NaNO}_2$  is used to ensure that all the plutonium is converted to the +4 state to effect complete exchange.

## 2. Reagents

$^{236}\text{Pu}$  standardized tracer solution in 3M HCl  
HDEHP solution: 0.75M solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane  
DBHQ solution: 0.2M solution of 2,5-di-tertiary butylhydroquinone in 2-ethyl-1-hexanol  
HCl: 6M; 3M  
 $\text{NaNO}_2$ : 10M

## 3. Procedure

*Step 1.* Pre-equilibrate the 0.75M HDEHP solution with an equal volume of 3M HCl in a separatory funnel. (The size of the funnel should be about twice that of the sample aliquot.) Add sufficient 10M  $\text{NaNO}_2$  to an aliquot of the sample and the plutonium tracer (in either a narrow-necked conical centrifuge tube or an erlenmeyer flask) to make the final concentration of the salt  $\sim 0.2M$ ; for example, add 1 ml of 10M  $\text{NaNO}_2$  to 50 ml of aliquot of sample. Heat the solution to boiling and then permit it to cool to room temperature. Add the sample to one-third its volume of pre-equilibrated HDEHP, shake for 1 min, and allow the two phases to separate; centrifuge if necessary (Note). Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 6M HCl, and discard the wash.

*Step 2.* To the organic phase add one-third volume of the 0.2M DBHQ solution and shake for  $\sim 10$  s. Add one-half volume of 6M HCl, shake for  $\sim 2$  min, and allow 5 min for the separation of the two phases. Drain, save the aqueous (lower) phase, and discard the organic layer.

*Step 3.* If the volume of the aqueous phase is  $< 5$  ml, add  $\text{H}_2\text{O}$  to make the solution 3M in acid and proceed to *Step 2* of the PLUTONIUM procedure. If the volume of the aqueous phase is  $> 5$  ml, transfer the solution to a 125-ml

erlenmeyer flask and evaporate over a burner. Transfer the solution to a 40-ml conical centrifuge tube, use water washes from the erlenmeyer flask to dilute the solution to 3M in acid, and then continue with *Step 2* of the PLUTONIUM procedure.

#### Note

If very large aliquots (150 to 200 ml) of sample are used, the volume of HDEHP solution may be increased to one-half volume of that of the sample and a second back-extraction with 6M HCl may be performed.

#### Addendum

If large amounts of thorium are present, complete the above procedure and carry out *Steps 2* through *4* of the regular PLUTONIUM procedure. Then dissolve the LaF<sub>3</sub> by stirring with 2 to 3 drops of saturated H<sub>3</sub>BO<sub>3</sub> solution. Add 3 ml of 10M HCl and transfer the solution to a 6-cm by 4-mm Bio-Rad AG 50W-X4, minus 400 mesh, cation resin (H<sup>+</sup> form) column. (Before using, wash the column with 10M HCl.) Collect the effluent in a 125-ml erlenmeyer flask. Wash the column once with 3 ml of 10M HCl and twice with 6 ml of conc HCl; collect the effluents in the erlenmeyer flask. Boil down the combined effluents to a small volume (0.5 to 2 ml) and transfer the solution to a 40-ml glass centrifuge tube. Dilute with sufficient H<sub>2</sub>O to make the solution 3M in HCl and proceed with *Step 2* of the PLUTONIUM procedure.

(October 1989)

# AMERICIUM AND CURIUM I

H. L. Smith

## 1. Introduction

The procedures given below are suitable for the isolation of americium and curium from a solution containing uranium, plutonium, thorium, and fission products that is obtained from underground nuclear debris.

The regular procedure, which is employed for relatively small samples, consists of (a) a  $\text{LaF}_3\text{-La(OH)}_3$  cycle to separate the actinides and lanthanides from massive contaminants, (b) anion-exchange steps to remove plutonium, (c) adsorption of the lanthanides and remaining actinides on a cation-exchange column, and (d) elution of the latter elements with alcoholic HCl.

The alternative procedure is somewhat more laborious because a number of extractions are performed, but it may be used for larger debris samples. That procedure uses extractions with di-2-ethylhexyl orthophosphoric acid (HDEHP).

## 2. Reagents

### A. Regular Procedure

$^{243}\text{Am}$  tracer: standardized by counting a known volume or known weight of solution

$^{244}\text{Cm}$  tracer: standardized by counting a known volume or known weight of solution

Lanthanum carrier: 5 mg lanthanum/ml, added as  $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

HCl: 1M; 2M; 6M; conc

$\text{HNO}_3$ : conc

HF: conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

HF-HCl wash solution: 1M in each component

$\text{NH}_4\text{OH}$ : conc

Alcoholic HCl solution: 20% by volume of ethanol in conc HCl; saturated with gaseous HCl

Anion-exchange resin: AG 1-X10, 100 to 200 mesh

Cation-exchange resin: AG 50-X4, finer than 400 mesh; tested to ensure that it is suitable for the separation of the lanthanides from the actinides

Methyl red indicator solution

### B. Alternative Procedure (in addition to those in A)

HCl: 0.05M; 5M

HDEHP solution: 0.5M solution in *n*-heptane  
*n*-Heptane

Diethyl ether: pre-equilibrated with 6M HCl

## 3. Procedures

The regular procedure will ordinarily handle the solution obtained from 0.1 to 0.3 g of debris. If it is necessary to take a larger sample or if the sample contains a large amount of calcium, the alternative procedure should be used. The extractions may be performed in separatory funnels or in centrifuge tubes. The phases are mixed with transfer pipettes and then centrifuged to separate the phases. The volumes may, of course, be increased as desired for larger samples.

### A. Regular Procedure

*Step 1.* To an aliquot of sample in an 125-ml erlenmeyer flask, add amounts of  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  tracers approximately equal to those of the  $^{241}\text{Am}$  and  $^{242}\text{Cm}$  expected. Adjust the acid concentration to  $\sim 1\text{M}$ , and add some HCl if none is present. Allow the sample to stand on a steam bath overnight.

*Step 2.* Boil the sample to dryness and then add 10 ml of conc HCl and 3 drops of conc  $\text{HNO}_3$ . Pass the solution through an AG 1-X10 anion resin column, 8 mm by 8 cm; collect the effluent in a clean 40-ml long-taper glass centrifuge tube. Wash the column with 4 to 5 ml of conc HCl and combine this effluent with the previous one.

*Step 3.* Boil the sample to dryness. Take up the residue in 5 ml of 2M HCl, add 4 drops of lanthanum carrier, and make the solution 2M in HF. Allow the mixture to stand for 5 min, then centrifuge, and discard the supernate. Wash the precipitate with 2 ml of HF-HCl solution and discard the washings.

*Step 4.* Dissolve the precipitate by slurring with 1 to 4 drops of saturated H<sub>3</sub>BO<sub>3</sub> solution and adding an equal volume of conc HCl. Dilute to 4 to 5 ml with H<sub>2</sub>O, and precipitate La(OH)<sub>3</sub> by the dropwise addition of conc NH<sub>4</sub>OH. Let the mixture stand on a steam bath for 5 min, centrifuge, and discard the supernate. Wash the precipitate with 2 to 3 ml of H<sub>2</sub>O, heat on a steam bath, centrifuge, and discard the supernate.

*Step 5.* Dissolve the precipitate in 5 ml of 2M HCl, make the solution 2M in HF, let stand for 5 min, centrifuge, and discard the supernate. Wash the precipitate with HF-HCl wash solution, centrifuge, and discard the supernate. Dissolve the precipitate by slurring with 1 drop of H<sub>3</sub>BO<sub>3</sub> solution; then add 10 drops of conc HCl and ~0.02 ml of conc HNO<sub>3</sub>.

*Step 6.* Pass the solution through two successive AG 1-X10 anion resin columns, 3 mm by 3 cm. Collect the effluent in a clean 40-ml long-taper centrifuge tube. Wash the original centrifuge tube and the resin columns successively with 3 drops of conc HCl, and combine the washings with the previous effluent. Discard the resin columns. Evaporate the solution to dryness.

*Step 7.* Dissolve the residue in 1 drop (50  $\mu$ l) of conc HCl and transfer the solution to a 3-mm by 10-cm, AG 50-X4 cation resin column that has been washed with alcoholic HCl solution. Pass the solution into the resin column by means of a slight air pressure. Add 1 drop of conc HCl to the centrifuge tube and pass through the resin column, again passing the solution into the column. Elute the americium-curium with alcoholic HCl; collect

fractions of ~0.1 ml each in 0.5-ml beakers or planchets.

*Step 8.* Dry the fractions and locate the americium-curium peak by alpha-counting. Transfer the activities to a plating cell with 6M HCl. Add 5 drops of methyl red indicator solution, make alkaline with conc NH<sub>4</sub>OH, and then make barely acidic with 1M HCl. Electroplate onto a 1-in. platinum disk for 20 min at 2 A. The <sup>241</sup>Am and <sup>242</sup>Cm are related to the <sup>243</sup>Am and <sup>244</sup>Cm tracers by alpha-pulse analysis.

## B. Alternative Procedure

*Step 1.* (As in the regular procedure.)

*Step 2.* Boil the sample to dryness and dissolve the residue in 10 ml of 0.05M HCl. Ignore any insoluble residue. Transfer the solution (and any residue) to a 60-ml separatory funnel or 40-ml conical centrifuge tube, add 10 ml of HDEHP solution, and mix the phases thoroughly. Separate the phases and discard the aqueous (lower) layer.

*Step 3.* If there is a precipitate in the HEDHP phase, filter it through dry filter paper. Wash the HDEHP phase with three 10-ml portions of 0.05M HCl and discard the washes. The americium and curium activities are now in the organic phase.

*Step 4.* Back-extract the americium and curium with 10 ml of 5M HCl and discard the HDEHP. Wash the HCl phase with 10 ml of heptane and discard the washings.

*Step 5.* Add sufficient conc HCl to make the solution 6 to 7M in acid. Extract twice with volumes of diethyl ether equal to that of the acid solution. (The ether should be pre-equilibrated with 6M HCl.) Discard the ether washings.



*Step 6.* Cautiously evaporate the aqueous solution to dryness; evaporation should be carried out on a steam bath in a large enough vessel to prevent loss of sample through any violent ebullition of the ether.

*Step 7.* Add 4 drops of lanthanum carrier and proceed with *Steps 5* through *8* of the regular procedure.

(October 1989)

# AMERICIUM AND CURIUM II

D. W. Efurud and F. R. Roensch

## 1. Introduction

The following procedure was devised to separate trace quantities of americium and curium from up to 10 g of debris from underground detonations. The lanthanides and actinides are concentrated by a  $\text{LaF}_3\text{-La(OH)}_3$  cycle. They are extracted with di-2-ethylhexyl orthophosphoric acid (HDEHP). Final purification of americium and curium is accomplished by a series of anion exchange steps. If required, americium can be separated from curium on a cation-exchange column. This procedure was developed by modifying chemistries described in Refs. 1 through 3.

It is strongly recommended that the final purification be performed in a Class 100 clean area and that the HCl,  $\text{HNO}_3$ , and  $\text{HClO}_4$  acids be prepared by subboiling distillation. Ultrapure reagents must be used. All glassware and quartz should be leached in aqua regia and rinsed in Type 1 reagent-grade water. Samples prepared by this procedure are suitable for analysis by alpha and mass spectrometric measurement techniques.

## 2. Reagents

$^{243}\text{Am}$  tracer: standardized by alpha-counting known weights of solutions and by isotope dilution mass spectrometry

$^{244}\text{Cm}$  tracer: standardized by alpha-counting known weights of solutions and by isotope dilution mass spectrometry

Lanthanum carrier: 1 mg lanthanum/ml, added as  $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

HCl: conc; 6M; 3M; 0.05M

HF: conc

HCl-HF: 3M HCl-3M HF

$\text{HClO}_4$ : conc

$\text{HNO}_3$ : 90%  $\text{HNO}_3$ ; conc; 10M; 0.1M; 0.01M

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

NaOH: 6M

$\text{NH}_4\text{OH}$ : conc

HDEHP solution: 0.5M solution of unpurified material in heptane

Heptane

Acetone-HCl mixture: 25% conc HCl-75% acetone distilled from glass

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ : solid

$\text{AgNO}_3$ : 10%  $\text{AgNO}_3$  by weight in  $\text{H}_2\text{O}$

Anion-exchange resin: Bio-Rad macroporous resin AGMP-1, 50 to 100 mesh

Cation-exchange resin: PHOZIR, P9411A Inorganic Ion Exchanger; source: Atomergic Chemetals Corp.

## 3. Procedure

*Step 1.* Place an aliquot of the sample in a 500-ml erlenmeyer flask and add  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  tracers in amounts equal to those of the  $^{241}\text{Am}$  and  $^{242}\text{Cm}$  expected. Add 1 ml of lanthanum carrier. To equilibrate the sample and tracer, add 20 ml of  $\text{HClO}_4$  and 10 ml of 90%  $\text{HNO}_3$ ; fume over a burner at 180°C or higher. The equilibration step is omitted for untraced samples.

*Step 2.* Boil almost to dryness. Cool the contents of the flask. Add 25 ml of 3M HCl and warm slightly to dissolve solids. Transfer the solution to a 50-ml polycarbonate centrifuge tube. Rinse the erlenmeyer flask with 5 ml of 3M HCl. Add 6 ml conc HF to the centrifuge tube, stir, and place in a heating block at 80°C for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 20 ml of 3M HCl-HF. Centrifuge and discard the wash.

*Step 3.* Add 2 ml of saturated  $\text{H}_3\text{BO}_3$  and 2 ml of conc HCl to the precipitate and warm slightly to dissolve any solids. Transfer the solution to a 40-ml glass centrifuge tube. Make the solution alkaline with 6M NaOH. Centrifuge and discard the supernate. Add 10 ml of 6M NaOH and boil over a burner while stirring constantly. Centrifuge and discard supernate. Add 20 ml  $\text{H}_2\text{O}$ , stir, and centrifuge. Discard the supernate.

*Step 4.* Dissolve the sample in 3 ml of 6M HCl. Add 10 ml of  $\text{H}_2\text{O}$  and make the solution

alkaline with  $\text{NH}_4\text{OH}$ . Place in a heating block at  $80^\circ\text{C}$  for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$  that contains 1 drop of  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 5.* Dissolve the sample in conc HCl. Place in a heating block and evaporate to dryness. Cool the centrifuge tube. Add 10 ml of 0.05M HCl and 10 ml of 0.5M HDEHP solution. Extract for 2 min. Centrifuge and discard the aqueous layer. Wash the organic phase by shaking with an equal volume of 0.05M HCl for 1 min. Centrifuge and discard the aqueous phase. Strip the lanthanides and actinides from the organic phase by shaking with 5 ml of 6M HCl for 1 min. Use another 5 ml of 6M HCl to repeat the back extraction. Combine the 6M HCl from the two back-extractions. Wash the 6M HCl by adding 10 ml of heptane and shaking for 1 min. Centrifuge and discard the organic layer.

*Step 6.* Place the 6M HCl that contains the lanthanides and actinides in a  $80^\circ\text{C}$  heating block for 30 min. Make the solution alkaline with  $\text{NH}_4\text{OH}$ . Place in a heating block for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$  that contains 1 drop of  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate.

*Step 7.* Dissolve the precipitate in 10 ml of conc HCl that contains 1 drop conc  $\text{HNO}_3$ . Pass the solution through a 1.3- by 3-cm anion-exchange column that has been conditioned with 3 ml of conc HCl containing 1 drop of conc  $\text{HNO}_3$  (Note 1). Collect the effluent in a 40-ml glass centrifuge tube. Record the time when 50% of the solution has passed through the column as the plutonium separation time. Wash the resin with 5 ml of conc HCl that contains 1 drop of conc  $\text{HNO}_3$ ; collect the wash in the same tube. Evaporate the solution to dryness. Add 1 ml of  $\text{HClO}_4$  and evaporate to dryness.

*Step 8.* Add 5 ml of conc HCl and dissolve the sample. Add 15 ml of glass-distilled acetone. Let the mixture stand for 5 min before passing it

through a 1.3- by 3-cm anion-exchange column, that has been conditioned with 10 ml of acetone-HCl mixture (Note 2). Rinse the column with 10 ml of acetone-HCl mixture. Elute the americium and curium with 10 ml of conc HCl into a 40-ml glass centrifuge tube. Evaporate the sample to dryness on a heating block.

*Step 9.* Add 3 ml of acetone-HCl mixture to the sample. Let the sample stand for 5 min before passing it through a 6- by 25-mm anion-exchange column that has been conditioned with 3 ml of acetone-HCl mixture. Rinse the column with 5 ml of acetone-HCl mixture. Elute the americium and curium with 4 ml of conc HCl into a 13- by 100-mm quartz test tube. Evaporate the sample to dryness on a heating block.

*Step 10.* Add 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  to the quartz test tube that contains the americium and curium; heat at  $130^\circ\text{C}$  for 1 h. Raise the temperature of the heating block to  $180^\circ\text{C}$  and evaporate the sample to dryness. The sample is ready for analysis or an americium-curium separation can be performed.

*Step 11.* If an americium-curium separation is required, add 1 ml of conc  $\text{HNO}_3$  and evaporate the sample to dryness. Add 10 ml 0.01M  $\text{HNO}_3$ , 1 drop of 10%  $\text{AgNO}_3$  solution, and 0.023 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Mix gently by swirling. Heat the sample in a water bath at 80 to  $90^\circ\text{C}$  for 10 min. Remove the tube and cool for 7 min in a beaker of water at room temperature.

*Step 12.* Pass the sample through a 6- by 25-mm cation-exchange column that has been conditioned with 5 ml of 0.01M  $\text{HNO}_3$  (Note 3). Catch the effluent, which contains the americium, in a 40-ml glass centrifuge tube. Rinse the column with 10 ml of 0.1M  $\text{HNO}_3$  and catch the rinse in the same centrifuge tube. Elute the curium from the column into a second 40-ml glass centrifuge tube with 10 ml of 10M  $\text{HNO}_3$ . Evaporate the samples to dryness on a heating block. Repeat Steps 7 through 10 to prepare the americium sample and the curium sample for analysis.

## Notes

1. The anion-exchange resin was prepared by warming it overnight in 5M HCl. It was washed 20 times with Type 1 reagent-grade water.

2. Fresh acetone-HCl mixture must be prepared daily.

3. The cation-exchange resin was prepared by washing 20 times with 0.1M HNO<sub>3</sub>.

## References

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(October 1989)

# SEPARATION OF AMERICIUM AND CURIUM FROM TRANSCURIUM ELEMENTS

H. L. Smith

## 1. Introduction

The separation of americium and curium from the transcurium elements is effected by adsorbing transcurium elements from dilute HCl solution onto a Kel-F column treated with 2-ethylhexylphenylphosphonate [2-EH( $\phi$ P)A].

## 2. Reagents

HClO<sub>4</sub>: conc

HCl: 4M; 1M

2-EH( $\phi$ P)A: 1M in *n*-heptane [29 ml of 2-EH( $\phi$ P)A made up to 100 ml with *n*-heptane].

Kel-F: Kel-F 6051; source: Applied Science Laboratories, State College, Pennsylvania; slurry in *n*-heptane.

Column: 3.5 mm by 5 cm; plugged with glass wool or sand and filled with the Kel-F slurry in heptane; treated before use with 5 ml of 2-EH( $\phi$ P)A reagent and 5 ml of 1M HCl.

## 3. Preparation of 2-Ethylhexylphenylphosphonate [2-EH( $\phi$ P)A] from Di-2-Ethylhexylphenylphosphonate

To a 2-l quartz erlenmeyer flask, add 200 g of di-2-ethylhexylphenylphosphonate, 60 g of NaOH, and 500 ml of H<sub>2</sub>O. Add a Teflon stirring bar, cover with a watch glass, and heat on a heater-stirrer for ~72 h. The saponification reaction is complete when the volume of the organic phase has increased by ~50%. Remove the watch glass and continue heating to permit the 2-ethylhexanol formed to evaporate; add H<sub>2</sub>O, as necessary, to prevent bumping. When all the 2-ethylhexanol has evaporated, the monoester will be dissolved in the sodium hydroxide solution, and a single phase will remain. Acidify the solution with HCl, decant the organic (upper) phase into centrifuge cones, and centrifuge to remove any solid contaminant.

The compound may be used without further purification.

## 4. Procedure

*Step 1.* Evaporate the sample to dryness with conc HClO<sub>4</sub>.

*Step 2.* Take up the sample in 100  $\lambda$  of 1M HCl and allow the solution to run into the column. Wash the sample tube with 50  $\lambda$  of 1M HCl and add the washings to the column (Note 1). Add several milliliters of 1M HCl to the column reservoir.

*Step 3.* Collect 10 free column volumes; (Note 2) these will contain americium and curium. Californium starts eluting at 10 free column volumes.

*Step 4.* Remove what remains of the 1M HCl in the reservoir and add 4M HCl to the column. The next four free column volumes of eluate should contain 99% of the californium.

## Notes

1. Americium and curium start eluting immediately.

2. A free column volume denotes the amount of liquid in the column. For the size column employed in the procedure, this amounts to 6 to 8 drops.

(October 1989)

# PURIFICATION OF AMERICIUM FOR GAMMA COUNTING

K. Wolfsberg and W. R. Daniels

## 1. Introduction

This procedure has been used for the separation of americium from samples of up to 2 g of debris from underground detonations. Purification of the sample involves the isolation of a fraction that contains both americium and curium and consists of the following sequence of major steps: (a) initial fluoride precipitation; (b) hydroxide precipitations; (c) extraction of lanthanides and actinides into HDEHP (di-2-ethylhexyl orthophosphoric acid) from 0.05M HNO<sub>3</sub>; (d) back-extraction of only the lighter lanthanides and actinides into 0.8M HNO<sub>3</sub>; (e) passage through an anion-exchange resin column to remove contaminants such as tellurium, zirconium, and plutonium; (f) additional fluoride and hydroxide precipitations; and finally (g) adsorption of the remaining lanthanides and actinides on a cation-exchange column, elution with ethanol-HCl solution, and collection of the americium-curium fraction. The determination of <sup>240</sup>Am and <sup>241</sup>Am can be effected by gamma-ray counting in the presence of curium.

## 2. Reagents

HNO<sub>3</sub>: fuming; conc; 4M; 0.8M; 0.05M

HClO<sub>4</sub>: conc

HF: conc

HCl: conc

HCl-HF: 4M in each acid

H<sub>3</sub>BO<sub>3</sub>: saturated aqueous solution

NaOH: 6M

NH<sub>4</sub>OH: conc

NH<sub>2</sub>OH•HCl: solid

Tellurium(IV) carrier: 10 mg tellurium/ml, added as Na<sub>2</sub>TeO<sub>3</sub> in 6M HCl

Tellurium(VI) carrier: 10 mg tellurium/ml, added as Na<sub>2</sub>TeO<sub>4</sub>•2H<sub>2</sub>O in 3M HCl

Neodymium carrier: 5 mg neodymium/ml, added as NdCl<sub>3</sub>•6H<sub>2</sub>O

0.5M HDEHP: dilute 645 g of di-2-ethylhexyl orthophosphoric acid to 4 l with n-heptane  
EtOH-HCl reagent: 20% absolute ethanol—80% conc HCl—0.1% NH<sub>2</sub>OH•HCl; saturated with HCl gas

Anion-exchange resin: Bio-Rad AG 1-X10, 100 to 200 mesh

Cation-exchange resin: Bio-Rad AG 50W-X4 (H<sup>+</sup> form), nominal minus 400 mesh; batch selected to give satisfactory separation

Cation-exchange resin: Bio-Rad AG 50W-X4, 200 to 400 mesh (H<sup>+</sup> form)

## 3. Procedure

*Step 1.* From 4 to 24 h before beginning *Step 2*, prepare a cation-exchange column that contains Bio-Rad resin AG 50W-X4, minus 400 mesh (H<sup>+</sup> form). Treat the resin (a quantity equivalent to a resin volume of 25 ml when centrifuged from a slurry in water) three times with 50 ml of conc HCl and three times with EtOH-HCl reagent. This treatment is performed in a Büchner funnel with a medium frit, and the resin is sucked dry between treatments. Slurry the resin with EtOH-HCl and transfer to a glass column (9-mm o.d. by 38-cm length); fill to a height of >32 cm under 10 psi of air pressure. Pass EtOH-HCl reagent through the column until the column is ready to be used. Just before the column is used in *Step 12*, reduce the height of the resin to 30 cm.

*Step 2.* Treat ~2 g of ground debris in a Vycor or Teflon beaker with 10 ml of fuming HNO<sub>3</sub>, 20 ml of conc HClO<sub>4</sub>, and 25 ml of conc HF. Boil to heavy fumes of HClO<sub>4</sub>. Repeat treatment and boiling once or twice. Add 40 ml of 4M HNO<sub>3</sub>, transfer the solution to 40-ml Vycor centrifuge tubes, centrifuge, transfer the supernates to clean Vycor tubes, and discard the residues. Make the supernates ~4M in HF, centrifuge, and discard the supernates. Wash the precipitates three times with 4M HCl-4M HF, and combine them in a single centrifuge tube.

*Step 3.* Treat the precipitate with 5 ml of saturated  $\text{H}_3\text{BO}_3$  and 2 ml of conc  $\text{HNO}_3$ , and boil. If the sample is not dissolved, add 2 ml of  $\text{H}_3\text{BO}_3$  and 1 ml of  $\text{HNO}_3$  and boil again. If a small quantity of solid still remains, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the residue (Note 1).

*Step 4.* Dilute the solution to at least 20 ml with  $\text{H}_2\text{O}$  and make alkaline with 6M NaOH. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of 6M NaOH, boil the mixture, and then wash with  $\text{H}_2\text{O}$ . Discard the washes.

*Step 5.* Dissolve the precipitate in  $\sim 3$  ml of conc HCl, dilute to 20 ml with  $\text{H}_2\text{O}$ , and make alkaline with conc  $\text{NH}_4\text{OH}$ . Centrifuge, wash the precipitate with  $\text{H}_2\text{O}$ , and discard the wash.

*Step 6.* Dissolve the precipitate in  $\sim 1$  ml of conc  $\text{HNO}_3$ . Boil the solution to incipient dryness. (A flash evaporator is useful for this purpose.) Dissolve the residue in 10 ml of 0.05M  $\text{HNO}_3$  and transfer the solution to a 40-ml long-tapered centrifuge tube. Add 10 ml of 0.5M HDEHP in heptane. Plug the tube with a plastic stopper, shake vigorously for 20 to 30 s, and centrifuge for  $\sim 15$  s. Draw off and discard the aqueous (lower) phase; also discard any interface. Scrub the organic phase twice with 10-ml portions of 0.05M  $\text{HNO}_3$ . Back-extract the americium and the lighter tripositive lanthanides and actinides with two 10-ml portions of 0.8M  $\text{HNO}_3$ . Wash the combined back-extract with 10 ml of heptane and discard the wash. Transfer the solution to a 125-ml erlenmeyer flask and boil to incipient dryness (Note 2).

*Step 7.* Add 10 ml of conc HCl, 1 drop of conc  $\text{HNO}_3$ , and 1 drop each of tellurium(IV) and tellurium(VI) carriers. Heat the solution, but avoid boiling; pass through an AG 1-X10, 100 to 200 mesh anion column (8-mm o.d. by 10-cm length) that has been pre-equilibrated with 10 ml of conc HCl. Collect all effluents in an erlenmeyer flask.

*Step 8.* Boil to  $\sim 2$  ml, add 10 to 20 mg of neodymium carrier (or any tripositive lanthanide carrier), and dilute to  $\sim 20$  ml with  $\text{H}_2\text{O}$ . Add 4 ml of conc HF, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of 4M HCl-4M HF and discard the wash.

*Step 9.* Dissolve the precipitate in a mixture of 1 to 2 ml each of saturated  $\text{H}_3\text{BO}_3$  and conc HCl. Dilute the solution to 15 ml with  $\text{H}_2\text{O}$ , and make alkaline with 6M NaOH. Centrifuge and discard the supernate. Wash the precipitate with 15 ml of  $\text{H}_2\text{O}$  and discard the wash.

*Step 10.* Dissolve the precipitate in 1 ml of conc HCl, add  $\sim 100$  mg of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , dilute to 15 ml with  $\text{H}_2\text{O}$ , and reprecipitate the hydroxides with conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate. Wash the precipitate with 15 ml of  $\text{H}_2\text{O}$  and discard the wash.

*Step 11.* Dissolve the precipitate in 3 to 5 drops of conc HCl and dilute to  $\sim 30$  ml with  $\text{H}_2\text{O}$ . Add the equivalent of 1 to 2 ml of centrifuged Bio-Rad AG 50W-X4, 200 to 400 mesh cation resin ( $\text{H}^+$  form) in water-slurry form, stir for 1 min, and centrifuge. Discard the supernate, wash the resin with 30 ml of  $\text{H}_2\text{O}$ , and discard the wash.

*Step 12.* Slurry the resin from *Step 11* in 1 to 2 ml of  $\text{H}_2\text{O}$ ; transfer to the top of the cation-exchange column prepared in *Step 1*. Complete the transfer with a small  $\text{H}_2\text{O}$  wash. Allow the resin to settle and draw off the  $\text{H}_2\text{O}$ . Start eluting with EtOH-HCl reagent (Note 3) under  $\sim 10$  psi of air pressure. Collect the americium-curium fraction (Note 4).

## Notes

1. If a large amount of solid remains, add 20 ml of 6M NaOH and boil for  $\sim 2$  min. Centrifuge, discard the supernate, and wash the precipitate with  $\text{H}_2\text{O}$ ; discard the wash. Treat the solid with 2 to 5 ml of saturated  $\text{H}_3\text{BO}_3$  and 2 ml of conc  $\text{HNO}_3$ ; boil, centrifuge, and combine the supernate with the original one.

2. If the heavier lanthanides and actinides are to be recovered, adapt *Steps 8* and *9* of the procedure for CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM UNDERGROUND NUCLEAR DEBRIS for the back-extraction of all the tripositive lanthanides and actinides.

3. The  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in the EtOH-HCl reagent ensures that all the cerium present remains in the +3 condition and that no trace of this element elutes early as a +4 species.

4. The elution curve shown in Fig. 2 of the procedure for CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM UNDERGROUND NUCLEAR DEBRIS is reproducible on a volume basis.

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**CONCENTRATION OF  
TRANSPLUTONIUM ACTINIDES  
FROM UNDERGROUND  
NUCLEAR DEBRIS**

K. Wolfsberg and W. R. Daniels

### 1. Introduction

In this procedure, lanthanides and transplutonium actinides are extracted into tri-*n*-butylphosphate (TBP) from large volumes of solutions of low acidity that are heavily salted with  $\text{Al}(\text{NO}_3)_3$ . Following extraction, the TBP is scrubbed with an  $\text{NH}_4\text{NO}_3$  solution and the elements are back-extracted into  $\text{H}_2\text{O}$ . To keep the volumes of TBP and  $\text{H}_2\text{O}$  reasonable, a relatively small volume of TBP is repeatedly brought into contact with small volumes of feed solutions. This is done at the expense of  $\sim 10\%$  of the product yield.

The actinides and lanthanides are extracted into di-2-ethylhexyl orthophosphoric acid (HDEHP) from a solution of low acidity and are recovered in an aqueous phase after the HDEHP is boiled with decanol. Further decontamination is accomplished by passing a conc HCl solution of these elements through an anion-exchange resin column.

The actinides are then separated from the lanthanides by elution from a cation-exchange resin column with an ethanol-hydrochloric acid (EtOH-HCl) solution. A separation between the transcurium actinides and americium and curium can be effected on this column. [The lanthanides are separated from one another by elution with alpha-HIB(alpha-hydroxyisobutyric acid) from a cation-exchange resin column as described in THE LANTHANIDES procedure.]

The purpose of the procedure is to concentrate the tripositive actinide elements produced in underground detonations. Samples in a range of weights are encountered, and therefore it is necessary to use equipment of various sizes. This procedure is written for samples weighing  $\sim 250$  g. (For handling samples of 2 to 7 g see Note 1.)

### 2. Special Equipment

Extraction vessels: (see Fig. 1) TBP vessel, 25-cm length by 12.5-cm o.d.; HDEHP vessel, 20-cm length by 9-cm o.d.

Transfer vessels: (see Fig. 1) TBP vessel, 20-cm length by 9-cm o.d.; HDEHP vessel, 20-cm length by 7-cm o.d.

Stainless steel centrifugal stirrers

Stirring motors

Teflon glands: source: Arthur F. Smith Co., 201 S.W. 12th Avenue, Pompano Beach, Florida

Separatory funnels with Teflon stopcocks

Bottles: 2, 4, and 9  $\ell$

pH meter with combination glass and Ag-AgCl probe (Beckman 39030)

Rotary flash evaporator with a water-cooled condenser

Vacuum pump

Vinyl tubing

Teflon stopcocks

Solenoid valves

Switches for operating solenoid valves

Dispensing burettes with Teflon stopcocks

Glass columns for anion-exchange resin: 8-cm length by 10-mm o.d.

Glass columns for cation-exchange resin: 38-cm length by 9-mm o.d.; standard taper joint at top

Glass wool: used as plugs in tips of all columns

### 3. Special Reagents

$\text{Al}(\text{NO}_3)_3$ : saturated;  $\sim 2.5M$ , made by dissolving 5 lb of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 1050 ml of  $\text{H}_2\text{O}$  to produce  $\sim 2400$  ml of solution;  $1.9M$ , made by diluting three volumes of saturated  $\text{Al}(\text{NO}_3)_3$  with one volume of  $\text{H}_2\text{O}$

$\text{NH}_4\text{NO}_3$ - $\text{HNO}_3$  reagents:  $10M$  in  $\text{NH}_4\text{NO}_3$  and  $0.2M$  in  $\text{HNO}_3$ , made by dissolving 7 lb of  $\text{NH}_4\text{NO}_3$  in  $\text{H}_2\text{O}$ , adding 50 ml of conc  $\text{HNO}_3$ , and diluting to 4  $\ell$  with  $\text{H}_2\text{O}$ ;  $0.65M$   $\text{NH}_4\text{NO}_3$ - $0.05M$   $\text{HNO}_3$ , made by combining 28 ml of conc  $\text{HNO}_3$  and 570 ml of saturated  $\text{NH}_4\text{NO}_3$  and making up to 9  $\ell$  with  $\text{H}_2\text{O}$

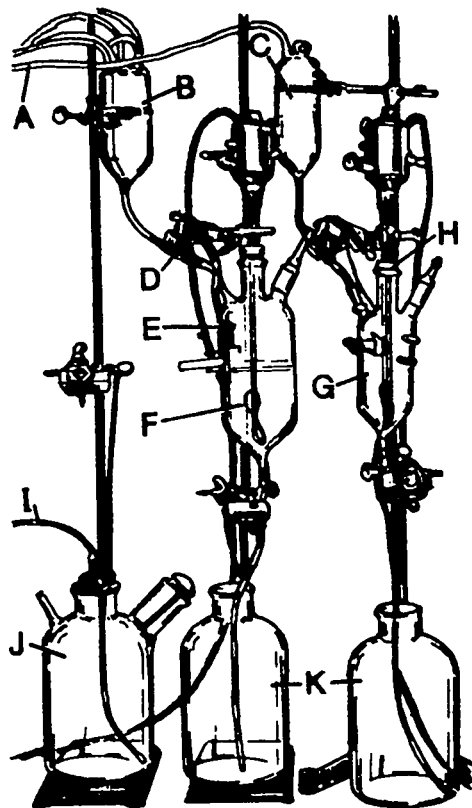


Fig. 1. TBP and HDEHP extraction apparatus. (A) lines to  $\text{Al}(\text{NO}_3)_3$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{HNO}_3$  wash solutions and to  $\text{H}_2\text{O}$ ; (B) TBP transfer vessel; (C) HDEHP transfer vessel; (D) typical solenoid valve; (E) TBP mixing vessel; (F) stainless steel centrifugal stirrer; (G) HDEHP mixing vessel; (H) Teflon gland; (I) air pressure line; (J) feed solution vessel; and (K) vessels for receiving waste solutions or product.

$\text{LiOH}$ : 4M, made by dissolving 671 g of  $\text{LiOH}\cdot\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  and diluting to 4 l

Buffer solution: (pH 1) for standardizing pH meter

$\text{HCl}$ : 10M

Tri-*n*-butylphosphate (TBP)

HDEHP: 0.5M, made by diluting 645 g of di-2-ethylhexyl orthophosphoric acid to 4 l with *n*-heptane

Decanol

$\text{HCl-HF}$ : 4M in each acid

Tellurium(IV) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_3$  in 6M  $\text{HCl}$

Tellurium(VI) carrier: 10 mg tellurium/ml, added as  $\text{Na}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$  in 3M  $\text{HCl}$

$\text{NH}_2\text{OH}\cdot\text{HCl}$ : solid

*n*-heptane

$\text{EtOH-HCl}$ : 20% absolute ethanol-80% conc  $\text{HCl}$ -0.1%  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , saturated with  $\text{HCl}$  gas

Anion-exchange resin: Bio-Rad AG 1-X10, 100 to 200 mesh

Cation-exchange resin: Bio-Rad AG 50W-X4 ( $\text{H}^+$  form), nominal minus 400 mesh; batch-selected to give satisfactory separations.

#### 4. Procedure

The ground-up sample is dissolved in a mixture of conc  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{HF}$  and is boiled to fumes of  $\text{HClO}_4$  after each addition. The solution is made 4M in  $\text{HNO}_3$  and then 4M in  $\text{HF}$ ; the insoluble fluorides (including the tripositive actinide fluorides) are filtered. The precipitate is washed twice with 4M  $\text{HF}$ -4M  $\text{HNO}_3$ , dissolved in conc  $\text{HClO}_4$ , and diluted to make a solution 1 to 2M in  $\text{HClO}_4$ . Details of this process are outlined below. For samples of 25-50 g, use the alternative steps described in Sec. 5.

*Step 1.* To the sample, add enough saturated  $\text{Al}(\text{NO}_3)_3$  and 4M  $\text{LiOH}$  to make the solution 1.7 to 1.9M in  $\text{Al}(\text{NO}_3)_3$  and  $\sim 0.1\text{M}$  in  $\text{H}^+$  (pH 1). This is done by pouring the sample into a 9-l bottle and adding first  $\sim 4000$  ml of saturated  $\text{Al}(\text{NO}_3)_3$  and then 4M  $\text{LiOH}$  slowly from a dispensing burette while stirring the solution vigorously. Stop the addition of  $\text{LiOH}$  when the indicated pH is 0.9 to 1.1. Adjust the  $\text{Al}(\text{NO}_3)_3$  concentration up to 1.7 to 1.9M ( $\sim 75\%$  saturated; Note 2).

*Step 2.* Pour 1 kg of TBP into the extraction vessel. Then add 500 ml of 1.9M  $\text{Al}(\text{NO}_3)_3$  and stir for 2 min. Draw off the pre-equilibrating  $\text{Al}(\text{NO}_3)_3$  wash (the lower phase) and discard. (Fig. 1 shows the extraction apparatus. In general, solutions are transferred by means of air pressure, pumps, or gravity flow.)

*Step 3.* Drain 500 ml of feed (the solution from *Step 1*) from the transfer vessel into the TBP in the extraction vessel. As soon as the addition of feed is begun, start the stirrer and continue stirring for 3 min. After the phases separate, drain off the aqueous phase and discard. Repeat the procedure with successive 500-ml portions of feed; the total number of such contacts should not exceed 20 (Note 3).

*Step 4.* Wash the TBP phase with one 500-ml portion of 1.9M Al(NO<sub>3</sub>)<sub>3</sub> and stir for 2 min; wash with five 500-ml portions of 10M NH<sub>4</sub>NO<sub>3</sub>-0.2M HNO<sub>3</sub> and stir for 5 min each time. Discard the washings.

*Step 5.* Back-extract the lanthanides and actinides with three 500-ml portions of H<sub>2</sub>O; stir for 2 min. Collect the aqueous phases in a plastic bottle.

*Step 6.* Concentrate the back-extracted sample to ~200 ml by boiling in an appropriate glass vessel or by using a rotary flash evaporator with a water-cooled condenser. (The concentration step should be terminated before any material comes out of solution.) Pass the concentrated solution through a filter to remove any remaining TBP.

*Step 7.* To the concentrated solution, slowly add conc NH<sub>4</sub>OH until a pH of 1.5 to 1.75 is reached. Transfer the solution directly to the HDEHP extraction vessel, add 200 ml of 0.5M HDEHP, and stir for ~2 min. After the phases separate, drain the aqueous phase and discard. Wash the HDEHP phase with three 200-ml portions of 0.65M NH<sub>4</sub>NO<sub>3</sub>-0.05M HNO<sub>3</sub> that have drained from the transfer vessel into the extraction vessel. Discard the washings.

*Step 8.* Drain the HDEHP phase into a 1-l erlenmeyer flask; add 100 ml of decanol, 50 ml of conc HCl, and a magnetic stirring bar. Heat the flask on a stirrer-hot plate, and gently boil the mixture for 15 to 20 min. If necessary, add enough conc HCl to maintain an aqueous phase.

*Step 9.* Pour the hot mixture into a separatory funnel. Drain the aqueous phase into a second separatory funnel. Extract the organic phase with 25 ml of 6M HCl and add the aqueous phase to the second separatory funnel. Scrub the combined aqueous phase with ~10 ml of heptane and discard the heptane. Boil the sample in an erlenmeyer flask almost to dryness.

*Step 10.* Fill a glass column (see Sec. 2) with anion-exchange resin and pretreat the resin with ~15 to 20 ml of 10M HCl that contains 2 drops of conc HNO<sub>3</sub>. Dissolve the sample from *Step 9* in 10 ml of conc HCl. Add 1 drop each of conc HNO<sub>3</sub>, tellurium(IV) carrier, and tellurium(VI) carrier; warm gently. Pass the solution through the resin column (~1 drop/s) and collect the eluate in an erlenmeyer flask. Rinse the column twice with 5-ml portions of 10M HCl that contains 1 drop of conc HNO<sub>3</sub>; collect the eluates in the same flask.

*Step 11.* Boil the sample to ~2 ml; dilute with H<sub>2</sub>O to ~20 ml. Add 4 ml of conc HF, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of 4M HCl-4M HF and discard the wash. Dissolve the precipitate in 1 to 2 ml each of saturated H<sub>3</sub>BO<sub>3</sub> and conc HCl; dilute the solution to 15 ml with H<sub>2</sub>O and make the solution alkaline with 6M NaOH. Centrifuge and discard the supernate. Wash the precipitate with H<sub>2</sub>O and discard the washings. Dissolve the precipitate in 1 to 2 ml of conc HCl, dilute to ~20 ml with H<sub>2</sub>O, and add ~100 mg of NH<sub>2</sub>OH•HCl. Warm the solution gently, make alkaline with conc NH<sub>4</sub>OH, and centrifuge. Discard the supernate, wash the precipitate with H<sub>2</sub>O, and discard the washings.

*Step 12.* Dissolve the precipitate in 3 to 5 drops of conc HCl and dilute to ~30 ml with H<sub>2</sub>O. Add the equivalent of 2 ml of centrifuged cation-exchange resin in water-slurry form, stir for 1 min, and centrifuge. Discard the supernate and wash the resin twice with H<sub>2</sub>O.

*Step 13.* About 1 d before the next step, prepare the cation-exchange column. Treat the cation-exchange resin (a quantity equivalent to a resin volume of 25 ml when it has been centrifuged from a slurry in H<sub>2</sub>O) twice with 50 ml of conc HCl and three times with EtOH-HCl solution. Perform the treatment in a Büchner funnel with a medium frit, and suck the resin dry between treatments. Slurry the resin with EtOH-HCl and transfer to a glass column for cation-exchange; fill to a height of ~32 cm under 10 psi of air pressure. Pass EtOH-HCl through the column under 10 psi of pressure until the column is ready to be used. Just before use, reduce the height of the resin to 30 cm.

*Step 14.* Slurry the resin from *Step 12* in 1 to 2 ml of H<sub>2</sub>O and transfer to top of the cation-exchange column. Complete the transfer with a small H<sub>2</sub>O wash. Allow the resin to settle and draw off the H<sub>2</sub>O. Start eluting with EtOH•HCl under ~10 psi air pressure at a flow rate of ~0.1 ± 0.015 ml/min. The elution curve shown in Fig. 2 is reproducible on a volume basis. The free column volume is ~6 ml. The valley between lutetium and americium-curium (with the eluant used, there is essentially no separation between these latter two elements) occurs between 32 and 40 ml. The method of collecting fractions (by volume, time, or drop number), counting them, and combining them will vary with the nature and intent of the purification (Note 4).

## 5. Alternative Procedure for Samples Weighing 25 to 50 g

In *Step 2*, reduce the amount of TBP by 50% and add 300 ml (rather than 500 ml) of 1.9M Al(NO<sub>3</sub>)<sub>3</sub>.

In *Step 3*, wherever 500 ml is indicated, replace with 300 ml.

In *Step 4*, use three 300-ml portions of NH<sub>4</sub>NO<sub>3</sub>-HNO<sub>3</sub> wash.

In *Step 5*, use three 300-ml portions of H<sub>2</sub>O.

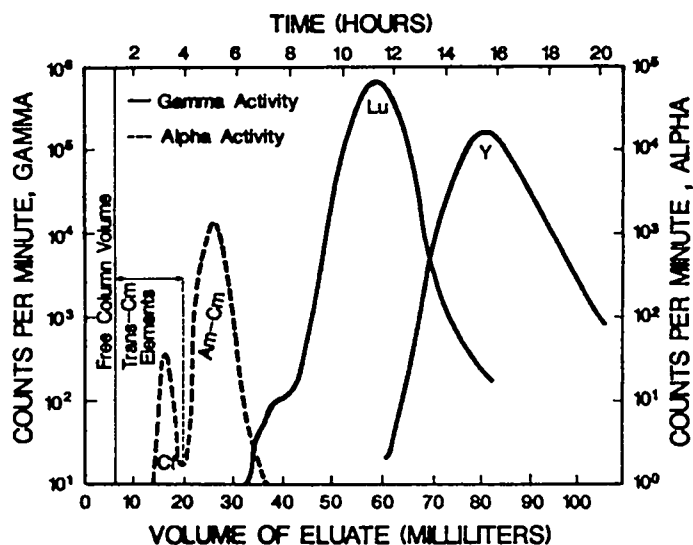


Fig. 2. Elution curve for transplutonium actinides.

Add another step—*Step 9a* to follow 9. This step is the same as *Step 10* except that when tellurium carriers are added, also add 5 mg of neodymium carrier (5 mg neodymium/ml in 3M HCl).

Add another step—*Step 11a* to follow 11. Dissolve the hydroxide precipitate in 1 to 2 ml of conc HCl and dilute to ~20 ml with H<sub>2</sub>O. Add 100 mg of NH<sub>2</sub>OH•HCl, warm the solution gently, make alkaline with conc NH<sub>4</sub>OH, and centrifuge. Discard the supernate, wash the precipitate with H<sub>2</sub>O that contains a few drops of conc NH<sub>4</sub>OH, and discard the washing.

Replace *Step 12* with the following process. Dissolve the precipitate in 3 to 5 drops of conc HCl and dilute to ~30 ml with H<sub>2</sub>O. Centrifuge for 3 min and transfer the supernate to a clean centrifuge tube. (Usually, no solid is visible.) Add the equivalent of 2 ml of centrifuged cation-exchange resin in water-slurry form, stir for 1 min and centrifuge. Discard the supernate and wash the resin twice with H<sub>2</sub>O.

## Notes

1. In *Step 1*, use a 4-ℓ bottle and 1400 ml of saturated  $\text{Al}(\text{NO}_3)_3$ . In *Step 2*, use 0.5 kg of TBP. In *Steps 3* through *5*, reduce the volumes listed to 400 ml. In *Step 9*, before boiling the sample to dryness, add 10 mg of neodymium carrier. In *Step 10*, substitute conc HCl for 10M acid and double the size of the washes. Boil the eluate almost to dryness and repeat the step. In *Step 11*, carry out the precipitation with NaOH twice. In *Step 12*, after dissolving the precipitate and diluting to 30 ml with  $\text{H}_2\text{O}$ , centrifuge for 3 min and transfer the liquid to a clean centrifuge tube. Then complete the step.

2. The pH is not necessarily a real indication of the hydrogen-ion concentration in the concentrated solution, but it appears to be a good way to arrive at a reproducible starting solution of low hydrogen-ion concentration.

3. In general, treat each contact as an individual organic-aqueous system with an apparent distribution coefficient,  $K(o/a)$ , between 20 and 40. If the relative volume of organic phase to aqueous phase is 2:1, between 97.5 and 98.8% of the actinides in the extraction vessel will be in the organic phase after each extraction. The following table shows how the overall yield drops as a function of the number of extractions.

Number of Extractions	Extracted (%)	
	<u>K = 40</u>	<u>K = 20</u>
1	99	98
5	96	93
10	94	87
15	91	82
20	88	78

In fact, the distribution coefficient probably changes with the number of contacts. The TBP becomes more viscous, and phase separation times increase with the number of contacts.

A value of 20 to 40 for the apparent K is probably fairly representative of yttrium. For neodymium, the value is between 10 and 20. In general, the value of K (and recovery) varies in the order: neodymium europium tellurium yttrium terbium californium fermium. This difference might result in ~10% fractionation of the actinides.

4. The americium-curium fraction from the column is suitable for the determination of americium by gamma-counting.

(October 1989)

# SEPARATION OF TRACE AMOUNTS OF TRANSPLUTONIUM ELEMENTS FROM FISSION PRODUCTS

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## 1. Introduction

The following procedure was devised to separate the transplutonium elements from day-old fission product samples that contain  $10^{15}$  to  $10^{16}$  fissions. These elements are carried with  $YF_3$  or  $LaF_3$  and  $La(OH)_3$  precipitates, which are subsequently dissolved. The HCl solution is passed through several anion-exchange resin columns to remove uranium, neptunium, plutonium, and most of the remaining fission products (in particular, zirconium and tellurium). An ethanol-HCl elution from a cation resin column is used to remove the lanthanides. Final separation of the individual transplutonics is accomplished by elution from a cation resin column with ammonium alpha-hydroxyisobutyrate.

## 2. Reagents

Yttrium carrier: 10 mg yttrium/ml, added as  $Y(NO_3)_3 \cdot 6H_2O$  in  $H_2O$

Lanthanum carrier: 5 mg lanthanum/ml, added as  $La(NO_3)_3 \cdot 6H_2O$  in  $H_2O$

Zirconium carrier: 10 mg zirconium/ml, added as  $ZrO(NO_3)_2$  in 1M  $HNO_3$

Tellurium carrier: 10 mg tellurium/ml, added as  $Na_2TeO_3$  in 1M HCl

Strontium carrier: 10 mg strontium/ml, added as  $Sr(NO_3)_2 \cdot 4H_2O$  in  $H_2O$

$NH_4OH$ : conc

HCl: 0.1M; 0.5M; 3M; conc

10M Solution I: 0.1 ml conc  $HNO_3$ /15 ml of 10M HCl

HF: conc

HF- $HNO_3$ : equal volumes of 2M solutions

HF-HCl solution: 0.006M in HF and 0.1M in HCl  
 $HNO_3$ : conc

$H_3BO_3$ : saturated solution

Phenolphthalein indicator solution

Ethanol-HCl eluant: 20% ethanol-80% conc HCl (by volume); saturated with HCl gas at room temperature. (If a cold solution is passed through a resin column, bubbles will form and disturb the resin bed.) This solution should be prepared just before use.

Ammonium alpha-hydroxyisobutyrate eluant:

The stock solution of alpha-hydroxyisobutyric acid (alpha-HIB) is prepared (usually 0.5 or 1M) and is kept refrigerated to inhibit possible mold formation. From the stock solution, small quantities are withdrawn and partially neutralized with  $NH_4OH$  to obtain an eluant of the desired pH. The pH of the eluant should be chosen so as to elute the activities in a convenient volume; the column volume and the speed with which the separation must be made should be considered. If 0.5M isobutyrate solution is used, the peak position in FCV (free column volume units) may be estimated directly from Table I (see Note 1) and Fig. 1. If stronger or weaker acid is used, the pH corresponding to a given anion activity (as shown in Fig. 2) must be calculated from the relationship

$$K_1 = \frac{(H^+)(A^-)}{(HA)} \sim \frac{10^{-pH}(A^-)}{(MHA) - (A^-)},$$

or

$$10^{-pH} \sim \frac{K_1 [(MHA) - (A^-)]}{(A^-)},$$

where

$$K_1 \sim 10^{-3.9},$$

(MHA) = molarity of alpha-hydroxyisobutyric acid,  
and

( $A^-$ ) = anion activity (isobutyrate) read from Fig. 2 .

Anion-exchange resin: Bio-Rad AG 1-X10, 100 to 200 mesh for large columns and 200 to 400 mesh for the small column (Note 2). The resin is stored as a slurry in  $H_2O$ .

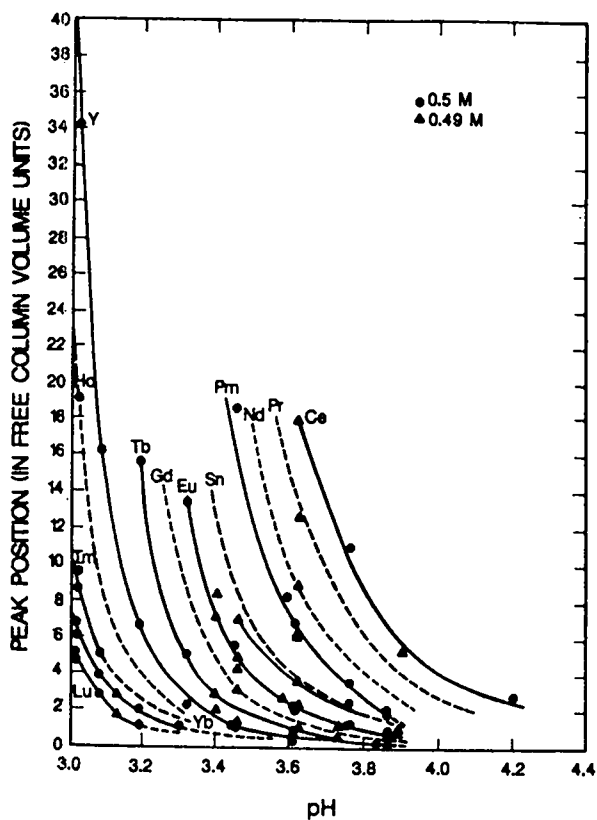


Fig. 1. Lanthanide elution positions *vs* pH with 0.5M  $\alpha$ -hydroxy isobutyric acid.

Cation-exchange resin: Bio-Rad AG 50-X4, 400 mesh or finer. The resin is prepared by washing successively with H<sub>2</sub>O, NH<sub>4</sub>OH, H<sub>2</sub>O, and three times with conc HCl. For the ethanol-HCl columns, the resin is stored as an HCl slurry. For the slurry in H<sub>2</sub>O, the resin should be washed an additional three times with H<sub>2</sub>O.

Cation-exchange resin: Dowex 50 is used for the "isobutyrate" column. It contains from 2 to 8% DVB (the percent of divinylbenzene is proportional to cross-linkage and choice depends on individual preference and what is available). The time required to attain equilibrium and the volume required to elute will increase with the percentage of DVB in the resin. The data in the accompanying graphs were taken with 4% DVB resin. The resin should be 400 mesh or finer; if wet-graded, that fraction is used that settles at a rate of

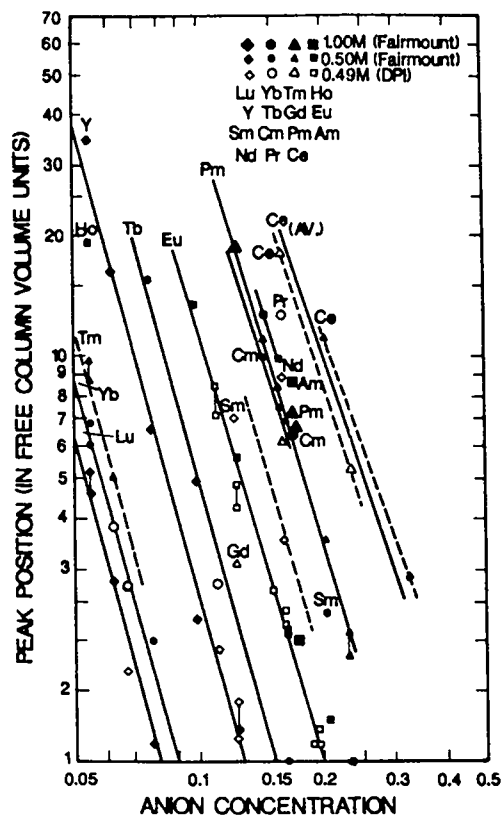


Fig. 2. Lanthanide and actinide elution positions *vs* hydroxy isobutyrate anion concentration.

0.1 to 1.5 cm/min. If the resin has not been specially treated by the supplier, it should be washed thoroughly with 6M NH<sub>4</sub>SCN, 6M NH<sub>4</sub>OH, H<sub>2</sub>O, and HCl, and then stored as the ammonium form in H<sub>2</sub>O. (If no resin can be found that achieves a good separation at room temperature, 12% DVB Dowex 50 may usually be used successfully in a column heated to 80 to 90°C.)

Ion-exchange columns: The ion-exchange columns are fabricated by fusing a length of glass tubing to a centrifuge cone and drawing out the tip to make 6-cm by 2-mm-i.d. and 12-cm by 8-mm-i.d. glass columns. The column tip is plugged with glass wool or sand. A slurry of resin is introduced and allowed to settle; the supernate is discarded. The resin is washed by passing several milliliters of eluant through the column. (Just before use, the "isobutyrate"

column is slurried with the eluant and allowed to settle again.) A uniformly deposited bed of resin, free from air bubbles or channels, is essential to a successful elution. The FCV is approximately equal to half the apparent volume of the resin bed.

### 3. Procedure

*Step 1.* To an aliquot of the sample in a 40-ml glass centrifuge tube, add 2 drops each of zirconium, tellurium, and strontium carriers and 1 drop of yttrium carrier. Use phenolphthalein indicator and add conc  $\text{NH}_4\text{OH}$  to precipitate the  $\text{Y}(\text{OH})_3$ . Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 to 1.0 ml  $\text{H}_2\text{O}$ .

*Step 2.* Dissolve the precipitate in a minimum of 3M HCl and transfer to a plastic test tube. Add 2 two drops of conc HF/ml of solution. (If the solution contains a large amount of iron or uranium, add HF to decolorize the solution and then 2 drops/ml in addition.) Let the solution stand for 5 min, centrifuge, discard the supernate, and wash the precipitate with 0.5 ml of the 2M HF-2M  $\text{HNO}_3$  solution.

*Step 3.* Dissolve the fluoride precipitate by adding 1 drop of saturated  $\text{H}_3\text{BO}_3$ , stirring, and then adding 2 ml of conc HCl. Transfer the solution to a 40-ml glass centrifuge tube. Add 2 drops of strontium carrier and then boil the solution briefly. Precipitate the  $\text{Y}(\text{OH})_3$  with  $\text{NH}_4\text{OH}$ , centrifuge, discard the supernate, and wash the precipitate twice with 0.1 to 1.0 ml of  $\text{H}_2\text{O}$ .

*Step 4.* Dissolve the precipitate in 3 ml of 10M HCl. Add 1 drop of conc  $\text{HNO}_3$ . Transfer the solution to a 5-cm by 2-mm AG 1 anion resin column that has been washed with several column volumes of 10M Solution I. Push through under pressure. After adding 1 drop each of zirconium and tellurium carriers, pass the solution through two 10-cm by 8-mm anion columns that have also been treated with 10M Solution I. Wash the centrifuge tube and then all three columns in succession

with two 3-ml portions of 10M Solution I. (The small column contains the plutonium, which can be determined by the PLUTONIUM procedure.)

*Step 5.* Add conc  $\text{NH}_4\text{OH}$  to the combined 10M Solution I fractions to precipitate  $\text{Y}(\text{OH})_3$ . Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 ml of  $\text{H}_2\text{O}$ .

*Step 6.* Dissolve the precipitate in a minimum of 0.1M HCl; pass the solution through a 1-cm by 2-mm AG 50 cation resin column that has been washed with several column volumes of 0.1M HCl. Wash the column with 1 ml of 0.1M HCl, then 2 ml of the 0.006M HF-0.1M HCl solution, and finally 1 ml 0.5M HCl (Note 3).

*Step 7.* Using a transfer pipette and a minimum of  $\text{H}_2\text{O}$ , transfer the cation resin from the 1-cm column to the top of a 12-cm by 2-mm Dowex 50 resin column that has been washed with several column volumes of the ethanol-HCl eluant. After the resin has settled, withdraw the excess  $\text{H}_2\text{O}$  and wash out the column above the resin with a small portion of ethanol-HCl. Elute the activity with the 20% ethanol-HCl solution; use sufficient pressure to give  $\sim 1$  drop/45 s. Collect the desired fraction (Note 4) in a 40-ml centrifuge tube (see Fig. 3).

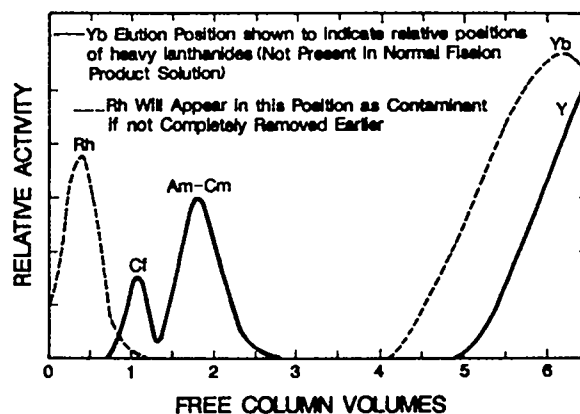


Fig. 3. Twenty percent ethanol-saturated HCl elution from AG 50-X4 cation resin.



*Step 8.* Place the tube that contains the sample in an oil or steam bath and evaporate to  $\sim 0.5$  ml; use a stream of air over the solution if rapid evaporation is desired. Add 1 drop of  $\text{La}(\text{NO}_3)_3$  solution (5 mg lanthanum/ml), and transfer the sample to a 3-ml centrifuge cone. The final solution should consist of 1.5 ml of 2 to 4M HCl.

*Step 9.* Precipitate  $\text{La}(\text{OH})_3$  with gaseous  $\text{NH}_3$  or carbonate-free  $\text{NH}_4\text{OH}$ . Centrifuge, discard supernate, and wash the precipitate with 0.5 ml of  $\text{H}_2\text{O}$ .

*Step 10.* Dissolve the precipitate in a few drops of 0.1M HCl and equilibrate this solution with a small quantity of resin from the top of the "isobutyrate" (Dowex 50) column. (The quantity of resin used for equilibration is small compared to the size of the column.) Transfer the slurry carefully to the column reservoir and allow to settle. Withdraw the supernate and discard.

*Step 11.* Introduce carefully several milliliters of the ammonium alpha-hydroxyisobutyrate solution, so as not to disturb the active band at the top of the column. Apply slight air pressure, if necessary, to produce a flow rate of 1 drop/1 to 3 min. (Pressure may be applied with a 10-ml syringe fitted with a rubber stopper or, more conveniently, from a pressure reduction valve that is attached to a source of compressed air.)

*Step 12.* Collect the eluate dropwise on platinum plates or in 1-ml beakers. Assay all fractions and combine the drops that make up a peak. If additional chemistry is necessary, the isobutyrate may be destroyed by evaporating the solution to dryness and then destroying residual organic matter with  $\text{HNO}_3$  and  $\text{HClO}_4$ .

## Notes

1. TABLE I  
Separation Factors with Ammonium  
Alpha-Hydroxyisobutyrate  
( $C_m = 1.0$ )

<u>Element</u>	<u>Relative Peak Position</u>
Einsteinium	0.13
Californium	0.19
Berkelium	0.37
Curium	1.00
Americium	1.39
Lutetium	0.011
Ytterbium	0.016
Thulium	0.022
Erbium	—
Holmium	0.039
Yttrium	0.069
Dysprosium	0.076
Terbium	0.14
Gadolinium	0.22
Europium	0.34
Samarium	0.7
Promethium	1.1
Neodymium	2.3
Cerium	3.4

2. Resins vary from batch to batch in their ability to achieve various separations, so several samples of resin should be tried before discarding the method.

3. The small cation column was used as an alternative to equilibrating and washing the resin in a test tube and then transferring the resin to the top of the column. This column seemed to be more rapid, provide better decontamination, and require less direct handling of the rather "hot" solution.

4. Essentially no separation of americium and curium was observed in these ethanol-HCl elutions.

(October 1989)

## CURIUM-242

J. W. Barnes

### 1. Introduction

In this procedure, curium is sufficiently decontaminated from other activities so that a pulse analysis of the final product gives the ratio of the unknown quantity of  $^{242}\text{Cm}$  present to the known quantity of added  $^{244}\text{Cm}$  tracer. The procedure has an advantage over one that uses a cation-exchange resin column because an equally effective separation of curium from lanthanide activities can be obtained with less time and effort. This procedure does not separate americium and curium from other tripositive actinides.

The first major step is the adsorption of some of the impurities on an anion-exchange column from conc HCl. The curium is then adsorbed on an anion column as a thiocyanate complex from 5M  $\text{NH}_4\text{SCN}$  at pH 1.5. This step gives effective decontamination from alkali and alkaline earth metal activities. The lanthanides are poorly adsorbed; any that are fixed on the column are eluted by washing with  $\text{NH}_4\text{SCN}$  solutions. The curium is finally removed from the column by elution with a more dilute  $\text{NH}_4\text{SCN}$  solution and is collected on a platinum disk. After drying and ignition at red heat, the sample is pulse-analyzed.

### 2. Reagents

Yttrium carrier: 10 mg yttrium/ml, added as  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$^{244}\text{Cm}$  standard solution: 100 to 1000 counts/min/ml

$\text{HClO}_4$ : conc

HCl: conc; 3M

$\text{HNO}_3$ : conc

$\text{NH}_4\text{OH}$ : 3M

$\text{NH}_4\text{CNS}$ : 5M; 1M in a 3:1 ethanol-to- $\text{H}_2\text{O}$  mixture

Solution A: a mixture that contains 2 to 3 drops of conc  $\text{HNO}_3$  to 15 ml conc HCl

Ethanol: 95%

Hydrion paper: pH range 1.2 to 2.4

Bio-Rad AG 1-X8, 100 to 200 mesh anion-exchange resin

Bio-Rad AG 1-X2, 200 to 400 mesh anion-exchange resin

### 3. Procedure

*Step 1.* To the  $^{244}\text{Cm}$  tracer (Note 1) in a 50-ml erlenmeyer flask, add an aliquot of the sample, 3 drops of yttrium carrier, and 0.5 to 0.7 ml of conc  $\text{HClO}_4$ . Boil to dryness and allow to cool.

*Step 2.* Prepare a 6-mm by 7- to 8-cm column of Bio-Rad anion resin AG 1-X8, 100 to 200 mesh, and pretreat with 3 to 5 ml of Solution A. Dissolve the dry residue from *Step 1* in 1 to 2 ml of Solution A (do not heat, even though all the solid does not dissolve). Pass the resulting solution through the resin column; ignore any precipitate. Rinse the erlenmeyer flask with 1 ml of Solution A and pass the rinsings through the column. Collect the effluent and the wash in a 50-ml erlenmeyer flask, add 0.5 ml of conc  $\text{HClO}_4$ , and fume to dryness. Cool.

*Step 3.* Prepare a 3.5-mm by 7- to 8-cm column of Bio-Rad anion resin AG 1-X2, 200 to 400 mesh, and wash the column with 2 ml of 5M  $\text{NH}_4\text{CNS}$ . Add 2 ml of 5M  $\text{NH}_4\text{CNS}$  to the dry residue in the erlenmeyer flask and swirl to obtain solution. Use Hydrion paper (pH range 1.2 to 2.4), 3M  $\text{NH}_4\text{OH}$ , and 3M HCl to adjust the pH to  $\sim 1.5$ . Add the solution to the anion column and push it through at the rate of 1 drop every 7 to 15 s. Rinse the top of the column with 2 ml of 5M  $\text{NH}_4\text{CNS}$  that has been adjusted to pH 1.5 with 3M HCl, and push this solution through at the same rate. Make up a 1M  $\text{NH}_4\text{CNS}$  solution in a 3:1 ethanol-to- $\text{H}_2\text{O}$  mixture, and adjust the pH to 1.5 with 3M HCl. Wash the column with 3 ml of this solution and collect the washings in a clean 40-ml conical centrifuge tube. (This wash is kept in case curium happens to be eluted at this stage.) Dilute the 1M  $\text{NH}_4\text{CNS}$  solution with an equal volume of  $\text{H}_2\text{O}$ , and add 1 drop of conc HCl for each

4 ml of the resulting solution. Pass 1 ml of the final solution through the column and collect the eluate in a clean 40-ml conical centrifuge tube.

*Step 4.* Transfer this eluate, which contains the curium activity, to a 1.75-in.-diam platinum disk on a brass ring on a hot plate. Turn up the heat gently, and evaporate the liquid on the platinum disk to dryness. When the disk is dry, adjust the hot plate to its maximum heat and volatilize the  $\text{NH}_4\text{CNS}$ . Finally, heat the disk to redness in a Fisher burner flame. Place the disk in the pulse analyzer and count (Note 2).

### Notes

1. The quantity of  $^{244}\text{Cm}$  tracer employed is 3 to 5 times that of the estimated  $^{242}\text{Cm}$  content of the aliquot.

2. If the pulse analysis curve is unsatisfactory because of too much beta-gamma activity, the material on the platinum disk must be further purified. This is accomplished in the following manner. Warm the disk under a heat lamp with several small portions (each  $\sim 0.5$  ml) of Solution A. Pass the resulting solution through a Bio-Rad 1-X8 column as in *Step 2*. Complete *Step 2* and the rest of the procedure. If experience with gamma readings on the final eluate from *Step 3* indicates that further purification is necessary, do not dry the eluate. To the eluate add sufficient solid  $\text{NH}_4\text{CNS}$  to make the solution 4 to 5M in the salt. Pour the solution onto a clean Bio-Rad AG 1-X2 column, as in *Step 3*, and repeat this step.

(October 1989)

# A RAPID SEPARATION OF THE TRANSCURIUM ELEMENTS FROM UNDERGROUND NUCLEAR DEBRIS

W. G. Warren and D. C. Hoffman

## 1. Introduction

This procedure is suitable for the separation of transcurium elements from solutions of high ionic strength that are obtained by dissolving underground nuclear debris.

Following an initial concentration of the heavy elements by precipitating them as hydroxides, the lanthanides and actinides are extracted into di-2-ethylhexyl orthophosphoric acid (HDEHP) from a solution of pH 1.2 to 2.0. They are then recovered as an aqueous phase after esterification of the HDEHP with decanol. A number of the lighter actinides are removed by adsorption onto an anion-exchange resin column from 10M HCl; this step is preceded and followed by hydroxide precipitations. The lanthanides and the remaining actinides are further purified by adsorption onto a cation-exchange resin column and subsequent elution with 6M HCl. After another hydroxide precipitation, the transcurium actinides are separated from the lanthanides, americium, and curium by elution from a cation-exchange resin column with an ethanol-HCl solution.

## 2. Reagents

HCl: conc; 10M; 6M; 0.1M

HNO<sub>3</sub>: conc; 0.05M

Lanthanum carrier: 10 mg lanthanum/ml, added as La(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O in H<sub>2</sub>O

NH<sub>3</sub>: gas

NH<sub>4</sub>OH: 6M

Ethanol-HCl solution (EtOH-HCl): 20% absolute ethanol-80% conc HCl (by volume); saturated with HCl gas at room temperature

0.5M HDEHP: Dilute 645 g of di-2-ethylhexyl orthophosphoric acid to 4 l with *n*-heptane

*n*-Heptane

Decanol

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh; slurry in H<sub>2</sub>O

Cation-exchange resin: Bio-Rad AG 50W-X4, 200 to 400 mesh; slurry in H<sub>2</sub>O

Cation-exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh; slurry in H<sub>2</sub>O

## 3. Procedure

*Step 1.* Pass gaseous NH<sub>3</sub> into a solution of the sample in a 40-ml long-taper Pyrex centrifuge tube until precipitation is complete. Centrifuge and wash the hydroxide precipitate with H<sub>2</sub>O that contains a small amount of NH<sub>4</sub>OH. Centrifuge and discard the washings. Repeat the washing process.

*Step 2.* Dissolve the precipitate in 20 to 25 drops of conc HNO<sub>3</sub>, and adjust the pH to 1.2 to 2.0 by the dropwise addition of 6M NH<sub>4</sub>OH. Dilute to ~10 ml with H<sub>2</sub>O and add the solution to a 60-ml separatory funnel. Add 10 ml of 0.5M HDEHP and shake the mixture gently for ~1 min. Allow the two phases to separate and drain the aqueous (lower) layer into a clean separatory funnel. Add 5 ml of HDEHP to the aqueous phase, shake gently, discard the aqueous phase, and combine the two HDEHP phases. Wash the combined HDEHP phases four times with 15-ml portions of 0.05M HNO<sub>3</sub>; discard the aqueous phase in each case.

*Step 3.* Drain the HDEHP phase into a 125-ml erlenmeyer flask, and add 7.5 ml of conc HCl and 4 ml of decanol. Boil while using a magnetic stirrer on a hot plate for 15 min to convert the HDEHP to the decanol ester. (Add more HCl, if necessary.) Add the mixture to a 60-ml separatory funnel, allow the two phases to separate, and transfer the HCl layer (top) into a clean separatory funnel. To the ester phase, add ~4 ml of 6M HCl. Shake and allow the two layers to separate. Combine the HCl fraction with that previously isolated and discard the ester fraction. Wash the combined HCl fractions with 11.5 ml of heptane, discard the washings, and transfer the HCl fraction to a clean 40-ml long-taper Pyrex centrifuge tube.

*Step 4.* Add 1 drop of lanthanum carrier if necessary, and bubble in  $\text{NH}_3$  gas until precipitation is complete. Centrifuge and discard the supernate. Wash the precipitate with  $\sim 2$  ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the washings.

*Step 5.* Dissolve the hydroxide precipitate in 1 ml of 10M HCl and 1 drop of conc  $\text{HNO}_3$ ; pass the solution through a Bio-Rad AG 1-X8, 100 to 200 mesh, anion-exchange resin bed 2.5 cm long in an 8-cm by 1-cm-o.d column. (The column is prepared by washing with three separate mixtures of 1 ml of 10M HCl that contains 1 drop of conc  $\text{HNO}_3$ .) Collect the eluate in a 40-ml long-taper Pyrex centrifuge tube.

*Step 6.* Dilute the eluate to  $\sim 8$  ml with  $\text{H}_2\text{O}$ . Bubble in  $\text{NH}_3$  gas until precipitation is complete, centrifuge, and discard the supernate. Wash the precipitate with  $\sim 2$  ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the washings.

*Step 7.* Dissolve the precipitate in 1 drop of conc HCl, dilute the solution to 12 ml with  $\text{H}_2\text{O}$ , and pass it through a Bio-Rad AG 50W-X4, 200 to 400 mesh, cation-exchange resin column (same dimensions as the anion column). Wash the centrifuge tube with two 1-ml portions of 0.1M HCl and add the washings to the column. Elute with three 1-ml portions of 6M HCl; catch the eluates in a clean long-taper centrifuge tube.

*Step 8.* Bubble  $\text{NH}_3$  gas into the combined eluates to precipitate hydroxides. Centrifuge and discard the supernate. Wash the precipitate with 1 ml of water, centrifuge, and discard the washings.

*Step 9.* To the precipitate add 1 to 2 drops of EtOH-HCl solution; add the resulting solution to the top of a Bio-Rad AG 50W-X4, minus 400 mesh, cation-exchange resin column, 12- to 14-cm length by 3-mm i.d.; the tip should have a drip rate of  $\sim 120$  drops/ml. Add 1 to 2 drops of EtOH-HCl solution to the centrifuge tube, centrifuge, and add the solution to the top of

the resin column. Repeat the EtOH-HCl wash of the centrifuge tube. Add 3 ml of EtOH-HCl solution to the resin column and apply sufficient pressure (2 to 3 psi) to produce a drop rate of  $\sim 40$  s/drop. Collect dropwise in fractions and alpha-count. The transcurium elements elute first, followed by americium and curium ( $\sim 1.9$  column volumes after the free column volume; see Fig. 3 of the procedure for SEPARATION OF TRACE AMOUNTS OF TRANSPLUTONIUM ELEMENTS FROM FISSION PRODUCTS).

After identification of the americium-curium peak, combine all the previous fractions for the transcurium sample. Evaporate to dryness at  $\sim 120^\circ\text{C}$  in an oil bath with an air jet. Take up in 1 ml of conc HCl and proceed as in *Step 2* of the procedure for ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING.

(October 1989)

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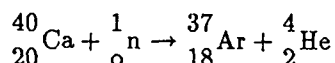
## II. Separation of Products from Irradiated Targets

# THE SEPARATION OF $^{37}\text{Ar}$ FROM IRRADIATED CALCIUM OXIDE

J. W. Barnes, J. Balagna, R. J. Prestwood,  
and B. P. Bayhurst

## 1. Introduction

This procedure describes the separation of  $^{37}\text{Ar}$  from a CaO pellet that has been irradiated with 2.5- to 14.5-MeV neutrons.



In an evacuated system, the CaO pellet is treated with an excess of dilute HCl in the presence of added argon carrier. The resulting solution is distilled to bring about complete mixing of  $^{37}\text{Ar}$  with carrier. The argon is then cryopumped into a thin-windowed (1-mil beryllium) gas sample container that is fabricated from stainless steel and sealed with a bellows valve. The 2.62-keV x-ray from  $^{37}\text{Cl}$ , formed from  $^{37}\text{Ar}$  by electron capture, is counted on a lithium-drifted silicon crystal.

## 2. Reagents

Argon carrier: high-purity gas  
HCl: 4M  
Tantalum turnings

## 3. Procedure

*Step 1.* Add the irradiated CaO pellet (~90 to 100 mg, compressed before irradiation in a hydraulic press at high temperatures and pressures) to the dissolver of the apparatus (Fig. 1). On another vacuum line, fill the two sections of the argon carrier tube with the gas to a pressure of 250 torr and connect the tube to the apparatus as shown in Fig. 1 (Note 1). Add ~2.5 ml of 4M HCl to the HCl reservoir and evacuate the system in the following manner. Start the pumping at room temperature with a mechanical pump; when the pressure has dropped to 0.2 to 0.5 torr, connect the

system to a diffusion pump. When the pressure reaches 20 to 50 mtorr, freeze the HCl solution with liquid nitrogen. Open the bellows valve to the stainless steel sample container (Fig. 2). Continue pumping until the pressure is  $\sim 2 \times 10^{-5}$  torr (1 to 2 h). Close the stopcock to the pumping system and follow the pressure rise with the differential capacitance manometer. If the pressure rise within 5 min is <2 mtorr, proceed with *Step 2*. If the rise is >2 mtorr, continue the evacuation process until the pressure rise is satisfactory. Open the stopcock to the pumping system.

*Step 2.* Close the dissolver stopcock, open the stopcock to the first half of the argon carrier, melt the HCl solution with an electric heat gun, and pour the solution onto the CaO pellet. Stir for 10 min with a magnetic stirrer to obtain a clear solution (Note 2).

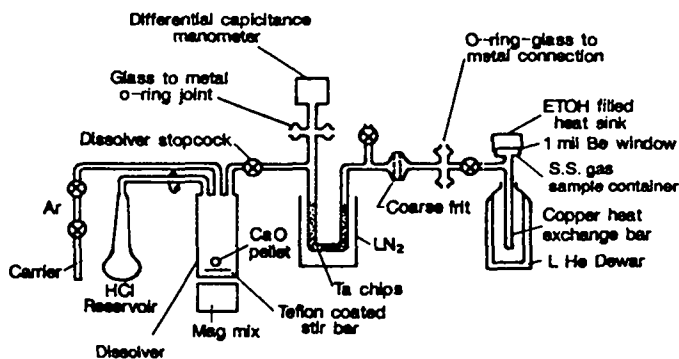


Fig. 1. Dissolver apparatus.

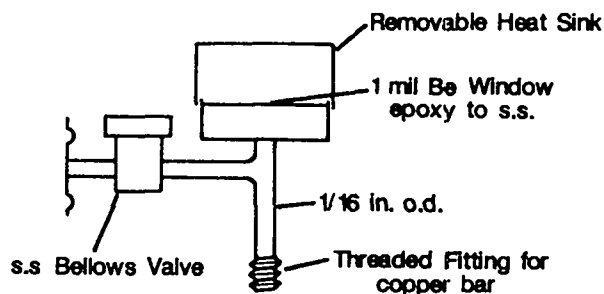


Fig. 2. Stainless steel sample container.

*Step 3.* Chill the HCl reservoir by means of liquid nitrogen; with an electric heat gun, apply heat intermittently to the dissolver (while stirring) until the solution distills into the reservoir and only solid  $\text{CaCl}_2$  remains. (The argon is not condensed by the liquid nitrogen, but the distillation permits complete mixing between carrier gas and the  $^{37}\text{Ar}$  released from the CaO pellet.) Place a Dewar filled with liquid nitrogen around a U-tube that is filled with the tantalum turnings (glass beads would probably work as well). Melt the solid plug of HCl solution (with a heat gun) and refreeze in the bottom of the reservoir to eliminate plugging at the upper portion by frozen HCl solution.

*Step 4.* Close the stopcock to the pumping system and cool the copper heat-exchange bar with liquid nitrogen. Slowly open the dissolver stopcock and record the pressure indicated by the differential capacitance manometer (Note 3). Replace the liquid nitrogen around the copper bar with liquid helium and record the pressure decrease at 2-min intervals for 8 min; then record at 1-min intervals until the pressure drops to zero or remains constant (10 to 12 min). Shut the dissolver stopcock and the bellows valve and remove the liquid helium container. Be certain that the stopcock to the pumping system remains closed.

*Step 5.* Open the stopcock to the second half of the argon carrier, remove the liquid nitrogen from around the HCl reservoir, and melt the HCl ice (with a heat gun). Pour the solution onto the  $\text{CaCl}_2$  in the dissolver and stir for  $\sim 10$  min.

*Step 6.* Repeat *Step 3*.

*Step 7.* Cool the copper heat-exchange bar with liquid nitrogen and then replace the nitrogen with liquid helium. Slowly open the dissolver stopcock and record the pressure shown on the differential capacitance manometer. After the copper bar has been cooled with liquid helium for 1.5 to 2 min, open the bellows valve. Record the pressure decrease at 2-min intervals for 8 min and then at 1-min intervals until the pressure

drops to zero or remains constant. Close the bellows valve, the dissolver stopcock, and the top argon-carrier stopcock. Observe the pressure in the manometer for another 5 min to be certain that the bellows valve is sealed tightly. Open the stopcock to the pumping system and check the manometer for possible zero drift. Remove the liquid nitrogen container from the U-tube that contains the tantalum turnings, warm the turnings with an electric heat gun, and pump for  $\sim 10$  min. Disconnect the sample container and count the 2.62-keV x-ray from  $^{37}\text{Cl}$  on a lithium-drifted silicon crystal.

### Notes

1. The quantity of carrier gas should be held constant from run to run to eliminate errors caused by self-absorption of the gas.
2. The  $^{37}\text{Ar}$  will not be released quantitatively from the CaO pellet if it is not completely dissolved in HCl.
3. The manometer reading will verify whether approximately half of the argon carrier gas has been introduced. The P-V calibrations of the apparatus should have already been done.

(October 1989)



# SEPARATION OF THALLIUM FROM LEAD AND BISMUTH TARGETS

R. J. Prestwood

## 1. Introduction

These procedures are used for examining thallium isotopes produced by the 800-MeV proton bombardment of lead and bismuth targets. The targets are dissolved in  $\text{HNO}_3$  and thallium is precipitated as TII. The target metals are left in solution as iodocomplexes,  $\text{PbI}_4^{2-}$  and  $\text{BiI}_4^-$ . In each case, the thallium is purified by  $\text{La}(\text{OH})_3$  scavenges and then precipitated as  $\text{Tl}_2\text{CrO}_4$ . Chemical yields are ~50%.

## 2. Reagents

Thallium carrier: 10 mg thallium(I)/ml, made by dissolving the pure metal in 6M  $\text{HNO}_3$  and bringing to volume so that final solution is 1.5M in the acid

Lanthanum carrier: 10 mg lanthanum/ml, added as aqueous  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

$\text{HNO}_3$ : conc; 6M; 2M

$\text{NH}_4\text{OH}$ : conc

NaI: solid

NaI reagent: 3M in NaI and 2M in  $\text{HNO}_3$

$\text{Na}_2\text{CrO}_4$ : 10% aqueous solution

## 3. Procedure

### A. Separation of Thallium from a Lead Target

*Step 1.* To a 125-ml erlenmeyer flask, add 2.0 ml of thallium carrier and up to 500 mg of lead target foil. Dissolve the lead in a minimum of 6M  $\text{HNO}_3$ . Evaporate the solution to ~2ml, and then use 2M  $\text{HNO}_3$  to transfer the solution to a 40-ml glass centrifuge tube. Make up to 20 ml with the 2M acid. Add 10 g of NaI and stir to precipitate TII. Centrifuge and discard the supernate. Wash the precipitate three times with 20-ml portions of NaI reagent and discard the washes.

*Step 2.* Dissolve the TII in a minimum of 6M  $\text{HNO}_3$  (the thallium remains in the +1 state) and heat over a burner to volatilize any  $\text{I}_2$  present. Dilute the solution to ~20ml with  $\text{H}_2\text{O}$  and reprecipitate TII, this time with NaI reagent. Centrifuge and discard the supernate. Redissolve the TII in a minimum of 6M  $\text{HNO}_3$  and dilute to 20 ml with  $\text{H}_2\text{O}$ . Add 4 drops of lanthanum carrier and precipitate  $\text{La}(\text{OH})_3$  with an excess of conc  $\text{NH}_4\text{OH}$ . Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate.

*Step 3.* Add 1 g of NaI to reprecipitate TII. Centrifuge and discard the supernate. Dissolve the TII in a minimum of 6M  $\text{HNO}_3$  and repeat the  $\text{La}(\text{OH})_3$  scavenge.

*Step 4.* To the supernate add 2 ml of 10%  $\text{Na}_2\text{CrO}_4$  solution; place on a steam bath for a few minutes to permit the  $\text{Tl}_2\text{CrO}_4$  to coagulate. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the wash. Slurry the  $\text{Tl}_2\text{CrO}_4$  in 10 ml of  $\text{H}_2\text{O}$ , filter through a weighed filter circle, dry, weigh, and mount for counting. Without the heating and washing, the small  $\text{Tl}_2\text{CrO}_4$  crystals would pass through the filter paper; the  $\text{Tl}_2\text{CrO}_4$  may be filtered satisfactorily through a Millipore filter.

### B. Separation of Thallium from a Bismuth Target

*Step 1.* To a 125-ml erlenmeyer flask, add 2.0 ml of thallium carrier and up to 3 g of bismuth metal target. Place the flask on a hot plate, add 5 ml of 6M  $\text{HNO}_3$ , and then add 5 ml of the conc acid in small portions to continue the dissolution process. Evaporate the solution to 2 to 3 ml and use 20 ml of 2M  $\text{HNO}_3$  to transfer the solution to a 40-ml glass centrifuge tube. Add 10 g of NaI to precipitate TII. (Some  $\text{I}_2$  is also formed.) Centrifuge and discard the supernate.

Wash the precipitate three times with 20-ml portions of NaI reagent and discard the washes. (Washing removes adhering  $\text{BiI}_3$  and  $\text{I}_2$  from the TII.)

*Step 2.* Repeat *Steps 2* through *4* of Procedure A.

(October 1989)

# THE CARRIER-FREE ISOLATION OF ASTATINE FROM THICK BISMUTH TARGETS

J. L. Clark

## 1. Introduction

A radiochemical study of the  $^{209}\text{Bi}(\pi^+, \pi^- \text{xn})^{209-x}\text{At}$  double-charge exchange reactions at LAMPF (The Los Alamos Meson Physics Facility) required the development of a rapid and highly selective chemical method for separating tracer-level quantities of astatine from thick bismuth targets. This procedure is based in part on the techniques of Bochvarova and coworkers.

The bismuth metal target is dissolved in a minimum of conc  $\text{HNO}_3$ , excess nitrate is removed with  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , and the astatine is reduced to the  $-1$  oxidation state by  $\text{SnCl}_2$  in  $8M$   $\text{HCl}$ . The astatine (with traces of polonium and iodine) is then adsorbed on a coarse-grain tellurium column under an  $\text{N}_2$  atmosphere. Following acid and  $\text{H}_2\text{O}$  rinses of the column to remove unwanted radioactive entities, the astatine is eluted with  $\text{NaOH}$ . This procedure provides a final astatine solution of high purity and small volume. A small volume is particularly desirable because it facilitates the preparation of a thin source that is suitable for alpha counting. Because all the known isotopes of astatine decay at least in part by alpha emission, such a source can be used for the rapid and efficient assay of tracer-level astatine. The time required for the chemical separation is  $\sim 20$  to  $40$  min and typical chemical yields range from  $25$  to  $50\%$ .

## 2. Reagents

$\text{HNO}_3$ : conc  
 $\text{HCl}$ : conc;  $8M$ ;  $1.5M$   
 $\text{NaOH}$ :  $2M$   
 $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution:  $0.1$  g of compound/ $\text{ml}$   $\text{H}_2\text{O}$   
 $\text{SnCl}_2$  solution:  $1M$  compound in  $8M$   $\text{HCl}$   
Silver foil:  $1$  mil; precleaned with  $\text{CCl}_4$  and dilute  $\text{HNO}_3$   
Tellurium powder:  $\sim 30$  mesh; purity  $99.999\%$

## 3. Procedure

### A. Column Preparation

In distilled  $\text{H}_2\text{O}$ , sediment the tellurium to be used for the column packing (Note). Decant the  $\text{H}_2\text{O}$  and wash the tellurium with hot  $1.5M$   $\text{HCl}$  and  $\text{H}_2\text{O}$ . Sediment the tellurium again and place in a glass column; be sure that the element remains under  $\text{H}_2\text{O}$ . A small wad of glass wool serves as a suitable support for the tellurium. Be certain that air bubbles are removed during the loading process. Pass a few milliliters of the  $\text{SnCl}_2$  solution through the column to remove smaller grains of tellurium, which may have been transferred to the column during loading. Store the loaded column under distilled  $\text{H}_2\text{O}$  until it is needed. Typically, columns with active regions of  $\sim 4$ -mm i.d. and  $40$ -mm length are prepared.

### B. Target Dissolution

Because of the reported volatility of astatine, the dissolution of the bismuth metal target should be carried out as gently as possible. Place the irradiated target into a small beaker (standard laboratory glassware is suitable) and dissolve it in a minimum of conc  $\text{HNO}_3$ . Remove excess  $\text{NO}_3^-$  ion from solution by the dropwise addition of the  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . Reaction occurs with vigorous bubbling and the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  should be added carefully. When reaction is complete, add conc  $\text{HCl}$  to the solution until the concentration of that acid is  $\sim 8M$ . Add a few milliliters of  $\text{SnCl}_2$  solution to reduce astatine to the  $-1$  oxidation state.

### C. Column Loading and Elution

Pass the solution obtained from the bismuth target through the tellurium column under  $3$  to  $15$  psi of  $\text{N}_2$  pressure. (The adsorption of astatine onto the tellurium appears to be independent of the flow rate for loading—up to several milliliters per minute.) Wash the column with  $8M$   $\text{HCl}$  and then with  $\text{H}_2\text{O}$  to remove unwanted activities. Activities commonly encountered in

medium-energy proton and pion irradiations of bismuth are due to polonium, bismuth, and lead isotopes. Characteristic purification factors for the tellurium column separation of astatine from these activities are: Po  $> 2 \times 10^3$ ; Bi  $> 10^5$ ; and Pb  $> 10^6$ . Finally, elute the astatine with 1 to 2 ml of 2M NaOH. Nearly all the adsorbed astatine can be eluted with such small volumes of base.

#### D. Alpha Source Preparation

Neutralize the eluate from the tellurium column with a few drops of conc HCl. Place the solution into a glass chimney under which a clean 1-mil silver foil has been secured. Stir to deposit the astatine on the foil. Plating times of 10 to 20 min can give nearly quantitative yields of the astatine from the solution. Air dry. The sources prepared in this manner are thin enough to permit the recording of alpha spectra that have characteristic resolution of  $\sim 20$ - to 25-keV FWHM.

#### 4. Chemical Yield Determination

Because there are no stable isotopes of astatine, the determination of separation efficiencies and chemical yields cannot be done through standard carrier techniques. Instead, one must resort to certain "spike" procedures in which a known quantity of a particular astatine isotope is added to the target solution. A good candidate for such "spikes" is 7.2-h  $^{211}\text{At}$  ( $E_\alpha = 5.87$  and 7.45 MeV), which can be made in high yield by the  $^{209}\text{Bi}(\alpha, 2n)^{211}\text{At}$  reaction. Nanocurie strength  $^{211}\text{At}$  "spikes" are sufficient for yield determinations in experiments in which astatine formation cross-sections are in the range of microbarns. Details of the astatine "spike" procedure can be found in work by J. L. Clark.

#### Note

Sedimentation of the tellurium allows the selection of a more or less uniform grain size, thus facilitating the packing of the column and optimizing its flow characteristics.

#### References

1. M. Bochvarova *et al.*, Radiokhimiya 14, 858 (1972).
2. J. L. Clark, Ph.D. thesis, Carnegie-Mellon University (1980).

(October 1989)

## RECOVERY OF RADIOPOTASSIUM FROM A VANADIUM TARGET

V. R. Casella, P. M. Grant,  
and H. A. O'Brien, Jr.

### 1. Introduction

This procedure describes the recovery of  $^{43}\text{K}$  that is produced by the bombardment of vanadium targets with 800-MeV protons. The targets were 0.25 mm thick and had a purity of  $\sim 99.9\%$ . Typical proton bombardments were for a duration of  $\sim 3 \mu\text{A}\cdot\text{h}$  integrated intensity.

An irradiated foil is dissolved in 8M  $\text{HNO}_3$ , the solution is diluted to 4M in acid, and scandium and potassium carriers are added. The solution is then passed through a hydrated antimony pentoxide (HAP)-exchange column; potassium and other alkali metals, as well as alkaline earth metals, are adsorbed on the column. The column is washed with 4M  $\text{HNO}_3$ , and then with 1M  $\text{HCl}$ ; the latter removes  $\text{NO}_3^-$  ion, a biological poison. Potassium is eluted from the column with 12M  $\text{HCl}$ . The conc acid also carries some antimony from the HAP, and it is removed by adsorption on an anion-exchange resin from a solution 8M in  $\text{HCl}$ . The final decontamination step consists of passing the effluent, adjusted to pH 10, through a chelating-ion-exchange resin and washing the resin with  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer of pH 9.4. The chelating resin has little affinity for alkali metal cations. The overall chemical yield is  $91 \pm 3\%$ .

Potassium-43 decays by beta emission with a half-life of 22.6 h, and the isotope can be readily imaged with conventional scintillation cameras or rectilinear scanners. This technique is used in diagnostic nuclear medicine for body electrolyte and cardiovascular studies.

### 2. Reagents

Potassium carrier:  $\text{KCl}$  in  $\text{H}_2\text{O}$ ; of known concentration  
Scandium carrier:  $\text{ScCl}_3$  in very dilute  $\text{HCl}$ ; of known concentration  
 $\text{HCl}$ : 12M; 8M; 1M  
 $\text{HNO}_3$ : 8M; 4M  
 $\text{NH}_4\text{OH}$ : 6M  
 $\text{H}_2\text{O}_2$ : 30% aqueous solution  
 $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer: 0.1M in both  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ ; pH 9.4  
Carbazole reagent: 2 to 3 mg of carbazole ( $\text{C}_6\text{H}_5\text{-NH-C}_6\text{H}_5$ , diphenylimide)/ml of conc  $\text{H}_2\text{SO}_4$   
Hydrated antimony pentoxide (HAP)-exchanger: source: Carlo Erba, Industrial Chemicals Division, Milan, Italy; washed with distilled  $\text{H}_2\text{O}$  before use to remove fine particulates  
Bio-Rad AG 1-X8, 50 to 100 mesh, anion-exchange resin  
Bio-Rad Chelex-100, 100 to 200 mesh, cation-exchange resin

### 3. Procedure

*Step 1.* Dissolve the vanadium target in 8M  $\text{HNO}_3$  and dilute with  $\text{H}_2\text{O}$  to make the solution 4M in acid. Add 150  $\mu\text{g}$  each of potassium and scandium carriers.

*Step 2.* Pass the solution through a column (0.8-cm i.d. and 2-cm length) of hydrated antimony pentoxide (HAP)-exchanger at a rate of  $\sim 0.2 \text{ ml/min}$ . Discard the effluent. Wash the column with several column volumes of 4M  $\text{HNO}_3$  and discard the washes. Wash the column with 1M  $\text{HCl}$  until the effluent gives a negative test for  $\text{NO}_3^-$  ion with carbazole reagent. (If  $\text{NO}_3^-$  is present, a deep green color will form.) Discard the effluent.

*Step 3.* Elute potassium with several column volumes of 12M  $\text{HCl}$ . Add 2 ml of 30%  $\text{H}_2\text{O}_2$  to the effluent to enhance the Sb(V) oxidation state and evaporate to near dryness. Take up the residue in 15 ml of 8M  $\text{HCl}$ ; pass the solution at a flow rate of  $\sim 0.3 \text{ ml/min}$  through a column (0.8-cm i.d. and

10-cm length) of Bio-Rad AG 1-X8 anion-exchange resin to remove any antimony present. Collect the effluent.

*Step 4.* Adjust the pH of the effluent to 10 by evaporation and addition of  $\text{NH}_4\text{OH}$ . Pass the solution through a column (0.8-cm i.d. and 10-cm length) of Bio-Rad Chelex-100 cation-exchange resin. Collect the effluent. Wash the column with several column volumes of  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer (pH 9.4) to effect quantitative elution of potassium. Combine the effluents.

(October 1989)

## RECOVERY OF RADIOHAFNIUM FROM A TANTALUM TARGET

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### 1. Introduction

This procedure was designed to isolate  $^{172}\text{Hf}$  produced by the bombardment of tantalum foils with 800-MeV protons. The tantalum targets had a purity of >99.9%, weighed  $\sim 2.5$  g, and had a thickness of 0.25 mm. The length of proton irradiation was 12  $\mu\text{A}\cdot\text{h}$  of integrated intensity. The separation process consists of dissolution of the target in a mixture of conc HF and  $\text{HNO}_3$ ; coprecipitation of hafnium (presumably as anionic fluorocomplexes) on  $\text{CaF}_2$ ; extraction of hafnium from  $\text{HClO}_4$  solution into thenoyltrifluoroacetone (TTA); and back-extraction into conc HCl. The overall chemical yield is  $93 \pm 5\%$ .

The  $^{172}\text{Hf}$  decays (with a half-life of 1.87 y) to  $^{172}\text{Lu}$  and the latter isotope transforms (with a half-life of 6.70 d) to stable  $^{172}\text{Yb}$ . The  $^{172}\text{Hf}$ - $^{172}\text{Lu}$  combination offers a possible medical generator system, in which the  $^{172}\text{Lu}$  has potential applications in compound labeling and biodistribution studies in animal models. The availability of millicurie quantities of  $^{172}\text{Hf}$  should serve to stimulate preclinical investigations of the lanthanide compounds in nuclear medicine.

### 2. Reagents

Hafnium carrier: 500 to 600  $\mu\text{g}$  of metal in  
hafnium solution

HF: conc

$\text{HNO}_3$ : conc

$\text{HClO}_4$ : conc

HCl: conc

$\text{CaCl}_2$ : solution of known concentration

$^{47}\text{Ca}^{2+}$  tracer (optional)

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ : solid

Thenoyltrifluoroacetone (TTA) reagent: 0.5M  
solution in benzene (stored in the dark)

Benzene

### 3. Procedure

*Step 1.* To the tantalum foil in a Teflon beaker, add 500 to 600  $\mu\text{g}$  of hafnium carrier and 2 to 3 ml of conc HF/g of the target. Then add conc  $\text{HNO}_3$  (dropwise initially) until dissolution is complete. The dissolution process usually requires  $\sim 3$  h and a volume of  $\text{HNO}_3$  that is slightly under half that of the HF.

*Step 2.* Dropwise, add 45 mg of  $\text{Ca}^{2+}$  as  $\text{CaCl}_2$  solution (Note 1) and an additional ml of conc HF. Permit the fine white  $\text{CaF}_2$  precipitate that forms to equilibrate with the rest of the solution by stirring and mild heating for 15 min on a steam bath. After the mixture cools, centrifuge and decant the supernate. Add 10 mg of  $\text{Ca}^{2+}$  to the supernate and repeat the coprecipitation procedure. Combine the  $\text{CaF}_2$  precipitates (Note 2).

*Step 3.* Dissolve the  $\text{CaF}_2$  precipitate in conc  $\text{HClO}_4$  ( $\sim 0.25$  ml of acid/mg of  $\text{Ca}^{2+}$  precipitant), and dilute the solution to 2M in  $\text{HClO}_4$ . Add  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  to complex fluoride ion (Note 3). Transfer the solution to a separatory funnel with 25 to 30 ml of TTA reagent. Equilibrate the mixture on a Burrell wrist-action shaker for 1 h. If the radiohafnium did not extract quantitatively into the organic phase, add more  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and repeat the extraction.

*Step 4.* Dilute the organic phase from the TTA extraction tenfold with benzene. Extract twice with 25-ml volumes of conc HCl; combine the aqueous phases, which contain the radiohafnium.

### Notes

1. Calcium-47 tracer was included in some experiments to monitor the chemistry of the  $\text{Ca}^{2+}$  added in the coprecipitation procedure and to ensure its complete removal from the final product.

2. Coprecipitation of hafnium with  $\text{CaF}_2$  is most successful when carried out at high HF

concentrations and small volumes. When less than quantitative coprecipitation of radiohafnium occurs, it generally is associated with the presence of appreciable residual  $\text{Ca}^{2+}$  in solution, as is indicated by the added  $^{47}\text{Ca}^{2+}$ . Volume reduction and addition of conc HF usually are successful in causing more  $\text{CaF}_2$  to precipitate; sometimes only the addition of more  $\text{Ca}^{2+}$  will effect the complete removal of  $^{172}\text{Hf}$ . The latter procedure is to be avoided whenever possible to minimize the volumes required in the TTA extraction step.

3. Fluoride ion interferes with the TTA extraction process. The quantity of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  added depends upon the amount of fluoride in the  $\text{CaF}_2$  precipitate; 2.5 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  is typical, although up to 15 g did not adversely affect the extraction.

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# SEPARATION OF STRONTIUM, YTTRIUM, AND ZIRCONIUM FROM A MOLYBDENUM TARGET

Spallation reactions have been induced in molybdenum targets by using 200- to 800-MeV protons to produce microcurie amounts of various radioelements. The targets were in the form of 99.9%-pure foils (usually 0.51 mm thick) and were irradiated for 1 to 2  $\mu\text{A}\cdot\text{h}$  of integrated intensity. Following irradiation, a target is permitted to stand for several days to permit the activities to decay to reasonable levels. The target is then radiographed and the hot spot is cut away from surrounding inactive metal. The radioactive section is cleaned of surface contaminants by immersion in chromic acid cleaning solution for 1 to 2 min, rinsed with distilled water, dried, and weighed. Typical molybdenum weights ranged from 1 to 10 g.

## (A) SEPARATION OF STRONTIUM

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### 1. Introduction

Strontium is quantitatively separated from the irradiated molybdenum by a six-step procedure using precipitation, solvent extraction, and ion-exchange techniques. The molybdenum metal is first dissolved in 30%  $\text{H}_2\text{O}_2$  to give a solution of molybdic acid,  $\text{H}_2\text{MoO}_4$ . Following removal of excess  $\text{H}_2\text{O}_2$ , the acid is converted to its ammonium salt and then  $\text{Pb}(\text{MoO}_4)$  is precipitated. Extraction of the  $\text{Pb}(\text{MoO}_4)$  with a 50% solution of di-2-ethylhexyl orthophosphoric acid (HDEHP) in toluene (from a solution 0.12M in HCl) effectively separates strontium from yttrium. The former is concentrated in the aqueous phase, whereas the yttrium and some other contaminants are extracted into the organic phase. Macroscopic amounts of lead and molybdenum are removed from the aqueous solution by precipitation as sulfides. Last traces of contaminants are removed

by adsorption on a  $\text{ZrO}_2$  ion exchanger at pH 6.0; strontium is not retained by the exchanger. The yield of strontium, determined by radioactivity levels, is  $94 \pm 2\%$ ; separation is effected from molybdenum, technetium, niobium, zirconium, yttrium, rubidium, selenium, arsenic, zinc, and cobalt.

The long-lived  $^{82}\text{Sr}$  and  $^{85}\text{Sr}$  isotopes are obtained from the irradiation process. Because  $^{82}\text{Sr}$  has a reasonably long half-life (25.55 d) and decays to an alkali metal of very short half-life ( $^{82}\text{Rb}$ ; 1.273 min), this system is of potential interest for cardiovascular investigations in nuclear medicine.

If strontium activity is of primary interest and the irradiation of the molybdenum target has not been sufficiently intense to produce milligram quantities of the element, strontium carrier is added at an appropriate place in the procedure.

### 2. Reagents

Strontium carrier: 10 mg  $\text{Sr}^{2+}/\text{ml}$ , added as  $\text{Sr}(\text{NO}_3)_2$  solution  
 $\text{HNO}_3$ : 7 to 8M  
HCl: 0.12M  
 $\text{H}_2\text{S}$ : gas  
 $\text{H}_2\text{O}_2$ : 30% aqueous solution (unstabilized)  
 $\text{NH}_4\text{OH}$ : conc; 3.7M  
 $\text{NH}_4\text{Cl}$ : 0.1M aqueous solution  
 $\text{Pb}(\text{NO}_3)_2$ : 5 mg of  $\text{Pb}^{2+}/\text{ml}$  of aqueous solution  
Chromic acid cleaning solution: 35 ml of saturated aqueous  $\text{Na}_2\text{Cr}_2\text{O}_7$  in 1 l of conc  $\text{H}_2\text{SO}_4$   
HDEHP solution: 50% solution by volume of di-2-ethylhexyl orthophosphoric acid in toluene  
Hydrous  $\text{ZrO}_2$  ion exchanger: HZO-1 crystals; source: Bio-Rad Laboratories

### 3. Procedure

*Step 1.* To the molybdenum sample in a 400-ml beaker, add sufficient 30% H<sub>2</sub>O<sub>2</sub> to dissolve the metal with mild heating. (Typically, 10 to 20 ml of the peroxide is required per gram of molybdenum.) Heat the yellow molybdic acid solution gently to drive off excess H<sub>2</sub>O<sub>2</sub>.

*Step 2.* By a careful combination of evaporation with gentle heating and the addition of conc NH<sub>4</sub>OH, make the solution ~1M in molybdenum and 3 to 4M in base. (Care must be taken during this operation because of the molybdenum's tendency to escape from solution by a mass transport mechanism.) During the process, the solution's original bright yellow color becomes almost colorless, and a small amount of yellow-brown precipitate forms. The precipitate, which is thought to be molybdenum(V) or molybdenum(VI) hydroxide (hydrous molybdenum oxides) or a mixture of the two, carries with it a large amount of zirconium and yttrium activities. Place the mixture of precipitate and solution into a large centrifuge tube, centrifuge, transfer the supernate into a clean centrifuge tube, and set aside the precipitate.

*Step 3.* To the supernate, add 1 ml of Pb(NO<sub>3</sub>)<sub>2</sub> solution (5 mg of Pb<sup>2+</sup>). A white precipitate of PbMoO<sub>4</sub> forms immediately. Stir the suspension, heat on a steam bath for 1 to 2 h, centrifuge, decant the supernate, and set aside. Wash the PbMoO<sub>4</sub> precipitate several times with a 0.1M NH<sub>4</sub>Cl solution that has been made slightly alkaline by the addition of NH<sub>4</sub>OH. After each wash, centrifuge and set aside the supernate.

*Step 4.* Add 10 ml of 0.12M HCl and 10 ml of HDEHP solution to the precipitate. Stopper the centrifuge tube and equilibrate the mixture on a Burrell wrist-action shaker for 1 to 2 h. (The PbMoO<sub>4</sub> should be dissolved completely after this time.) Transfer to a 60-ml separatory funnel and draw off the aqueous (lower) layer into a 250-ml beaker. Set aside the organic (upper) layer.

*Step 5.* Make the aqueous phase alkaline with 0.5 ml of 3.7M NH<sub>4</sub>OH. A white precipitate, probably Pb(OH)<sub>2</sub>, forms. Bubble H<sub>2</sub>S through the suspension for ~30 min. The white precipitate is converted to brownish-black PbS. Acidify the mixture with 0.5 ml of 7 to 8M HNO<sub>3</sub>, heat on a steam bath for 10 to 15 min, cool to room temperature, and filter into a 250-ml filter flask. Discard the precipitate, which is a mixture of PbS and MoS<sub>3</sub>.

*Step 6.* Heat the filtrate to drive off any excess H<sub>2</sub>S and adjust the pH to ~6.0 by the dropwise addition of conc NH<sub>4</sub>OH. If necessary, add a few milligrams of strontium carrier in the form of Sr(NO<sub>3</sub>)<sub>2</sub> solution. (See Introduction; milligram quantities of strontium are necessary to maintain a quantitative recovery of the element.) Pass the solution through a column (0.8-cm diam, 4-cm length) of untreated 100 to 200 mesh hydrous ZrO<sub>2</sub>-exchange crystals (HZO-1) at a rate of ~0.1 ml/min. Collect the strontium-containing effluent.

## (B) SEPARATION OF YTTRIUM

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### 1. Introduction

In the separation of strontium from the molybdenum target, practically all the yttrium is found in the hydrous molybdenum oxides (*Step 2* of Procedure A) and the HDEHP organic extractant (*Step 4*). Only niobium, zirconium, molybdenum, and a small amount of strontium contaminate the yttrium.

To separate the yttrium, the hydrous molybdenum oxides are dissolved in 0.12M HCl and extracted with HDEHP solution. The organic phase is subsequently combined with that from the prior molybdenum-strontium HDEHP extraction (Procedure A). The combined organic phases are back-extracted with 8M HCl, and the aqueous

phase from this extraction is converted to 12M in HCl and is passed through an anion-exchange resin. The yttrium remains in solution and is found in the column effluent, thus completing the separation from molybdenum. The overall chemical yield of yttrium is  $96 \pm 4\%$ .

Yttrium-88 (half-life, 107 d) and yttrium-87 (half-life, 80.3 h) are the main long-lived isotopes of the element that are produced in the molybdenum target by spallation. Yttrium-88 decays to stable  $^{88}\text{Sr}$  with prominent gamma emissions of 898.04 keV (93.4%) and 1836.13 keV (99.4%). The latter photon will interact with  $^9\text{Be}$  to produce monoenergetic neutrons of  $\sim 150$ -keV kinetic energy. The properties of  $^{88}\text{Y}$  make it attractive for use with  $^9\text{Be}$  as a photoneutron source in nuclear safeguards and other areas of research.

## 2. Reagents

HCl: 12M; 8M; 0.12M

HDEHP solution: 50% solution by volume of di-2-ethylhexyl orthophosphoric acid in toluene.

Anion-exchange resin: Bio-Rad AG 1-X10, 100 to 200 mesh; preconditioned with conc HCl; column parameters: 0.8-cm i.d., 9-cm length, and 0.1-ml/min flow rate.

## 3. Procedure

*Step 1.* Dissolve the hydrous molybdenum oxides from *Step 2* of Procedure A in 10 ml of 0.12M HCl. Add 10 ml of HDEHP solution and equilibrate the mixture on a Burrell shaker for 50 min. Combine the organic phase (upper layer) with that from *Step 4* of Procedure A. (If radiozirconium is to be isolated later, repeat the HDEHP extraction and add the organic layer to the other two layers.)

*Step 2.* Back-extract the combined organic phase twice with equal volumes of 8M HCl on the Burrell shaker, each time for 50 min. Combine the aqueous phases and set aside the organic phase for the separation of zirconium.

*Step 3.* Evaporate the aqueous solution to near dryness, and then dissolve the mixture in 10 ml of 12M HCl. Pass the solution through the Bio-Rad AG 1-X10 anion-exchange resin and collect the effluent that contains the yttrium.

## (C) SEPARATION OF ZIRCONIUM

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### 1. Introduction

If the HDEHP extraction of the yttrium procedure (*Step 1* of Procedure B) is performed twice, 99% of the zirconium is taken into the organic phase and remains there after back-extraction of the yttrium with 8M HCl. Subsequent treatment of the organic phase with 30%  $\text{H}_2\text{O}_2$  extracts molybdenum into the aqueous phase but has no effect on the zirconium. Extraction of the organic phase with 3.5M HF then removes the zirconium, as well as any niobium that is present. The latter is separated from the zirconium by extraction into diisobutylcarbinol after the aqueous phase has been made 5.8M in both HF and  $\text{H}_2\text{SO}_4$ . The overall yield of zirconium is  $96 \pm 6\%$ .

Zirconium-88 (half-life, 83.4 d) is the precursor of  $^{88}\text{Y}$ . There would be advantages to incorporating the parent isotope into an  $^{88}\text{Y}$ -Be photoneutron source as well. A combined  $^{88}\text{Y}$ - $^{88}\text{Zr}$  active component could ease hot-cell processing, eliminate the long storage time needed to attain radioactive equilibrium, and increase the useful life time of the photoneutron source.

### 2. Reagents

HF: conc; 3.5M

$\text{H}_2\text{SO}_4$ : conc

$\text{H}_2\text{O}_2$ : 30% aqueous solution (unstabilized)

Diisobutylcarbinol (DIBC)

### 3. Procedure

*Step 1.* Back-extract molybdenum from the HDEHP phase of the yttrium procedure (*Step 2* of Procedure B) with an equal volume of 30%  $\text{H}_2\text{O}_2$ . Discard the aqueous (lower) layer.

*Step 2.* Back-extract the HDEHP layer with an equal volume of 3.5M HF to remove zirconium. Discard the organic layer.

*Step 3.* Make the aqueous phase 5.8M in both HF and  $\text{H}_2\text{SO}_4$  and extract twice with equal volumes of DIBC; discard the organic (upper) phase after each extraction. Centrifugation facilitates phase separation in this step. The final radiozirconium solution is the aqueous phase of this extraction.

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# SEPARATION OF IRON AND SCANDIUM FROM A NICKEL TARGET

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## 1. Introduction

The metal target, which has been bombarded with 200- to 800-MeV protons, is dissolved in aqua regia. Iron(III) and scandium then are separated from the nickel by precipitation of the hydroxides with conc aqueous  $\text{NH}_3$ , and the nickel is converted to the  $\text{Ni}(\text{NH}_3)_6^{2+}$  ion. The iron(III) is extracted into isopropyl ether from a solution 7.9M in HCl. It is then back-extracted into  $\text{H}_2\text{O}$  and placed on an anion-exchange resin column from conc HCl medium. After removal of adsorbed cobalt from the column, the iron(III) is eluted by 0.1M HCl and, finally, is converted to the oxide.

After preliminary treatment, the scandium, which remains in the aqueous layer from the isopropyl ether extraction, is dissolved in conc HCl and passed through an anion-exchange column to remove the last traces of iron and cobalt. The scandium is converted to the  $\text{ScF}_6^{3-}$  complex, and fluoride and hydroxide scavenges are performed in the presence of lanthanum carrier and iron(III) holdback carrier. The fluorocomplex is then destroyed and  $\text{ScF}_3$  is precipitated. The latter is converted to the hydroxide and ignited to the oxide. The chemical yields are ~85% for iron and ~95% for scandium.

## 2. Reagents

Standard iron(III) carrier: 10 mg iron/ml, made up from pure iron wire (NBS standard)

Iron(III) holdback carrier: 10 mg iron/ml, added as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in dilute HCl

Scandium carrier: 20 mg  $\text{Sc}_2\text{O}_3$ /ml, added as  $\text{ScCl}_3$  in very dilute HCl; standardized (see SCANDIUM I procedure)

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in very dilute  $\text{HNO}_3$

HCl: conc; 10M; 7.9M; 5.5M; 0.1M

$\text{HNO}_3$ : conc

$\text{NH}_4\text{HF}_2$ -HF reagent: 4M in  $\text{NH}_4\text{HF}_2$  and 1M in HF

Aqua regia: 3:1 conc HCl and  $\text{HNO}_3$

$\text{NH}_4\text{OH}$ : conc

NaOH: 10M

Isopropyl ether

Methyl red indicator solution

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh (prewashed with 7.9M HCl)

## 3. Procedure

*Step 1.* To a sample of metal target in a 40-ml glass centrifuge tube, add 2 ml of standard iron(III) carrier and 1 ml of scandium carrier. Place on a steam bath and add sufficient aqua regia to dissolve the sample. Dilute to 30 ml with  $\text{H}_2\text{O}$  and add an excess of conc  $\text{NH}_4\text{OH}$ . [Iron(III) and scandium precipitate as hydroxides, and the nickel is in solution as the deep blue  $\text{Ni}(\text{NH}_3)_6^{2+}$  complex.] Centrifuge and discard the supernate.

*Step 2.* Add sufficient conc HCl to dissolve the precipitate. Dilute to 30 ml with  $\text{H}_2\text{O}$  and reprecipitate the hydroxides with conc  $\text{NH}_4\text{OH}$ . Centrifuge and discard the supernate. Repeat the dissolution and precipitation processes three times. Wash the final  $\text{Fe}(\text{OH})_3$ - $\text{Sc}(\text{OH})_3$  precipitate with 30 ml of  $\text{H}_2\text{O}$  and discard the wash.

*Step 3.* Dissolve the precipitate in a minimum of conc HCl and evaporate the solution to <1 ml. Add 10 drops of conc HCl and 10 ml of 7.9M HCl; transfer to a 60-ml separatory funnel. Wash the centrifuge tube with 2 ml of 7.9M HCl and add the wash to the separatory funnel. Add 10 ml of isopropyl ether, shake well, and transfer the aqueous (lower) layer, which contains the scandium, to a clean 60-ml separatory funnel. Wash the ether layer twice with 5 ml of 7.9M HCl and transfer the washes to the separatory funnel that contains the aqueous layer from the extraction.

*Step 4.* To the ether layer add 10 ml of  $\text{H}_2\text{O}$  and shake well to back-extract the iron(III). Transfer

the aqueous layer to a clean glass centrifuge tube. Repeat the back-extraction of the ether layer and combine the second H<sub>2</sub>O layer with the previous one. To the aqueous extract, add an excess of conc NH<sub>4</sub>OH to precipitate Fe(OH)<sub>3</sub>, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H<sub>2</sub>O and discard the wash.

*Step 5.* Dissolve the Fe(OH)<sub>3</sub> in a minimum of conc HCl and add the solution to a 13- by 1-cm Bio-Rad AG 1-X8, 100 to 200 mesh, anion-exchange resin column that has just been washed with 7.9M HCl. Discard the effluent. To remove the cobalt, wash the column with 10 ml of 7.9M HCl and then with a total of 30 ml of 5.5M HCl. Discard the washes.

*Step 6.* Elute the iron(III) with 30 ml of 0.1M HCl; collect the eluate in a clean glass centrifuge tube. Add an excess of conc NH<sub>4</sub>OH to precipitate Fe(OH)<sub>3</sub>, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, add 6 ml of filter paper pulp slurry, and reprecipitate Fe(OH)<sub>3</sub> with conc NH<sub>4</sub>OH. Filter through filter paper, transfer to a porcelain crucible, and ignite in a furnace that is brought slowly to 1000°C. Maintain at 1000°C for 1 h, and then cool, weigh, and mount the Fe<sub>2</sub>O<sub>3</sub>.

*Step 7.* Wash the aqueous layer that contains the scandium (*Step 3*) twice with 10 ml of isopropyl ether and discard the washes. Transfer the solution to a clean glass centrifuge tube and evaporate to ~5 ml. Add an excess of 10M NaOH to precipitate Sc(OH)<sub>3</sub>, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl and reprecipitate the hydroxide with conc NH<sub>4</sub>OH. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of H<sub>2</sub>O and discard the wash.

*Step 8.* Dissolve the Sc(OH)<sub>3</sub> in a minimum of conc HCl and pass the solution through an anion-exchange resin column like the one used in *Step 5*. Collect the effluent in a clean glass centrifuge tube. Add 20 ml of 10M HCl to the resin column and

combine the effluent with the previous one. (The last traces of iron and cobalt are adsorbed on the column.) Evaporate the combined effluent to ~5 ml and transfer to a clean plastic centrifuge tube.

*Step 9.* Add an excess of conc NH<sub>4</sub>OH to precipitate Sc(OH)<sub>3</sub>. Centrifuge and discard the supernate. To the precipitate add 3 ml of NH<sub>4</sub>HF<sub>2</sub>-HF reagent (the scandium is converted to ScF<sub>6</sub><sup>3-</sup>), and bring the solution to a methyl red end point with conc NH<sub>4</sub>OH. Add 2 drops of lanthanum carrier, centrifuge, and transfer the supernate to a clean plastic tube. Discard the precipitate. Repeat the LaF<sub>3</sub> scavenge twice. To the supernate add 1.5 ml of conc NH<sub>4</sub>OH and 2 drops each of iron(III) holdback and lanthanum carriers; centrifuge, transfer the supernate to a clean plastic centrifuge tube, and discard the precipitate. Add 6 ml of conc HCl and place on a steam bath until the ScF<sub>3</sub> precipitate coagulates. Centrifuge and discard the supernate.

*Step 10.* Add 1 ml of 10M NaOH to the ScF<sub>3</sub> and heat, while stirring, on a steam bath for a few minutes. Add 9 ml of H<sub>2</sub>O, centrifuge, and discard the supernate. Dissolve the Sc(OH)<sub>3</sub> formed in a minimum of conc HCl, and reprecipitate the hydroxide with conc NH<sub>4</sub>OH. Dissolve the precipitate in a minimum of conc HCl, add 6 ml of filter paper pulp slurry, and reprecipitate Sc(OH)<sub>3</sub> with conc NH<sub>4</sub>OH. Filter onto filter paper, transfer the paper to a porcelain crucible, and ignite at 1000°C for 15 min. Cool, weigh, and mount the Sc<sub>2</sub>O<sub>3</sub>.

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# SEPARATION OF CARRIER-FREE ALUMINUM FROM SILICON TARGETS

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## 1. Introduction

This procedure separates carrier-free  $^{26}\text{Al}$  from a large silicon target ( $\sim 100$  g) that has been bombarded by 750-MeV protons. The target is dissolved in a mixture of equal volumes of conc HF and  $\text{HNO}_3$ , and the silicon distills as  $\text{SiF}_4$  during the dissolution process. After successive evaporations to dryness with conc HF, fuming  $\text{HNO}_3$ , and conc  $\text{HClO}_4$  to destroy any fluoro aluminum complexes, the residue is taken up in  $0.25M$   $\text{H}_2\text{C}_2\text{O}_4$ - $0.1M$  HCl. This solution is then passed through an anion-exchange resin column. The aluminum stays on the column and  $^{22}\text{Na}$  and  $^7\text{Be}$ , the major contaminants, pass through. The aluminum is eluted with  $6M$  HCl and the column step is repeated. The aluminum is again eluted with  $6M$  HCl, the solution is evaporated to dryness, and the aluminum is taken up in  $1M$  HCl. The solution is then extracted with HDEHP (di-2-ethylhexyl orthophosphoric acid) in toluene. The aluminum remains in the aqueous phase, and +3 and +4 ions are extracted into the organic phase. The aluminum is again placed on an anion-exchange resin column and eluted with  $6M$  HCl. The chemical yield is  $>90\%$ . Decontamination factors of  $^{26}\text{Al}$  from  $^{22}\text{Na}$  and  $^7\text{Be}$  are  $>10^{14}$  and  $>10^{11}$ , respectively. It is of the utmost importance that reagents of the highest purity be used to avoid introduction of carrier aluminum.

## 2. Reagents

HCl: conc;  $6M$ ;  $1M$ ;  $0.1M$

HF: conc

$\text{HNO}_3$ : fuming; conc

$\text{HClO}_4$ : conc

$\text{H}_2\text{O}$ : triply distilled

$\text{H}_2\text{C}_2\text{O}_4$ : solid; made up  $0.25M$  in  $0.1M$  HCl, and passed through an anion-exchange resin column (see below) before use

HDEHP (di-2-ethylhexyl orthophosphoric acid) solution: one volume of HDEHP to three of toluene. The HDEHP was purified by a modification of the procedures of Gureev *et al.*

Toluene

AGMP-1 anion-exchange resin, 200 to 400 mesh.

Column dimensions: 10.5 cm by 2.2-cm i.d.

The free column volume was 24 ml and the column was preconditioned by successive treatments with conc HCl,  $\text{H}_2\text{O}$ , and  $0.25M$   $\text{H}_2\text{C}_2\text{O}_4$ - $0.1M$  HCl solution.

## 3. Procedure

*Step 1.* Dissolve the silicon target slowly (it may take several days) in a mixture of equal volumes of conc  $\text{HNO}_3$  and HF at  $\sim 100^\circ\text{C}$ . The dissolution is carried out in a closed system; the  $\text{SiF}_4$  is trapped in a LiOH solution as it is evolved.

*Step 2.* Transfer the solution to a Teflon beaker and take it to dryness several times, first with conc HF, then with fuming  $\text{HNO}_3$ , and finally with conc  $\text{HClO}_4$ . Slurry the residue with conc  $\text{HClO}_4$  and transfer to a 40-ml Vycor centrifuge tube. Heat the slurry to dryness in an open furnace at  $200^\circ\text{C}$ .

*Step 3.* Take up the residue in 10 to 15 ml of purified  $0.25M$   $\text{H}_2\text{C}_2\text{O}_4$ - $0.1M$  HCl solution. Load onto the AG MP-1 anion-exchange resin column (flow rate as determined by gravity,  $\sim 40$  ml/h). Discard the effluent. (It contains large amounts of  $^7\text{Be}$  and  $^{22}\text{Na}$ .) Wash the column with 10 ml of the  $\text{H}_2\text{C}_2\text{O}_4$ -HCl solution, 70 ml of  $\text{H}_2\text{O}$ , and 60 ml of  $0.1M$  HCl. (These washes remove significant amounts of  $^{22}\text{Na}$  and  $^7\text{Be}$ .) Discard the washes.

*Step 4.* Elute the aluminum with 150 ml of  $6M$  HCl. Carefully take the solution to dryness ( $\text{AlCl}_3$  is somewhat volatile), dissolve the residue in  $0.25M$   $\text{H}_2\text{C}_2\text{O}_4$ - $0.1M$  HCl solution, and again pass through an AGMP-1 column as in *Step 3*. Elute the aluminum with  $6M$  HCl and take the eluate carefully to dryness.

*Step 5.* Take up the aluminum in a few milliliters of 1M HCl and extract the solution with an equal volume of the HDEHP solution. (The aluminum remains in the aqueous phase.) Separate the phases and wash the aqueous phase with toluene. Wash the organic phase with 1M HCl. Then wash the resulting aqueous phase with toluene. Combine this aqueous phase with the one from the original extraction. Discard the organic phases.

*Step 6.* Repeat the entire extraction procedure.

*Step 7.* Take the aqueous fraction containing aluminum to dryness several times with fuming HNO<sub>3</sub> and conc HClO<sub>4</sub> and then pass through an AG-MP1 column as in *Steps 2 and 3*, but use 50 ml of 0.25M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-0.1M HCl (rather than 10 ml) as a wash. (Use of the larger amount improves the separation of <sup>7</sup>Be.)

#### Reference

E. S. Gureev, V. N. Kosyakov, and G. N. Yakovlev, *Radiochimia* **6**, 655 (1964).

(October 1989)



# SEPARATION OF HAFNIUM AND THE LANTHANIDES FROM A TANTALUM TARGET

K. E. Thomas

## 1. Introduction

This procedure describes the separation of curie quantities of hafnium and the lanthanides from tantalum targets irradiated with  $\sim 800$ -MeV protons. The targets were 8-cm-square, 32-mm-thick slabs of tantalum metal (weight  $\sim 250$  g). After irradiation, a target is dissolved in a mixture of conc HF and  $\text{HNO}_3$ ; calcium carrier is added to precipitate  $\text{CaF}_2$ , which carries hafnium and the lanthanides. The precipitate is dissolved in a  $\text{H}_3\text{BO}_3$ -HCl acid mixture, and the solution is diluted until the HCl concentration is  $< 0.5M$ . Hafnium and the lanthanides are extracted into di-2-ethylhexyl orthophosphoric acid (HDEHP)-toluene solution. The lanthanides are removed from this solution by means of  $10M$  HCl, and essentially pure hafnium is left in the HDEHP-toluene phase. The lanthanides are separated on a cation-exchange resin column by elution with alpha-hydroxyisobutyric acid (alpha-HIB). Overall yields are estimated to be  $>90\%$  for hafnium,  $\sim 90\%$  for lutetium, and  $\sim 70\%$  each for gadolinium and europium.

## 2. Reagents

HF- $\text{HNO}_3$  mixture: a 4:1 mixture by volume of the conc acids

HCl: conc;  $10M$ ;  $0.4M$

$\text{HNO}_3$ : fuming

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

Calcium carrier: added as  $\text{Ca}(\text{NO}_3)_2$  solution

HDEHP-toluene solution: 10% HDEHP (di-2-ethylhexyl orthophosphoric acid) by volume  
Toluene

Cation-exchange resin: AG 50W-X8, minus 200 mesh ( $\text{NH}_4^+$  form)

Alpha-HIB (alpha-hydroxyisobutyric acid) solutions:  $0.52M$  solutions of pH 3.24, 3.33, and 4.4

## 3. Procedure

All operations are carried out in a hot cell.

*Step 1.* To a slab of irradiated tantalum target, add 1  $\ell$  of HF- $\text{HNO}_3$  mixture in 50-ml portions; remove each portion after violent reaction slows. (The target dissolves completely.) Combine the solutions.

*Step 2.* To the combined solution, add  $\sim 250$  mg of calcium carrier and allow the  $\text{CaF}_2$  precipitate that forms to settle. Decant the clear solution and centrifuge the remaining slurry. Wash the precipitate twice with  $\text{H}_2\text{O}$ . If more than one target slab is used, combine all  $\text{CaF}_2$  precipitates.

*Step 3.* To the precipitate add  $\text{H}_3\text{BO}_3$  solution and the minimum volume of conc HCl necessary to dissolve the precipitate when the mixture is heated. Dilute the resulting solution with enough  $\text{H}_2\text{O}$  to make the HCl concentration  $< 0.5M$ . (If three slabs of tantalum target are used, the volume of solution is now  $\sim 500$  ml.)

*Step 4.* Add 100 ml of HDEHP-toluene solution and mix thoroughly. Separate the phases. Repeat the extraction twice and combine all three organic (upper) phases. Wash the combined organic phases with 200 ml of  $0.4M$  HCl and discard the wash.

*Step 5.* Back-extract the lanthanides from the organic phase with 50 ml of  $10M$  HCl. Repeat the extraction and combine the aqueous wash phases. Wash the combined aqueous phase with 50 ml of toluene and discard wash. All the hafnium remains in the organic phase.

*Step 6.* Evaporate the combined aqueous phases to near dryness. If a brown solid forms, add 10 ml of fuming  $\text{HNO}_3$  and boil to near dryness. Add 10 ml of conc HCl and boil to a volume of  $\sim 0.5$  ml. Dilute to  $\sim 20$  ml with  $\text{H}_2\text{O}$ . Add a slurry containing 1.5 ml of cation-exchange resin in  $\text{H}_2\text{O}$ , centrifuge, and discard the supernate. Wash the resin with 10 ml of  $\text{H}_2\text{O}$  and discard the wash.

*Step 7.* Transfer the solid onto a bed of cation-exchange resin, 6.5 cm long and 0.75-cm diam, that has been equilibrated with H<sub>2</sub>O. Elute the heavy lanthanides with 200 ml of alpha-HIB solution of pH 3.24. Then carry out a gradient elution of the remaining lanthanides using 375 ml each of alpha-HIB solutions pH 3.33 and 4.44. The flow of all elutions is 0.2 ml/min and samples are collected for 30-min intervals. Individual element fractions are detected by their radiations. (For further details of the ion-exchange separation of lanthanides see THE LANTHANIDES procedure.)

(October 1989)

# RECOVERY OF CURIE QUANTITIES OF $^{77}\text{Br}$ , $^{82}\text{Sr}$ , $^{85}\text{Sr}$ , AND $^{88}\text{Y}$ FROM THE 600- to 800-MeV PROTON IRRADIATION OF MOLYBDENUM

J. W. Barnes, G. E. Bentley, and P. M. Grant

## 1. Introduction

Molybdenum and all the spallation products (except bromine) that are formed by irradiation of the metal are dissolved in a  $\text{HNO}_3\text{-H}_3\text{PO}_4$  plus  $\text{Cl}^-$  carrier mixture. Bromine and chlorine are evolved as gaseous species and are trapped as  $\text{AgX}$  in a  $\text{AgNO}_3$  solution. The silver halide is dissolved in aqueous  $\text{NH}_3$  and the silver is adsorbed as  $\text{Ag}(\text{NH}_3)_2^+$  on a cation-exchange resin; the radioactive  $\text{Br}^-$  and carrier  $\text{Cl}^-$  pass through the resin.

Yttrium, strontium, rubidium, and other elements that do not form anionic phosphate complexes are removed from the molybdenum-containing solution by adsorption on a cation-exchange resin. Molybdate ion, zirconium(IV), and other cations that form strong phosphate complexes pass through the resin. The adsorbed cations are eluted with 6M HCl. The effluent, made  $\sim 9M$  in HCl, is passed through an anion resin column; those ions that give relatively stable anionic chloro complexes (for example,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ ) stick on the resin. From the effluent at pH 0 to 1, yttrium and niobium are extracted by a mixture of HDEHP (di-2-ethylhexyl orthophosphoric acid), acetylacetone (2,4-pentanedione), and toluene. Strontium and rubidium remain in the aqueous phase. Yttrium is separated from niobium in the organic phase by extraction into 6M HCl. The pH of the aqueous mixture that contains strontium and rubidium is adjusted to  $>10$ , and the solution is passed through a chelating cation resin. The strontium is adsorbed on the resin and is eluted with 0.5M HCl.

Other spallation products can be isolated by appropriate extensions of the procedure.

Chemical analysis of the target is performed in a hot cell. A description of the hot cell equipment can be found in the Reference.

## 2. Reagents

HCl: 0.1M; 0.5M; 6M; conc

$\text{HNO}_3\text{-H}_3\text{PO}_4$  reagent: 550 ml of conc  $\text{HNO}_3$ , 250 ml of conc  $\text{H}_3\text{PO}_4$ , 200 ml of  $\text{H}_2\text{O}$ , and 2 mg of  $\text{Cl}^-$  carrier, added as  $\text{NH}_4\text{Cl}$

NaOH: 0.1M; 4M; 50 wt% aqueous solution

$\text{NH}_4\text{OH}$ : 3M

$\text{AgNO}_3$ : 0.01M

1,4-Dioxane

Toluene

HDEHP (di-2-ethylhexyl orthophosphoric acid)

2,4-Pentanedione (acetylacetone)

Cation-exchange resin: Dowex 50-X4, 100 to 200 mesh,  $\text{NH}_4^+$  form

Cation-exchange resin: Dowex 50-X4, 100 to 200 mesh,  $\text{H}^+$  form

Anion-exchange resin: Dowex AG 1-X8, 100 to 200 mesh

Chelating cation-exchange resin: Bio-Rad Chelex-100, 100 to 200 mesh

## 3. Procedure

The procedure has been used for a 30- to 60-g molybdenum target (stacked columns of 5- to 15-mil foils, 0.75 to 1 in. thick), at least 99.9% pure, which had been irradiated at an integrated proton current of  $\sim 40$  mA $\cdot$ h.

*Step 1.* The dissolution of the target is carried out in the apparatus shown in Fig. 1. To the irradiated target in the 1- $\ell$  erlenmeyer flask, add 50- to 75-ml increments of  $\text{HNO}_3\text{-H}_3\text{PO}_4$  reagent until reaction subsides. Continue adding 50- to 75-ml increments of the reagent until solution is complete. (At this point, the volume of solution is  $\sim 500$  ml.) Bromine and carrier chlorine are absorbed in the trap containing  $\text{AgNO}_3$  solution (0.01M). Other gases (for example, oxides of nitrogen) collect in the NaOH (4M) trap.

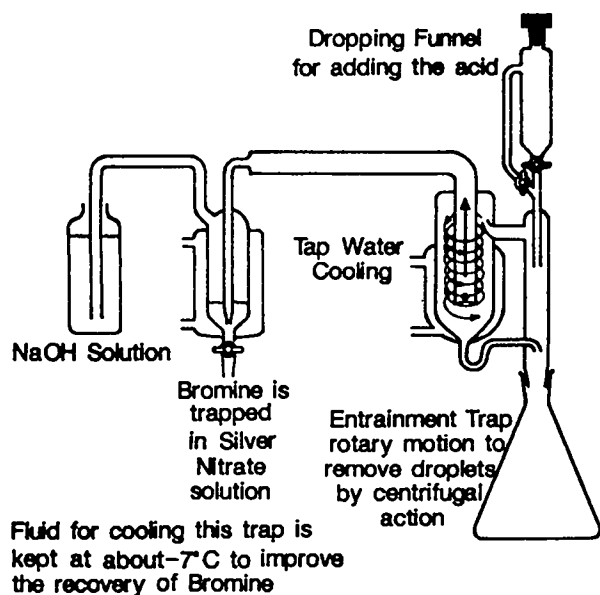


Fig. 1. Schematic of hot-cell equipment for recovering radioactive bromine from molybdenum.

*Step 2.* Centrifuge the silver halides in the  $\text{AgNO}_3$  trap and discard the supernate. Wash the precipitate with  $\sim 4$  ml of  $\text{H}_2\text{O}$ , centrifuge, and discard the wash. As quickly as possible, dissolve the precipitate in 5 ml of  $3M$   $\text{NH}_4\text{OH}$ . (Radiation reduces  $\text{AgBr}$  and  $\text{AgCl}$  to free silver and this process must be kept to a minimum.)

*Step 3.* Wash a Dowex 50-X4, 100 to 200 mesh, cation-exchange resin column ( $\text{NH}_4^+$  form; 4-mm i.d. by 50-mm length) with  $3M$   $\text{NH}_4\text{OH}$ . Pass the solution from *Step 2* through the column and collect the effluent in a calibrated glass centrifuge tube that contains 2 ml of  $0.1M$   $\text{NaOH}$ . The  $\text{Ag}(\text{NH}_3)_2^+$  ion is adsorbed on the column. Wash the column with 1 ml of  $\text{H}_2\text{O}$  and combine effluents.

*Step 4.* Heat effluents to drive off  $\text{NH}_3$ . The solution contains radioactive bromine as  $\text{Br}^-$ .

*Step 5.* Transfer the solution from the erlenmeyer flask that contains the dissolved molybdenum to a mixing vessel and add an

equal volume of  $\text{H}_2\text{O}$ ; then add two volumes of 1,4-dioxane. Pass the solution through a Dowex 50-X4, 100 to 200 mesh, cation resin column ( $\text{H}^+$  form; 30-mm i.d. by 100-mm length; preconditioned with a mixture of  $\text{HNO}_3$ - $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}$ , and dioxane of the same composition as the solution in the mixing vessel). Yttrium, strontium, and other metal cations stick on the column; the effluent contains molybdenum and other metals that form strong anionic complexes with phosphate ion (for example,  $\text{Zr}^{4+}$ ). (The 1,4-dioxane increases the degree of sorption of yttrium and strontium on the resin.)

*Step 6.* Wash the column with 100 ml of the  $\text{HNO}_3$ - $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{O}$ -dioxane mixture and discard the wash. Pass 500 ml of  $6M$   $\text{HCl}$  through the column to elute  $\text{Sr}^{2+}$ ,  $\text{Y}^{3+}$ , and other cations. (The progress of the elution is followed with a gamma survey meter.)

*Step 7.* Add an equal volume of conc  $\text{HCl}$  to the effluent and pass the solution through a Dowex AG 1-X8, 100 to 200 mesh, anion-exchange resin column (18-mm i.d. by 100-mm length). Zinc and iron are absorbed as anionic chloro complexes.

*Step 8.* Evaporate the effluent to near dryness and adjust the pH of the solution to 0 to 1 by the addition of  $0.1M$   $\text{HCl}$ . Extract the yttrium and niobium into 50 ml of a solution containing equal volume percentages of  $\text{HDEHP}$ , 2,4-pentanedione, and toluene. (The 2,4-pentanedione removes any aluminum impurity that might have contaminated the target.) Remove the aqueous (lower) phase that contains strontium and rubidium.

*Step 9.* Use a volume of  $6M$   $\text{HCl}$  equal to one-half the organic phase to extract yttrium from that phase. Niobium is left behind.

*Step 10.* To the aqueous solution that holds strontium and rubidium, add sufficient 50 wt%  $\text{NaOH}$  to bring the pH to a value  $>10$ . Pass the solution through a Bio-Rad Chelex, 100 to 200 mesh, cation-exchange resin column (18-mm i.d. by 100-mm length). Wash the column

with ~25 ml of H<sub>2</sub>O to remove any remaining rubidium. Elute strontium with 50 to 100 ml of 0.5M HCl. Essentially no gamma activity should be left on the column.

#### Reference

*Proceedings of the 26th Conference on Remote Systems Technology*, American Nuclear Society (1978), p. 372.

(October 1989)

# RECOVERY OF CURIE QUANTITIES OF $^{82}\text{Sr}$ , $^{85}\text{Sr}$ , $^{88}\text{Y}$ , AND $^{88}\text{Zr}$ FORMED BY 600- to 800-MeV PROTON IRRADIATION OF MOLYBDENUM

J. W. Barnes, G. E. Bentley, and P. M. Grant

## 1. Introduction

In this procedure, the irradiated molybdenum target first is dissolved in 30%  $\text{H}_2\text{O}_2$  and the solution is passed through a cation-exchange resin that adsorbs strontium, yttrium, zirconium, zinc, iron, rubidium, and niobium. Then these elements are stripped from the column with 6M HCl. The effluent, made  $\sim 9M$  in HCl, is passed through an anion-exchange resin on which zinc and iron are adsorbed as chloro complexes. The solution that comes off the resin is saturated with HCl gas and passed through another anion-exchange column. This time, zirconium adheres to the resin, and it is eluted by means of 3M HCl. From the effluent of this second passage at pH 0 to 1, yttrium and niobium are extracted by a mixture of HDEHP (di-2-ethylhexyl orthophosphoric acid), 2,4-pentanedione (acetylacetone), and toluene. Strontium and rubidium remain in the aqueous phase. Yttrium is separated from niobium in the organic phase by extraction with 6M HCl. The pH of the aqueous mixture of strontium and rubidium is adjusted to  $>10$ , and the solution is passed through a chelating cation resin. The strontium, which is adsorbed on the resin, is then eluted with 0.5M HCl.

Other spallation-produced elements (for example, the zinc, iron, and rubidium mentioned above) can also be isolated by appropriate extensions of the procedure.

## 2. Reagents

HCl: gas; 0.1M; 0.5M; 3M; 6M; conc  
NaOH: 50 wt% aqueous solution  
 $\text{H}_2\text{O}_2$ : 30% aqueous solution (unstablized); 3%  
HDEHP (di-2-ethylhexyl orthophosphoric acid)  
2,4-pentanedione (acetylacetone)  
Toluene

Cation-exchange resin: Bio-Rad AG 50W-X4, 100 to 200 mesh

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh

Chelating cation-exchange resin: Bio-Rad Chelex-100, 100 to 200 mesh

## 3. Procedure

The procedure was developed for a massive (450-g) molybdenum target, at least 99.9% pure, that had been irradiated with 600- to 800-MeV protons at an integrated current of 1.2 A·h. The irradiation produced  $\sim 100$  Ci of gamma activity, which was measured 10 d after the end of bombardment.

Chemical analysis of the target is performed in equipment especially designed for hot cell use. A description of this equipment and its use can be found in the Ref.

*Step 1.* Dissolve the molybdenum target by adding 100-ml amounts of 30% unstabilized  $\text{H}_2\text{O}_2$ . Then add sufficient  $\text{H}_2\text{O}_2$  to make the color of the solution yellow. A total of  $\sim 9.3$  l of the peroxide is required.

*Step 2.* Pass the solution through a Bio-Rad AG 50W-X4, 100 to 200 mesh, cation-exchange resin column (30-mm i.d. by 100-mm length). Wash the column with 100 ml of 3%  $\text{H}_2\text{O}_2$  and then with 100 ml of  $\text{H}_2\text{O}$  and discard the wash. Strontium, yttrium, zirconium, zinc, iron, rubidium, and niobium are adsorbed on the resin.

*Step 3.* Elute the bound ions with 1 l of 6M HCl. To the eluate, add an equal volume of conc HCl and pass the solution through a Bio-Rad AG 1-X8, 100 to 200 mesh, anion-exchange resin column (18-mm i.d. by 100-mm length). Zinc and iron are adsorbed as anionic chloro complexes.

*Step 4.* Saturate the effluent with HCl gas and pass it over a fresh anion resin column. Now zirconium adheres to the resin. Remove that element with 3M HCl; about seven free column volumes of the acid are required. (A free column

volume is equal to about one-half the volume of the resin bed.)

*Step 5.* Evaporate to near dryness the effluent from the second pass through the anion column. Adjust the pH of the solution to 0 to 1 by adding 0.1M HCl. Extract the yttrium and niobium into 50 ml of a solution containing equal volume percentages of HDEHP, 2,4-pentanedione, and toluene. (The 2,4-pentanedione removes any aluminum impurity that might have contaminated the target.) Remove the aqueous (lower) phase that contains strontium and rubidium.

*Step 6.* Use a volume of 6M HCl equal to one-half the organic phase to extract yttrium from that phase. Niobium is left behind.

*Step 7.* To the aqueous solution that holds the strontium and rubidium, add sufficient 50 wt% NaOH to bring the pH to a value >10. Pass the solution through a Bio-Rad Chelex, 100 to 200 mesh, cation-exchange column (18-mm i.d. by 100-mm length). Wash the column with ~25 ml of H<sub>2</sub>O to remove any remaining rubidium. Finally, elute strontium with 50 to 100 ml of 0.5M HCl. No gamma activity should be left on the column.

## Reference

*Proceedings of the 26th Conference on Remote Systems Technology*, American Nuclear Society (1978), p. 372.

(October 1989)

# LARGE-SCALE ISOLATION OF STRONTIUM FROM IRRADIATED MOLYBDENUM TARGETS

K. E. Thomas and J. W. Barnes

## 1. Introduction

This procedure describes the isolation of strontium from large amounts of molybdenum (60 to 460 g) that have been irradiated for 2 to 30 d at  $>500 \mu\text{A}$  by protons of energy  $<800 \text{ MeV}$ . The target is dissolved in either a mixture of  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  or in 30%  $\text{H}_2\text{O}_2$ . The former method of dissolution is preferred.

The dissolved sample is passed through a cation-exchange resin column;  $\text{MoO}_4^{2-}$  and other anions formed in the solution process pass through the column. The resin is then washed with 0.5M  $\text{NH}_4\text{Cl}$  solution to elute rubidium, the resin being converted to the  $\text{NH}_4^+$  form. Treatment of the resin with 0.5M alpha-HIB (alpha-hydroxyisobutyric acid) solution at a pH of five washes off yttrium, zirconium, zinc, manganese, and cobalt. The alpha-HIB is removed by treating the column with  $\text{H}_2\text{O}$  and the resin is then converted to the  $\text{H}^+$  form with 0.5M  $\text{HCl}$ , a process that removes more manganese. Strontium is finally eluted from the resin by 6M  $\text{HCl}$ . (If  $\text{H}_2\text{O}_2$  is used as the solvent, the strontium contains some zirconium and an anion column step is required.)

A radiochemically pure strontium fraction containing  $^{82}\text{Sr}$  and  $^{85}\text{Sr}$  is obtained; chemical yields are as high as 90%.

## 2. Reagents

$\text{HCl}$ : 0.5M; 6M; conc

$\text{HNO}_3\text{-H}_3\text{PO}_4$  solution: 500 ml of conc  $\text{HNO}_3$ ,  
250 ml of conc  $\text{H}_3\text{PO}_4$ , and 200 ml of  $\text{H}_2\text{O}$

Aqueous  $\text{H}_2\text{O}_2$  solutions: 10%; 30%

$\text{NH}_4\text{Cl}$ : 0.5M

Dioxane

Dioxane- $\text{H}_2\text{O}$ : equal volumes

Alpha-HIB (alpha-hydroxyisobutyric acid): 0.5M  
aqueous solution at pH 5

AG 50W-X8 cation-exchange resin, 100 to  
200 mesh; bed volume, 50 ml

AG 1-X8 anion-exchange resin

## 3. Procedure

*Step 1.* To the target in a glass container, add 50 to 100 ml of  $\text{HNO}_3\text{-H}_3\text{PO}_4$  or 30%  $\text{H}_2\text{O}_2$  solution. Allow the reaction to subside and transfer the liquid to a large bottle. Repeat with 50 to 100 ml portions of solvent until the target has dissolved completely. (A 1-l  $\text{HNO}_3\text{-H}_3\text{PO}_4$  solution has been used to dissolve 170 g of molybdenum, and 5 l of 30%  $\text{H}_2\text{O}_2$  to dissolve 3 g of metal.) Allow the solution to cool, and if  $\text{HNO}_3\text{-H}_3\text{PO}_4$  was used as solvent, add an equal volume of dioxane to the solution.

*Step 2.* Pass the solution through the AG 50W-X8 cation-exchange column at a flow rate of  $\sim 50 \text{ ml/min}$ . If the  $\text{HNO}_3\text{-H}_3\text{PO}_4$  solution was the solvent, wash the column first with 250 ml of dioxane- $\text{H}_2\text{O}$  solution and then with 250 ml of  $\text{H}_2\text{O}$ . If  $\text{H}_2\text{O}_2$  was the solvent, wash the column with 250 ml of 10%  $\text{H}_2\text{O}_2$  solution followed by 250 ml of  $\text{H}_2\text{O}$ . Discard all effluents.

*Step 3.* To the column, add successively 500 ml of 0.5M  $\text{NH}_4\text{Cl}$  solution, 500 ml of alpha-HIB solution (0.5M; pH 5), 100 ml of  $\text{H}_2\text{O}$ , and 250 ml of 0.5M  $\text{HCl}$ . Collect each of the eluates in a separate bottle. (These solutions may be used for the isolation of other elements.)

*Step 4.* To the column, add 250 ml of 6M  $\text{HCl}$ . Collect the first 25 ml of eluate and discard; collect the remainder in 100-ml portions. Check the resin column for radioactivity and, if there is still activity on the column, pass another 50 ml of 6M  $\text{HCl}$  through. Repeat until the column is free of activity. Combine those eluates that show activity.

*Step 5.* Evaporate the combined eluate to dryness and dissolve the residue in  $\text{H}_2\text{O}$ . Assay to determine the quantity and the purity of the strontium (Note).



## Note

If  $H_2O_2$  was used to dissolve the molybdenum target, the strontium fraction is contaminated with zirconium. The dried strontium fraction is dissolved in conc HCl, and the solution is passed through a small AG 1-X8 anion-exchange resin column. Zirconium is adsorbed on the resin and strontium passes through. The effluent containing the strontium is taken to dryness and then dissolved in  $H_2O$  and assayed.

(October 1989)

# SEPARATION OF YTTRIUM, ZIRCONIUM, ZINC, AND RUBIDIUM FROM SOLUTIONS OBTAINED IN THE LARGE-SCALE ISOLATION OF STRONTIUM FROM IRRADIATED MOLYBDENUM TARGETS

K. E. Thomas

## 1. Introduction

Zirconium can be separated in the procedures given here only if  $H_2O_2$  was used to dissolve the molybdenum target. For separation of the other elements, either method of dissolution— $HNO_3$ - $H_3PO_4$  or  $H_2O_2$ —may be employed. In *Step 3* of the procedure for the large-scale isolation of strontium, rubidium is eluted in impure form from the cation-exchange resin by  $0.5M$   $NH_4Cl$ . The procedure described below for the separation of this element allows recovery in a purer condition; the major contaminant is  $^{88}Y$ .

## 2. Reagents

HCl:  $0.05M$ ;  $0.1M$ ;  $1M$ ;  $2M$ ;  $6M$ ; conc

Aqueous  $H_2O_2$  solutions: 10%; 30%

HDEHP solution: a 10% by volume solution of di-2-ethylhexyl orthophosphoric acid in toluene

AG 50W-X8 cation-exchange resin, 100 to 200 mesh

AG 1-X anion-exchange resin

## 3. Procedure

### A. Separating Yttrium, Zirconium, and Zinc

*Step 1.* To the alpha-HIB solution from *Step 3* of the procedure for LARGE-SCALE ISOLATION OF STRONTIUM FROM IRRADIATED MOLYBDENUM TARGETS, add sufficient conc HCl to make the solution  $0.15M$  in this acid. Pass the solution through an AG 50W-X8 cation-exchange resin column. Wash the column with  $0.1M$  HCl. Save the effluents for recovery of zirconium (*Step 4*).

*Step 2.* Add  $1M$  HCl to the cation resin column and monitor the effluent to follow the elution of zinc. When the effluent is no longer radioactive, discontinue addition of HCl and save the effluent for purification of zinc (*Step 5*).

*Step 3.* Elute yttrium from the column with  $6M$  HCl. Save the eluate containing yttrium activity, and discard the cation resin column.

*Step 4.* To the effluents from *Step 1*, add 100 ml of the HDEHP solution, mix well, and separate the phases; save the organic (upper) phase, which contains zirconium. Wash the organic phase with  $6M$  HCl and discard the wash. The zirconium in the organic phase may be contaminated with  $^{46}Sc$ .

*Step 5.* To the effluent from *Step 2*, add sufficient conc HCl to make the solution  $2M$  in acid. Pass the solution through an AG 1-X8 anion-exchange resin column; zinc is adsorbed on the column. Wash the column with  $2M$  HCl to remove contaminants, and elute the zinc activity with  $0.05M$  HCl.

### B. Separating Zirconium and Rubidium

*Step 1.* To the  $H_2O_2$  solution from *Step 1* of the procedure for LARGE-SCALE ISOLATION OF STRONTIUM FROM IRRADIATED MOLYBDENUM TARGETS, add sufficient 30%  $H_2O_2$  solution to produce a bright yellow solution (peroxo complex?). Pass the solution through a fresh AG 50-X8 cation-exchange resin column, wash the resin with 10%  $H_2O_2$  solution and then with  $H_2O$ , and discard the effluents. Elute zirconium and rubidium with  $6M$  HCl until the resin exhibits no activity. Evaporate the solution to dryness.

*Step 2.* Dissolve the residue in conc HCl and pass the resulting solution through an AG 1-X8 anion-exchange resin column. Wash the column with conc HCl until no activity is eluted. Save the effluents for purification of rubidium. (*Step 4*).

*Step 3.* Wash the column with 1M HCl until the eluate, which contains the zirconium, shows no activity.

*Step 4.* Make the effluents from *Step 2* 1M in HCl and pass the solution through a fresh AG 50-X8 cation-exchange resin column. The  $^{88}\text{Y}$ , which has grown in from  $^{88}\text{Zr}$ , is adsorbed on the column and rubidium passes through.

(October 1989)

# SEPARATION OF CURIE QUANTITIES OF IRON FROM AN IRRADIATED NICKEL TARGET

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## 1. Introduction

Curie quantities of  $^{52}\text{Fe}$  are produced through spallation of a nickel target by 800-MeV protons. Following the irradiation process, the target is dissolved in conc  $\text{HNO}_3$ , the solution is made 6M in HCl, and the iron is extracted into methylisobutylketone (MIBK). Two washings of the organic layer with a mixture 6M in HCl and 3% in  $\text{H}_2\text{O}_2$  remove such contaminants as sodium, scandium, cobalt, and vanadium from the MIBK. Finally, iron is stripped from the MIBK phase by means of distilled water. The procedure gives an essentially quantitative separation of radioiron free from contaminants (Note).

Iron-52 (half-life 8.28 h) decays solely to  $^{52}\text{Mn}$  (half-life 21.1 min) by positron emission and electron capture. The radioiron is used directly in nuclear medicine in bone marrow studies or indirectly as the generator of its daughter, which finds application in cardiovascular investigations.

## 2. Reagents

$\text{HNO}_3$ : 10M

HCl: conc

$\text{H}_2\text{O}_2$ : 3%

MIBK (methylisobutylketone; 4-methyl-2-pentanone): equilibrated with 6M HCl just before use

## 3. Procedure

The nickel target ( $\sim 4$  g; 60 mil by 1.5 cm by 4 cm) is irradiated for 20 min at  $\sim 0.8 \mu\text{A}$ .

*Step 1.* Dissolve the target in  $\sim 50$  ml of 10M  $\text{HNO}_3$ , and make the solution 6M in HCl by the addition of the concentrated acid.

*Step 2.* Extract the solution with an equal volume of preequilibrated MIBK and discard the aqueous (lower) layer.

*Step 3.* Wash the MIBK layer twice by shaking with half volumes of a mixture 6M in HCl and 3% in  $\text{H}_2\text{O}_2$ . (The  $\text{H}_2\text{O}_2$  ensures that the vanadium is in the +5 state, in which condition it is removed from the MIBK.) Discard the washes.

*Step 4.* Strip the MIBK phase with three 33-ml portions of distilled  $\text{H}_2\text{O}$  and combine the aqueous phases, which now contain the iron.

## Note

This procedure is effective for isolating iron from nickel, cobalt, manganese, chromium, vanadium, titanium, scandium, calcium, and sodium.

(October 1989)

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### III. Preparation of Samples for Mass Spectrometric Analysis

# SEPARATION OF URANIUM AND PLUTONIUM FROM UNDER- GROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS

G. W. Knobeloch, V. M. Armijo,  
and D. W. Efurd

## 1. Introduction

The major steps in this procedure for the separation of uranium and plutonium include: (1) exchange of uranium in the sample with  $^{233}\text{U}$  and of plutonium with  $^{242}\text{Pu}$ ; (2) extraction of these elements as nitrates into ethyl acetate from a  $1M$   $\text{HNO}_3$  solution saturated with  $\text{NH}_4\text{NO}_3$ ; (3) back-extraction into  $\text{H}_2\text{O}$ ; (4) adsorption of the uranium and plutonium on an anion-exchange resin column; (5) washes with  $0.1M$   $\text{H}_2\text{SO}_4$  and  $10M$   $\text{HCl}$ , followed by elution of plutonium(III) by means of an  $\text{HI-HCl}$  mixture and uranium by  $\text{HNO}_3$  after washes with  $0.1M$   $\text{H}_2\text{SO}_4$  and  $8M$   $\text{HCl}$ ; and (6) separate treatment of the uranium and plutonium on macroporous anion-exchange resins; the elements are adsorbed from a  $\text{H}_2\text{O}_2\text{-HCl}$  solution, and after appropriate washes of the resins, the uranium is eluted with  $\text{H}_2\text{O}$  and the plutonium with  $\text{HBr}$ .

The extraction and back-extraction processes are quite effective in removing fission products and the elements present in macro amounts in soil samples (for example, sodium, potassium, magnesium, calcium, aluminum, silicon, and iron). After the back-extraction, the plutonium, about half of the neptunium, some  $^{95}\text{Zr}$  and  $^{97}\text{Zr}$ ,  $^{95}\text{Nb}$ ,  $^{99}\text{Tc}$ ,  $^{103}\text{Ru}$ ,  $^{229}\text{Th}$ ,  $^{131}\text{Te}$ , and  $^{132}\text{Te}$  remain with the uranium. Relatively large amounts of the salting out agent,  $\text{NH}_4\text{NO}_3$ , are also present and carry along enough of the alkali metals and iron to interfere with mass spectrometric analysis. The main purpose of the anion resin column step is the removal of these interferences. Last traces of iron are removed by the  $\text{H}_2\text{SO}_4$  wash. Large amounts of  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  used in washing the resin, relative to the free column volume, are necessary to remove all traces of

the alkali metals. At the completion of the column step, gamma-spectral analysis reveals that the major contaminant is zirconium and that only a little  $^{99}\text{Tc}$  and  $^{95}\text{Nb}$  are present. Emission-spectral analysis shows less than 1 ppm of sodium, potassium, calcium, aluminum, and iron in both the plutonium and uranium; there is also some uranium contaminant in the plutonium and some thorium and plutonium contaminant in the uranium. The macroporous anion-exchange resin column treatments are necessary to achieve additional levels of purity required for pulse-counting mass spectroscopy. Uranium recovery is  $\sim 80\%$  and plutonium recovery  $\sim 75\%$ .

The procedure has been used for samples containing as little as 5 ng of uranium and plutonium. A "clean" laboratory and the purest available reagents are required.

## 2. Reagents

$^{233}\text{U}$  tracer: source, National Bureau of Standards (NBS)  
 $^{242}\text{Pu}$  tracer  
 $\text{HClO}_4$ : conc  
 $\text{HNO}_3$ : conc;  $8M$ ;  $2M$ ;  $1M$   
 $\text{HBr}$ : 47%; source, MCB Reagents  
 $\text{HCl}$ :  $10M$ ;  $8M$ ;  $6M$ ;  $1.5M$   
 $\text{H}_2\text{SO}_4$ :  $0.1M$   
Aqua regia: 3:1 mixture, by volume, of  $10M$   $\text{HCl}$  and conc  $\text{HNO}_3$   
 $\text{HI-HCl}$  mixture: 1:9 mixture, by volume, of 48%  $\text{HI}$  and  $10M$   $\text{HCl}$   
 $\text{H}_2\text{O}$ : Type 1 reagent-grade water (deionized)  
 $\text{H}_2\text{O}_2\text{-HCl}$  reagent: 1 drop of 30%  $\text{H}_2\text{O}_2$  to 9 ml of  $10M$   $\text{HCl}$   
 $\text{NH}_4\text{NO}_3$ : solid  
Ethyl acetate  
Bio-Rad macroporous anion-exchange resin: AGMP-1, 50 to 100 mesh, granular, deionized water slurry. This resin is pretreated by warming overnight in a mixture of 50%  $10M$   $\text{HCl}$  and 50%  $\text{H}_2\text{O}$ . It is washed 20 times with deionized  $\text{H}_2\text{O}$  and stored as an  $\text{H}_2\text{O}$  slurry. The column uses a disposable automatic

pipette tip, ~7 cm long and 5 mm i.d. A plug of prewashed quartz wool is placed in the tip and resin is added to a depth of ~2 cm.

### 3. Procedure

*Step 1.* Place an aliquot of sample (Note 1) containing 100 to 200 ng of uranium in 3M HCl in a 40-ml centrifuge tube. Add  $^{233}\text{U}$  tracer in amount to provide approximately equivalent ratios of  $^{233}/^{235}$  and  $^{238}/^{233}$ , and then add  $^{242}\text{Pu}$  tracer equal to the estimated quantity of  $^{239}\text{Pu}$ . Add 2 ml of conc  $\text{HClO}_4$  and evaporate to dryness (Note 2).

*Step 2.* Add 5 ml of 2M  $\text{HNO}_3$  and sufficient solid  $\text{NH}_4\text{NO}_3$  to saturate the solution, and warm to room temperature. (The addition of the  $\text{NH}_4\text{NO}_3$  approximately doubles the volume of solution). Add 10 ml of ethyl acetate, stopper the tube with a plastic top, and shake for 1 min. Centrifuge lightly to separate the phases, remove the ethyl acetate (top) layer, and transfer it to a clean centrifuge tube. Repeat the extraction twice and combine the ethyl acetate phases. Discard the aqueous phase.

*Step 3.* Wash the combined ethyl acetate phases with 3 ml of 2M  $\text{HNO}_3$  that has been saturated with  $\text{NH}_4\text{NO}_3$  and equilibrated against ethyl acetate. Centrifuge and discard the wash. Wash twice more, discarding the washes. (The washes remove aqueous entrainments in the ethyl acetate.) Back-extract uranium and plutonium with 10 ml of  $\text{H}_2\text{O}$ , centrifuge, and transfer the aqueous layer to a clean centrifuge tube. Repeat the back-extraction twice more, combining the aqueous layers. Discard the ethyl acetate layer (Note 3).

*Step 4.* Evaporate the aqueous layer to dryness in a heating block. Wash down the walls of the tube with 1 ml of aqua regia and heat to dryness to destroy  $\text{NH}_4\text{NO}_3$ . Add 1 ml of 10M HCl and evaporate to dryness. Add 1 ml of 0.1M  $\text{H}_2\text{SO}_4$ , warm (Note 4), and place the solution on a Bio-Rad AGMP-1, 50 to 100 mesh, anion-exchange resin column that has previously been subjected to three

1-ml  $\text{H}_2\text{O}$  washes and one 1-ml 0.1M  $\text{H}_2\text{SO}_4$  wash. Discard the effluent. Wash the tube with 1 ml of 0.1M  $\text{H}_2\text{SO}_4$  and add the wash to the resin column (Note 5). Discard the effluent. Add 1 ml of 10M HCl containing a trace of  $\text{HNO}_3$  (10 ml of HCl + 1 drop of conc  $\text{HNO}_3$ ) to the column and discard the effluent. Rinse the tip of the column with a stream of deionized  $\text{H}_2\text{O}$ .

*Step 5.* To remove the plutonium remaining on the column, use three successive additions of 9 drops of HI-HCl mixture to reduce that element to the +3 state; collect the eluate that contains plutonium in a 40-ml centrifuge tube. Wash the column with 1 ml of 8M HCl. Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$ .

*Step 6.* Elute uranium with 1 ml of 1M  $\text{HNO}_3$  and 1 ml of conc  $\text{HNO}_3$  and collect the eluate in a 40-ml centrifugal tube.

*Step 7.* The uranium and plutonium samples at this point are not free enough of impurities to permit mass spectrometric analysis by the pulse-counting technique. Each fraction is evaporated to dryness in its centrifuge tube on a heating block. To destroy residual  $\text{I}^-$ , add 1 drop of conc  $\text{HNO}_3$  to the plutonium and evaporate the solution to dryness again. Repeat the evaporation, using 1 drop of 10M HCl. Add 1 ml of the  $\text{H}_2\text{O}_2$ -HCl reagent to dissolve each sample.

*The Uranium Sample:* Place the solution onto a Bio-Rad macroporous AGMP-1, 50 to 100 mesh, anion-exchange resin column that has been subjected to two 1-ml  $\text{H}_2\text{O}$  washes and three 1-ml  $\text{H}_2\text{O}_2$ -HCl reagent washes. Use one additional portion of 1 ml of the  $\text{H}_2\text{O}_2$ -HCl reagent to rinse the centrifuge tube and pass the rinsing through the column. Discard both effluents. Wash the zirconium off the column with 15 drops of 6M HCl. Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$  and elute the uranium with three successive 1-ml portions of deionized  $\text{H}_2\text{O}$ ; collect the eluates in a 40-ml centrifuge tube (Note 6). Transfer enough of the uranium solution

to supply 50 ng of the element to a quartz test tube. Evaporate the solution to dryness in a heating block. Add 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  and heat to  $130^\circ\text{C}$  for 1 h. Evaporate to dryness at a temperature  $>180^\circ\text{C}$ . Cool and cap the quartz tube. The sample is ready for mass spectrometric analysis.

*The Plutonium Sample:* The plutonium fraction still contains too much zirconium to permit mass spectrometric analysis and enough  $^{238}\text{U}$  to affect the determination of  $^{238}\text{U}$ . For purification, pass the  $\text{H}_2\text{O}_2$ - $\text{HCl}$  solution through a macroporous anion-exchange resin column like that used for uranium. Pass 1 ml of  $\text{H}_2\text{O}_2$ - $\text{HCl}$  reagent through the column and wash off the uranium and zirconium with 60 drops of 8M  $\text{HNO}_3$  (Note 7). Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$  and elute the plutonium with three 1-ml portions of 47%  $\text{HBr}$  into a quartz test tube. At this point, an aliquot is removed for alpha assay to ascertain the amount of plutonium that will be supplied for mass spectrometric analysis.

Evaporate the  $\text{HBr}$  solution of plutonium to dryness in a heating block. Destroy the traces of  $\text{HBr}$  and organic material from the remaining macroporous anion resin by adding 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  and heating to  $130^\circ\text{C}$  for 1 h in a heating block. Evaporate to dryness at a temperature greater than  $180^\circ\text{C}$ . Cool and cap the quartz tube. The sample is ready for mass spectrometric analysis.

## Notes

1. The usual size of sample is 10 to 100 mg. If more than 0.33 g of soil is required to meet plutonium requirements, it is suggested that fluoride precipitation, dissolution of the precipitate in  $\text{HCl} + \text{H}_3\text{BO}_3$  solution, and boiling with 9M  $\text{NaOH}$  be carried out as preliminary steps, after *Step 1* has been performed.

2. It is essential to achieve exchange between the tracers and sample atoms. This is accomplished

by allowing the sample plus tracer to evaporate to dryness overnight in a heating block (at  $\sim 110^\circ\text{C}$ ) followed by at least one strong fuming ( $\text{HClO}_4$ ) period over a burner.

3. At this point, the macro soil constituents, sodium, potassium, magnesium, calcium, aluminum, and iron, and most fission products have been removed. The remaining elements are:  $\sim 95\%$  of the uranium,  $\sim 80\%$  of the plutonium,  $\sim 50\%$  of the neptunium, 60 to 80% of the zirconium, and traces of niobium, technetium, ruthenium, tellurium, and iron; of course,  $\text{NH}_4\text{NO}_3$  also remains.

4. When dealing with nanogram quantities of uranium and plutonium, it is advisable to be thorough and patient in dissolving their nitrates from a dry state. Flaming the tubes to dryness should be avoided because the baked oxides formed will stick to the glass and be difficult to remove. Check for removal of  $^{237}\text{U}$  with a radiation meter, if possible.

5. The  $\text{H}_2\text{SO}_4$  is effective in the removal of the remaining  $^{239}\text{Np}$  and the last traces of iron that would interfere with the mass spectrometric measurement. Approximately 5% of the plutonium is washed off with the 0.1M  $\text{H}_2\text{SO}_4$ , but uranium sticks quantitatively. In *Step 4* when the uranium and plutonium are being dissolved in the warm 0.1M  $\text{H}_2\text{SO}_4$ , care must be taken to avoid concentration of the  $\text{H}_2\text{SO}_4$  by evaporation. A 0.5M  $\text{H}_2\text{SO}_4$  can remove 100% of the plutonium and 50% of the uranium. It is necessary to record the time here as the time of separation of plutonium and neptunium. This is also a convenient record of the separation of plutonium and curium, which is achieved here and in the extraction. This permits corrections to the  $^{238}\text{Pu}$  mass peak.

6. The final solution is assayed for  $^{233}\text{U}$  by alpha-counting to determine chemical yield. Also, at this point an aliquot may be removed for  $^{237}\text{U}$  measurement by beta- or gamma-counting.



7. Variations in the uranium, plutonium, zirconium, etc., ratios in the starting samples, as well as slight variances in column preparation, will result in slight differences in the amounts of 8M HNO<sub>3</sub> needed here and in the quantities of 6M HCl required on the macroporous anion resin cleanup column. Therefore, the relative amount of <sup>95</sup>Zr (by means of its 724- and 756-keV gammas) and of <sup>237</sup>U (by means of its 208-keV gamma) should be ascertained with a multichannel pulse height analyzer and the amount of <sup>239</sup>Pu should be determined by alpha-counting. With such information the quantities of column washes may be adjusted to obtain the best level of decontamination.

(October 1989)

# PREPARATION OF PLUTONIUM SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

R. E. Perrin and H. L. Smith

## 1. Introduction

To prepare plutonium samples for mass spectrometric analysis, the basic PLUTONIUM procedure is first carried out. After the element has been counted (*Step 10* of that procedure), it is removed from the platinum disk by repeated treatment with HF and HCl. The acidic solution is fumed to dryness with conc HNO<sub>3</sub> and HClO<sub>4</sub>, and the residue is dissolved in 9M HCl that contains enough H<sub>2</sub>O<sub>2</sub> to keep plutonium in the +6 oxidation state. The plutonium is then placed on a macroporous anion-exchange resin; uranium and iron are also adsorbed. The plutonium is removed from the column by elution with conc HBr; the uranium and iron stay on the column.

## 2. Reagents

HF: 2.7M

HCl: 3M; obtained by diluting National Bureau of Standards (NBS) sub-boiling distilled reagent

9M HCl: The reagent is used to pick up the sample after the HClO<sub>4</sub> fuming step and to rinse the column free of americium. The reagent is prepared by sub-boiling distillation or is purchased from NBS. Just before use, 10 ml of acid containing 1 drop of 30% H<sub>2</sub>O<sub>2</sub> is warmed at ~90°C for 20 to 30 min to ensure the presence of a small amount of free Cl<sub>2</sub>, which prevents reduction of plutonium on the column.

HNO<sub>3</sub>: conc; source: NBS

HClO<sub>4</sub>: conc; source: NBS

8.8M HBr: E. M. 306-7S Suprapur: source:  
E. Merck, Darmstadt, West Germany

Anion-exchange resin: Bio-Rad AGMP-1, 50 to 100 mesh

H<sub>2</sub>O: Use only H<sub>2</sub>O that has been deionized by passing through a Milli-Q H<sub>2</sub>O system.

## 3. Ion-Exchange Column Preparation

Disposable plastic pipette tips are used for ion-exchange columns. These are cleaned by immersion in 8M HNO<sub>3</sub> at 80°C for 48 h. The tips are then rinsed thoroughly with Milli-Q H<sub>2</sub>O and dried by two rinses in glass-distilled acetone. After air-drying in a class 100 clean-air hood, the tips are sealed in batches of 10 in plastic bags for storage.

Quartz wool is cleaned by immersion in 8M HNO<sub>3</sub> at ~80°C for 48 h. After thorough rinsing in Milli-Q H<sub>2</sub>O, the wool is air-dried under a heat lamp in a 100 plus hood. Small portions of the quartz wool are stored in 15-ml plastic vials that have been cleaned in a like manner.

Bio-Rad AGMP-1 resin, 50 to 100 mesh, is prepared by being washed thoroughly in 9M HCl three times. After the resin has settled, the excess HCl is poured off, and the resin is stored under fresh 9M HCl in 30-ml plastic bottles cleaned with 8M HNO<sub>3</sub> (as previously described for the disposable pipette tips).

All transfers are performed using transfer pipettes, which are cleaned by immersion in 8M HNO<sub>3</sub> for 48 h at 80°C. After thorough rinsing with Milli-Q H<sub>2</sub>O, the pipettes are air-dried in a 100 plus hood. The cleaned pipettes are stored in sealed plastic bags in batches of five.

All separations are performed using 13- by 100-mm Pyrex or quartz tubes that have been cleaned by immersion in 8M HNO<sub>3</sub> for 48 h at 80°C. After thorough rinsing with Milli-Q H<sub>2</sub>O, the tubes are air-dried (open end down) in a 100 plus hood. The tubes are then sealed in batches of two in plastic for future use. Pyrex tubes are used for column preparation and americium elution. Quartz tubes are used for the final elution step and boil down.

Prepare the ion-exchange column as follows.

1. Place a small quartz wool plug in the end of a clean plastic pipette tip. The plug should be  $\sim 2$  mm long. A clean transfer pipette tip works well for tamping the plug into the pipette tip.

2. Place a plastic collar over the ion-exchange column. This collar is made by cutting the end of a 3X tapered stopper with a razor blade. A small V is cut in the base of the stopper (see Fig. 1) to prevent formation of an air lock.

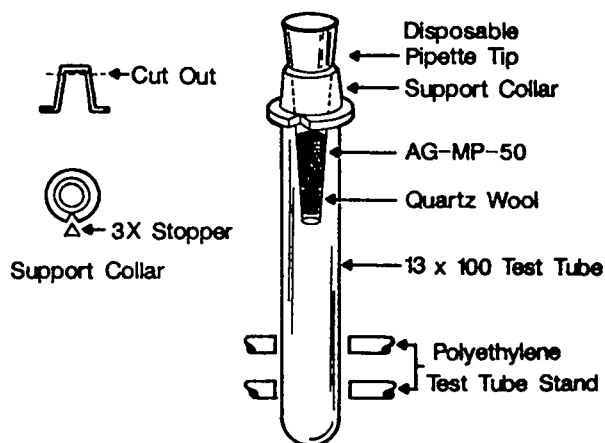


Fig. 1. Details of micro ion-exchange column.

3. Place the pipette tip with collar in a clean 13- by 100-mm Pyrex test tube supported in a plastic test tube rack.

4. Using a clean transfer pipette, transfer enough AGMP-1 resin to form a resin column 1 cm long in the pipette tip.

5. Rinse the resin column with 3 column volumes of 9M HCl containing a trace of free  $\text{Cl}_2$ .

#### 4. Procedure

This procedure assumes that the plutonium sample has been processed through the PLUTONIUM procedure.

*Step 1.* To the platinum disk from *Step 10* of the PLUTONIUM procedure, add sufficient 2.7M HF to cover the spots containing activity. Evaporate the liquid to dryness and add enough 3M (or more conc) HCl to cover the active sites. Warm gently and, by means of a transfer pipette, add the liquid to a Pyrex tube of appropriate size. Repeat the step (both HF and HCl additions) until the desired activity has been removed.

*Step 2.* Add a few drops of conc  $\text{HNO}_3$  and evaporate the solution to a small volume. Then add a few drops of conc  $\text{HClO}_4$  and fume to dryness.

*Step 3.* To the dry Pyrex tube containing the recovered plutonium, add  $\sim 1$  ml of 9M HCl containing a trace of free  $\text{Cl}_2$ . Warm to  $\sim 80^\circ\text{C}$  to ensure dissolution of the plutonium.

*Step 4.* Using a clean transfer pipette, load the solution on an anion-exchange column prepared as previously described. Support the column with a clean 13- by 100-mm Pyrex tube and discard the rinses. (It may be desirable to retain all effluents until the analysis is completed.)

*Step 5.* Using a clean transfer pipette, rinse the column with 5 column volumes of 9M HCl. Allow the fluid level to just reach the resin surface between rinses. This rinse will remove all alkali metals; the last traces of americium, uranium, iron, and plutonium are retained on the column.

*Step 6.* Remove the column from the test tube and thoroughly rinse the tip of the column with 9M HCl to remove the last traces of the impurities.

*Step 7.* Transfer the column to a clean 13- by 100-mm quartz tube. Rinse the column with 5 column volumes of 8.8M HBr. This rinse will elute the plutonium and leave all uranium and iron behind. This step is of particular importance because the presence of iron interferes with subsequent electrodeposition of plutonium.

*Step 8.* Remove and discard the ion-exchange column. Transfer the quartz tube to a heater block at  $\sim 130^{\circ}\text{C}$  and evaporate the solution to dryness using heat and a stream of filtered air.

*Step 9.* Wash down the sides of the tube with 1.0 to 1.5 ml of Milli-Q  $\text{H}_2\text{O}$  and fume to  $\sim 0.5$  ml. Add 3 to 4 drops of conc  $\text{HNO}_3$  and fume to dryness. Add 3 drops of conc  $\text{HClO}_4$  and evaporate to fumes at  $130^{\circ}\text{C}$ . Increase the temperature to  $180^{\circ}\text{C}$  and fume for 1 h, adding  $\text{HClO}_4$  as necessary. Then fume to dryness to ensure destruction of +3 plutonium polymers and oxidation of any organic matter present. The sample is ready for mass spectrometric analysis. After cooling, cap the test tube with a clean 3X plastic stopper (cleaned by immersion in 8M  $\text{HNO}_3$  for 48 h and rinsed with Milli-Q  $\text{H}_2\text{O}$ ). Seal the capped tube in plastic and submit for the mass spectrographic analysis. (The total plutonium submitted should be known to at least 10% to prevent errors in selecting the aliquot size for mass spectrometric analysis.)

(October 1989)

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#### IV. Dissolution Procedures

The Dissolution of Underground Nuclear Debris  
Samples

Hot-Cell Procedures for Dissolving Large Samples  
(up to 1 Kg) of Underground Nuclear Debris

The Dissolution of (A) Bulk Graphite Containing  
Uranium and Niobium

Carbides and (B) Activated Charcoal

# THE DISSOLUTION OF UNDERGROUND NUCLEAR DEBRIS SAMPLES

G. W. Knobloch

## 1. Introduction

The successful dissolution of underground nuclear debris samples depends basically on repeated evaporations with conc HF to convert  $\text{SiO}_2$  and silicates to volatile  $\text{SiF}_4$ . The actual steps in the procedure vary with the size of the sample and the nature of the analysis to be performed. The procedure given below is the one used for dissolving underground debris samples weighing up to 5 g.

## 2. Reagents

$\text{HNO}_3$ : fuming

$\text{HClO}_4$ : conc

HF: conc

HCl: 3M

NaOH: 6M

## 3. Procedure

*Step 1.* Place the dried, pulverized sample in a cylindrical Teflon vessel of  $\sim 700$ -ml capacity. Add 25 ml of fuming  $\text{HNO}_3$ , 100 ml of conc  $\text{HClO}_4$ , and, with care, 50 ml of conc HF. Heat to strong fumes of  $\text{HClO}_4$  on a hot plate (medium setting). The solution process may be accelerated by placing an aluminum jacket around the Teflon container.

*Step 2.* Cool, add another 50 ml of conc HF, and again evaporate to strong fumes of  $\text{HClO}_4$ .

*Step 3.* Repeat *Step 2* twice. (If 10 g of debris are being dissolved, repeat *Step 2* four times; add  $\text{HClO}_4$  as necessary to prevent the sample from becoming dry.)

*Step 4.* Evaporate until the volume is  $\sim 50$  ml, cool, and add 100 ml of 3M HCl. Warm slightly to dissolve any solids.

*Step 5.* Divide the solution among four 40-ml Vycor centrifuge tubes. Wash the Teflon vessel with 3M HCl and add the washes to the centrifuge tubes. Centrifuge for 2 min at 3500 rpm. During the centrifugation wash the Teflon vessel under a stream of  $\text{H}_2\text{O}$ . Rub the inner surfaces well and flush them with  $\text{H}_2\text{O}$  to remove adhering  $\text{SiO}_2$  particles, which may be discarded. The vessel is now ready for re-use in the following step.

*Step 6.* Transfer the supernate to the clean Teflon vessel, add 50 ml each of conc HF and  $\text{HClO}_4$ , and begin heating on a hot plate (medium setting).

*Step 7.* Wash the precipitates in the centrifuge tubes with 3M HCl, centrifuge, and add the supernates to the Teflon vessel on the hot plate.

*Step 8.* To each of the precipitates remaining in the centrifuge tubes add 2 to 3 ml of 6M NaOH and boil while stirring over a burner. Cool, acidify with 3M HCl, bring to a boil and centrifuge. Combine the supernates with those in the Teflon vessel. If more than a few grains of sand and/or any beta-gamma activity remain, repeat the NaOH-HCl treatment until no sand is left or until it is no longer active. (For complete destruction of solids, repeat the sequence of *Steps 2* through *8* until the sand is entirely dissolved.)

*Step 9.* Heat the contents of the Teflon vessel to strong fumes of  $\text{HClO}_4$ . Cool, add 50 ml of conc HF, and evaporate the solution until the volume is  $\sim 50$  ml. Cool.

*Step 10.* Add 100 ml of 3M HCl and warm slightly to dissolve any solid material. Divide the solution among four clean 40-ml Vycor centrifuge tubes and centrifuge at 3500 rpm.

*Step 11.* Filter the supernate through polypropylene "paper" into a labeled, graduated plastic bottle. Wash the Teflon vessel and the centrifuge tubes with 3M HCl, centrifuge, and filter the washes into the plastic bottle. If any precipitate

remains in the centrifuge tubes, add 2 to 3 ml of 6M NaOH and heat over a burner. Cool, neutralize with 3M HCl, centrifuge, and decant the supernate through the filter into the plastic bottle. Repeat the NaOH-HCl treatment if a precipitate still remains in the centrifuge tubes.

*Step 12.* Add 3M HCl to make the concentration of the original sample in solution  $\leq 7.5$  mg/ml. Heat the final solution overnight in a water bath at  $\sim 90^\circ\text{C}$ . (For reasons that are not at all clear, this heat treatment gives a sample solution that may be analyzed satisfactorily. Without such treatment, results may be erratic.)

(October 1989)

# HOT-CELL PROCEDURE FOR DISSOLVING LARGE SAMPLES (up to 1 kg) OF UNDERGROUND NUCLEAR DEBRIS

J. W. Barnes

## 1. Introduction

This procedure is designed for the recovery of zirconium, niobium, the lanthanides, and the actinides from samples (up to 1 kg in size) of debris from underground nuclear explosions. The samples are siliceous and have a wide range of particle size. The initial step in the separation is a leaching with conc HF at room temperature. This step is followed by removal of  $\text{SiO}_2$  by reaction with HF at  $\sim 0.25$  atm of pressure and a temperature near the boiling point of  $\text{H}_2\text{O}$ . The resulting fluoride slurry is centrifuged to separate the insoluble lanthanide and actinide fluorides from zirconium and niobium, which are in the form of soluble fluoride complexes. The insoluble fluorides are then treated with fuming  $\text{HNO}_3$  and conc  $\text{HClO}_4$ , and the mixture is evaporated to dryness. The residue is dissolved in dilute  $\text{HNO}_3$ .

All operations are carried out in a hot cell by using manipulators.

## 2. Reagents

HF: conc; gas  
 $\text{HNO}_3$ : 90% (yellow fuming); 1M  
 $\text{HClO}_4$ : 70%  
LiOH: 3.5M aqueous solution

## 3. Procedure

The procedure is carried out on debris samples that have undergone a preliminary treatment of (1) washing with  $\text{H}_2\text{O}$  to remove drilling mud, (2) selection of the portions of high specific activity, and (3) drying and grinding.

*Step 1.* Add the sample ( $\sim 250$  g; Note 1) to a polypropylene dissolver and gas chamber

(Fig. 1; Notes 2 and 3). Then, add 600 ml of conc HF in 50-ml portions over a 15-min interval. When the final portion has been added, bubble gaseous HF vigorously into the sample slurry at room temperature and under a slight vacuum ( $\text{H}_2\text{O}$  aspirator.)

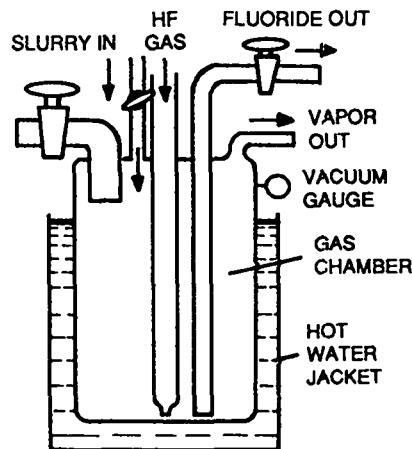


Fig. 1. Dissolver and gas chamber.

*Step 2.* After 15 minutes, begin to heat the  $\text{H}_2\text{O}$  jacket surrounding the chamber and decrease the pressure to  $\sim 0.25$  atm. While the HF flow is maintained, rapidly raise the temperature of the  $\text{H}_2\text{O}$  in the jacket to its boiling point. Permit the vapor effluent from the dissolver and gas chamber to pass first through an empty polypropylene pot and then into a pot containing 3.5M aqueous LiOH; this pot is connected to an  $\text{H}_2\text{O}$  aspirator. The HF treatment is carried out for 1 h.

*Step 3.* By air pressure, transfer the thin fluoride slurry into a 1-l polypropylene centrifuge bottle (Fig. 2). Centrifuge for  $\sim 10$  min (Note 4). Pour off the supernate containing the zirconium and niobium into a 2-l Teflon beaker. Wash the precipitate twice with  $\sim 0.75$  l of  $\text{H}_2\text{O}$ ; add the first wash to the supernate containing the zirconium and niobium and discard the second. The washing is effected by stirring with a high-speed plastic stirrer (Fig. 2).



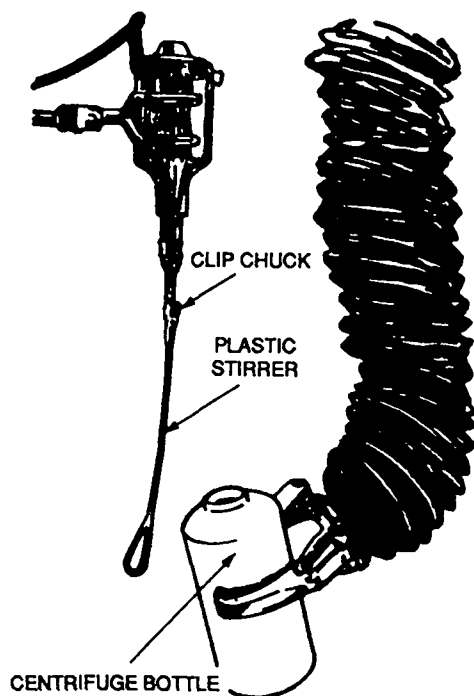


Fig. 2. Centrifuge bottle and stirrer.

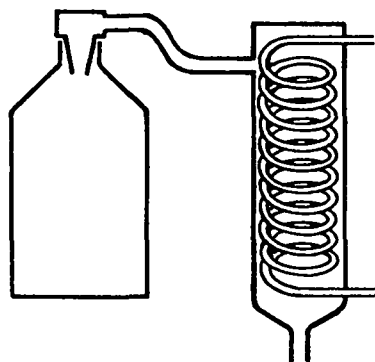


Fig. 3. Teflon evaporation equipment.

*Step 4.* Add 160 ml of 90%  $\text{HNO}_3$  and 240 ml of 70%  $\text{HClO}_4$  to the precipitate and stir. Pour the slurry into a 0.6- $\ell$  Teflon evaporation bottle (Fig. 3; Note 5). Evaporate the slurry to dryness by heating the bottle on a hot plate. The evaporation may be accelerated by wrapping aluminum around the bottle and introducing a stream of heated air into the bottle through an opening in the tapered Teflon joint. The evaporation process is complete when droplets of condensate no longer appear in the Kel F connecting tube. Cool the dry solid and separate the evaporation bottle at the tapered joint. Add 700 ml of 1 M  $\text{HNO}_3$  and stir magnetically to effect solution.

## Notes

1. Appropriate scale-up of quantities of reagents and sizes of equipment is made for larger samples.

2. The concentrated acids used in the procedure—conc HF, 90%  $\text{HNO}_3$ , and 70%  $\text{HClO}_4$ —are extremely corrosive. Polypropylene reaction vessels are suitable for use with these acids at room temperature and with conc HF at elevated temperatures; they are much more desirable than vessels constructed from polyethylene. Polypropylene has a higher working temperature limit and greater strength than polyethylene.

3. Specific details regarding the construction and operation of this piece of equipment and the others used in the procedure are described by J. W. Barnes.

4. A floor model centrifuge was modified by removing the base and cutting  $\sim 6$  in. from the top. It was equipped with a special head (source: International Equipment Company) for holding four 1- $\ell$  bottles.

5. Bottles of 0.6- to 2- $\ell$  capacity were used, depending upon the size of the original sample. They were equipped with a tapered Teflon joint and a Kel F connecting tube to the Teflon condenser shown.

## Reference

J. W. Barnes, *Proceedings of the 18th Conference on Remote Systems Technology*, American Nuclear Society (1970).

(October 1989)

# THE DISSOLUTION OF (A) BULK GRAPHITE CONTAINING URANIUM AND NIOBIUM CARBIDES, AND (B) ACTIVATED CHARCOAL

J. W. Barnes

## Introduction

The procedures described are designed for dissolving graphitic carbon containing fission products.

Bulk graphite containing both uranium carbide (which can be present in beads that are coated with pyrolytic graphite) and niobium carbide is brought into solution by wet ashing with 70%  $\text{HClO}_4$  in the presence of a small amount of  $\text{CrO}_3$ . Two points in the dissolution of the bulk graphite merit special mention. When heat is not removed from the graphite with sufficient rapidity, the dissolving process may accelerate to an uncontrollable rate and an explosion may occur. This condition results when the gases evolved interfere with heat exchange between the solid and the acid. The explosion hazard may arise early in the dissolving process either from the presence of a few chunks of graphite that have not yet disintegrated to powder form or from the use of too large a sample relative to the quantity of acid. Danger of explosion may also arise late in the dissolving process if the acid becomes so depleted that the mixture approaches dryness.

The second point to note is the possible loss of significant quantities of fission products, which may be entrained in droplets of solution that are carried away by the  $\text{CO}_2$  liberated in the dissolving process. This possibility is avoided through the use of a device for separating the droplets from the  $\text{CO}_2$  and returning them to solution.

Activated charcoal is first partially ignited in  $\text{O}_2$  and then dissolved in 90%  $\text{HNO}_3$  and 70%  $\text{HClO}_4$ . The ignition is performed because wet ashing of activated charcoal without such treatment is hazardous and may result in violent explosions.

Wet ashing is even more hazardous if carried out in the absence of 90%  $\text{HNO}_3$ .

## (A) Dissolution of Bulk Graphite That Contains Uranium and Niobium Carbides

### 1. Reagents

$\text{HClO}_4$ : 70%  
 $\text{HNO}_3$ : 90% (yellow fuming)  
HF: conc  
 $\text{HCl}$ : 6M  
 $\text{HCl-HF}$  solution: 4M in  $\text{HCl}$  and 0.3M in HF  
 $\text{CrO}_3$  solution: aqueous, 0.5 g/ml  
Activated charcoal

### 2. Remarks on Equipment

The apparatus used is depicted in Fig. 1. The dissolving flask is made of Vycor, which is resistant to thermal shock and much less reactive toward aqueous HF than is Pyrex. The baffles stop and return gas-carried liquid to the dissolving flask. The activated charcoal trap collects any volatile radioactive iodine species.

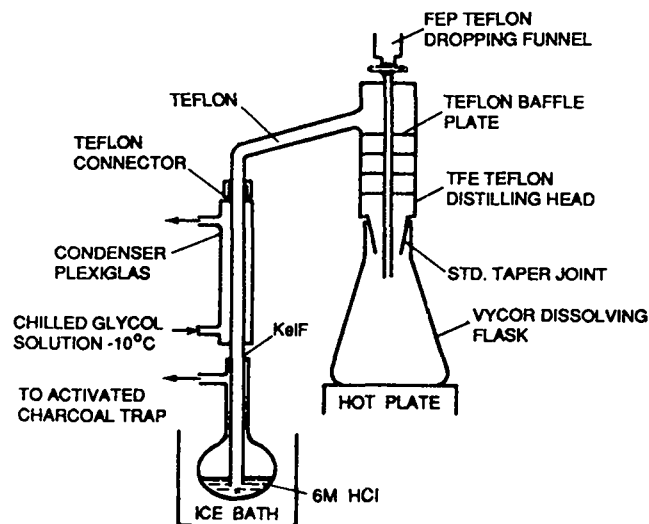


Fig. 1. Dissolution apparatus.

### 3. Procedure

*Step 1.* Place a 0.5-in. slice of sample (~6 g) in a Vycor flask equipped with a magnetic stirrer bar. Add 1 ml of  $\text{CrO}_3$  and 150 ml of 70%  $\text{HClO}_4$  (Note). Connect the flask to the condenser apparatus. The condenser trap should contain ~40 ml of 6M HCl; that is, enough to cover the outlet tube. Boil for ~1 h. Cool to ~100°C and add 10 ml 90%  $\text{HNO}_3$  slowly through the dropping funnel.

*Step 2.* Bring the solution again to a boil and continue boiling. The sample should be a reddish color ~2 h after the addition of  $\text{HNO}_3$ . There will probably be black specks of zirconium or niobium carbide present at this point. Boil for 2 h after the reddish color appears.

*Step 3.* Cool to near room temperature, disconnect the flask from the condenser, and add about half of the 6M HCl from the condensation trap. Reconnect the flask to the condenser and start warming and stirring. Add ~5 ml of conc HF through the dropping funnel. If the reaction appears to be too vigorous, which could result in loss of sample, it may be necessary to cool the flask. As the reaction permits, continue stirring and warming the solution; add HF as needed to dissolve the black particles.

*Step 4.* When the solution is clear and there is a white precipitate in the bottom of the flask, cool the solution and decant the clear supernate into a 500- or 1000-ml plastic volumetric flask. If a plastic volumetric flask is not available, the cool solution may be made up to volume in a Pyrex volumetric flask and then transferred to a plastic bottle for storage.

*Step 5.* Try to dissolve the white solid in the bottom of the flask with  $\text{H}_2\text{O}$ ; add a little HF and warm if necessary. If all the white solid does not dissolve, it may be necessary to repeat the procedure.

*Step 6.* Add the distillate in the cold trap to the volumetric flask. Rinse the cold trap and the dissolving flask with 10 to 15 ml of HCl-HF solution and add the rinse to the volumetric flask. Mix the contents of the volumetric flask and make up to volume; mix thoroughly. The solution is now ready for fission-product analysis.

### (B) Dissolution of Activated Charcoal

#### 1. Reagents

$\text{HClO}_4$ : 70%  
 $\text{HNO}_3$ : 90% (yellow fuming)  
HCl: 4M  
 $\text{O}_2$  gas: pure, tank

#### 2. Procedure

*Step 1.* In a fume hood, place 20 to 50 g of sample in a 1500-ml Vycor beaker; cover the beaker with a Pyrex watch glass that has a hole in the center for a glass tube of 5- to 6-mm o.d., which connects to an  $\text{O}_2$  tank. Heat the bottom of the beaker to raise the temperature of the sample to ~600°C. Pass  $\text{O}_2$  slowly over the sample and continue heating for 2 h. (Too rapid an  $\text{O}_2$  flow will blow solid oxide products from the beaker. It is not necessary that combustion be complete.)

*Step 2.* Add 50 ml of 90%  $\text{HNO}_3$  and 100 ml of 70%  $\text{HClO}_4$ . Boil on a hot plate while adding 50 ml of  $\text{HNO}_3$  dropwise into the mixture through the hole in the watch glass. Continue boiling for 20 min after a clear solution is obtained. (The total time of *Step 2* is 1 to 1.5 h. There may be a few chunks of unreacted sample present at the end of that time.) Cool the solution. At this point some salts may precipitate.

*Step 3.* Add 20 ml of 4M HCl to complex Fe(III) and enough  $\text{H}_2\text{O}$  to bring the volume to ~40 ml. Filter into a 500-ml volumetric flask and make up to volume with  $\text{H}_2\text{O}$ . The solution can now be analyzed for fission products.

## Note

It would not be necessary to add the  $\text{CrO}_3$  initially if it were possible to add the fuming  $\text{HNO}_3$  at that time. If  $\text{HNO}_3$  is added initially with the  $\text{HClO}_4$ , the reaction proceeds smoothly at first, but when the greenish fumes characteristic of  $\text{Cl}_2$  are replaced by the white fumes of  $\text{HClO}_4$ , enough pressure is generated in the system to blow the sample into the condenser or explode the equipment.

(October 1989)

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## V. Geochemical Procedures

A System for the Separation of Tritium and Noble Gases from Water Samples

The Separation of Iodine for Neutron Activation Analysis of Iodine-129 in Large Aqueous Samples

Analysis of Lead and Uranium in Geologic Materials by Isotope Dilution Mass Spectrometry

Determination of Ferrous Iron and Total Iron in Silicate Rocks

A Batch Method for Determination of Sorption Ratios for Partition of Radionuclides between Ground Waters and Geologic Materials

A Technique for the Measurement of the Migration of Radioisotopes through Columns of Crushed Rock

# A SYSTEM FOR THE SEPARATION OF TRITIUM AND NOBLE GASES FROM WATER SAMPLES

J. W. Barnes, M. A. Ott, and J. L. Thompson

## 1. Introduction

This system was developed to measure tritium (both as HTO and HT) and noble gases (krypton and xenon) present in water samples. In its current use, described here in detail, the only noble gas measured is krypton. The system consists of two parts—a collector of tritium and the noble gases and a separator of the latter. In the collector part of the system, all the tritium is retained as HTO and the noble gases are isolated in a zeolite molecular sieve trap. In the separator part of the system, the krypton is separated from the other noble gases, purified, and collected in a counter tube. A functional diagram of the vacuum system is shown in Fig. 1(a) and a detailed scheme is provided in Fig. 1(b).

This procedure gives a general overview of the functioning of this system, describes specific components of the system, and provides a detailed procedure for sample handling.

## 2. System Function

A portion of the water sample to be analyzed is distilled into the first water trap on the collector side of the system. Tritium initially present as HTO in the sample is detected in this trap. Tritium present in the sample as HT passes through this system to the CuO, where it is oxidized to HTO and collected in the second water trap. Known amounts of krypton and xenon are introduced into the water sample to act as carriers for the small quantities of noble gases that are dissolved in the sample. These carriers are also used for quantitative measurement of losses during gas handling. The noble gases pass through the system to the molecular sieve collection trap. Reactive gases such as O<sub>2</sub> and N<sub>2</sub> are removed by the titanium getter. Movement of gases and

vapors in the collector part of the system is by cryogenic pumping; the diffusion pump and forepump serve only to establish a good vacuum before the sample is introduced.

In the separator part of the system, the noble gases are collected under vacuum in a trap at liquid helium temperature and, with their helium carrier, are transported through the remainder of the system. The argon, krypton, and xenon elute sequentially from a charcoal trap as its temperature is raised. The elution of argon and krypton is monitored by a thermal conductivity detector. Argon is expelled from the system, krypton is retained, and the xenon later is pumped away. After a purification step that uses a titanium getter, the krypton pressure is measured in a bulb of known volume. Finally, krypton is condensed into a small counter tube in which the <sup>85</sup>Kr activity may be measured. The diffusion pump and forepump evacuate the traps between sample analyses.

## 3. Equipment

The major components of the collector and separator parts of the system are described below, and some operating conditions are specified. Some components (such as gauges, traps, and another thermal conductivity cell) present on the vacuum line are not discussed here because they are not used in the tritium/noble gas analyses. A brief description is given of an auxiliary vacuum line that fills the carrier gas bulbs.

### A. Collector

High-pressure water bottles: These contain the water samples (~2 ℓ) obtained under vacuum at depth in a well or from the surface.

Carrier gas bulbs: A set of bulbs of known volume (~12 ml each) filled sequentially with xenon and krypton at measured pressure and temperature.

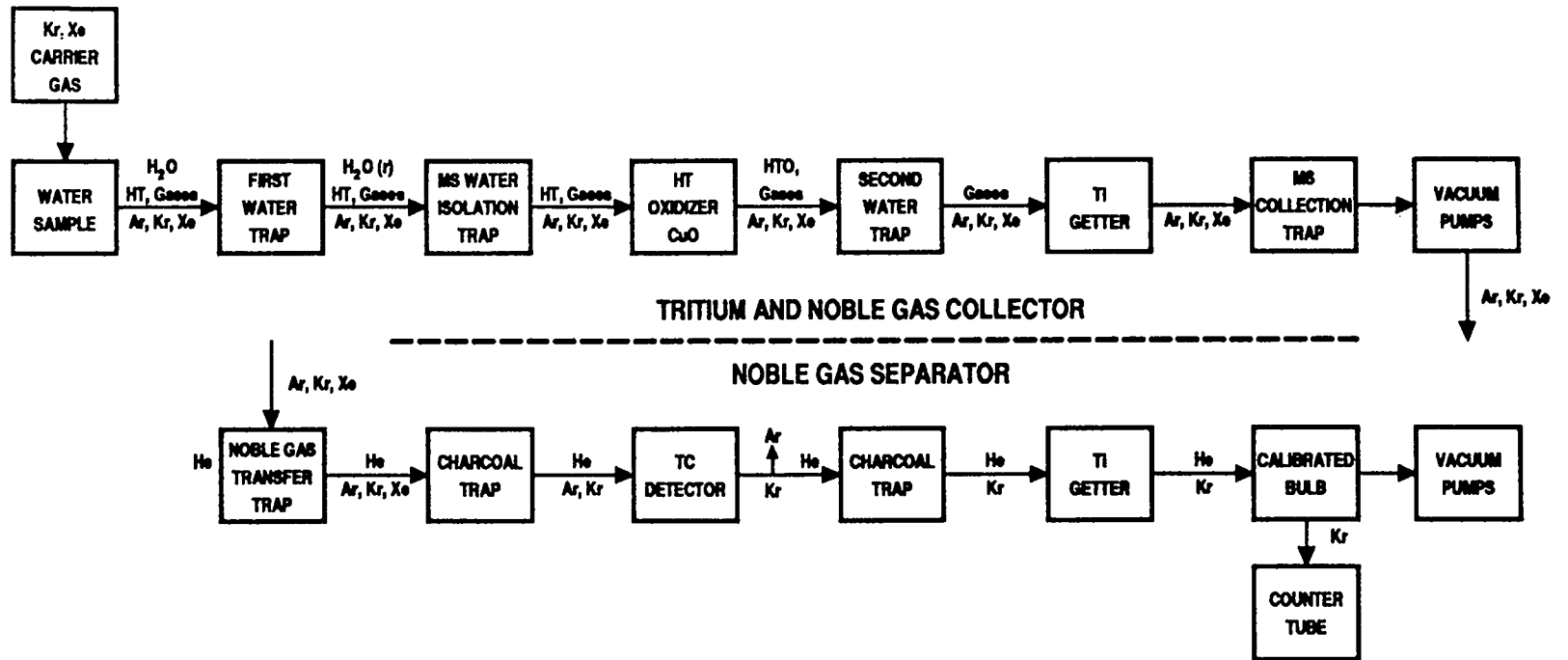


Fig. 1(a). Functional diagram of vacuum system.

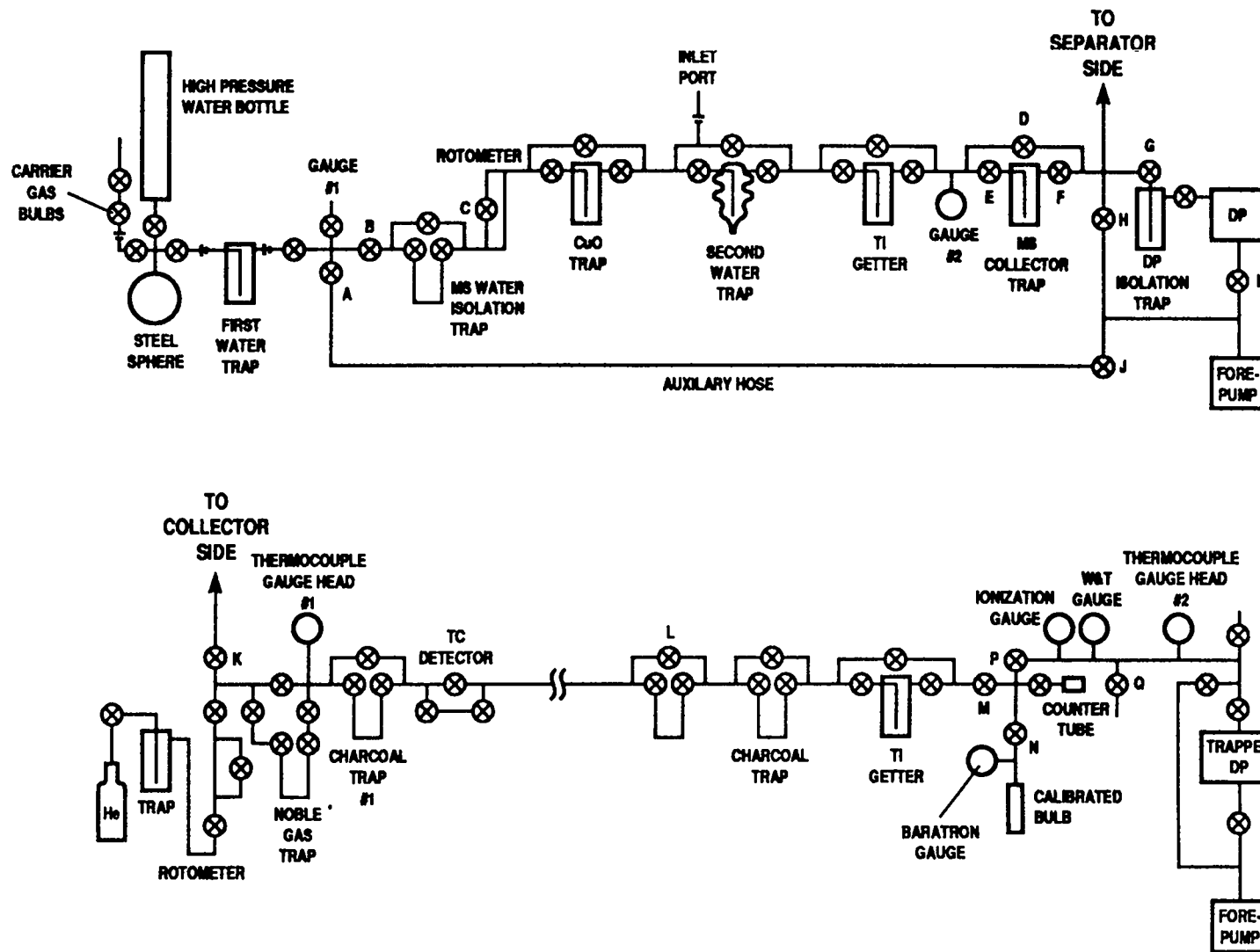


Fig. 1(b). Detailed scheme of both the collector side and the separator side of the vacuum system.



Steel sphere: The 15-ℓ container from which the water sample distills. Two spheres are available; No. 2 is used for samples likely to have high activity levels.

Water traps: Glass traps used to condense H<sub>2</sub>O and HTO vapor. They are cooled to -90°C with a dry ice-isopropyl alcohol slush.

Gauge No. 1: Thermister vacuum gauge, General Electric, Model 22GT.

Molecular sieve (MS) water-isolation trap: MS, Linde 4A,  $\frac{1}{16}$ -in. pellets, cooled with ice water to 0°C.

Rotometer: Fischer and Porter Co., catalogue No. 3654108, bottom ball stainless steel (ss).

CuO trap: For oxidation of HT to HTO at an operating temperature of 450°C.

Titanium getter: For reaction with N<sub>2</sub>, O<sub>2</sub>, etc., at an operating temperature of 900 to 1000°C.

Gauge No. 2: Hastings Vacuum Gauge, Model VT-5.

MS collector trap: MS, Linde 4A,  $\frac{1}{16}$ -in. pellets, cooled with liquid nitrogen to -196°C.

Diffusion pump isolation trap: Glass trap to remove oil vapor escaping from the diffusion pump, cooled with liquid N<sub>2</sub> to -196°C.

Diffusion pump (DP): Oil diffusion pump, Bendix, Type PMCS-2C, water-cooled.

Forepump: Welch Duo Seal, Model 1402.

## B. Separator

Helium supply: Tank helium is bled into the system through a molecular sieve (Linde, 4A,  $\frac{1}{16}$ -in. pellets), is cooled in the trap with liquid N<sub>2</sub> to -196°C, and flows through a rotometer (Fischer and Proctor Co., catalogue No. 3654108).

Noble gas trap: This stainless steel uranium-trap is cooled with liquid helium to -268°C.

Charcoal traps: These glass U-traps were made in the Laboratory glass shop, and replacements are on hand. The traps are filled with 40 to 60 mesh activated charcoal.

Thermal conductivity (TC) detector: Thermal conductivity detector head, Model 10-285, and power supply, Model 40-001, Gow-Mac

Instrument Co. The attached chart recorder is a Hewlett-Packard Model 7127A. The power supply is operated at 225 mA in the 0- to 10-V range at a sensitivity of 16. The chart recorder is run at 0.25 in./min.

Titanium getter: For reaction with N<sub>2</sub>, O<sub>2</sub>, etc., at an operating temperature of 900 to 1000°C.

Calibrated bulb: The volume is 81.2 ml.

Baratron gauge: This gauge, manufactured by MKS Instruments, consists of a meter head, Type 145 AHS-100, an electronics unit, Type 170M-6, a head selector, Type 170M-34, and a digital readout, Type 170M-27. Set the head range on the readout unit at 100, and the head selector switch in position 1. On the electronics unit, set the range multiplier to "Null" and adjust the potentiometer with a screwdriver until a zero reading is obtained. Turn the range multiplier to "F.S.," and adjust until a reading of 10 000 is obtained. Turn the range multiplier to ".01" and adjust the zero potentiometer located under the head selector switch to get a zero reading. Turn the range multiplier switch to "1". The unit is now ready. This procedure should be followed after the system has warmed up for at least 1 h.

Ionization gauge: Veeco Instruments, Model RG-830.

W&T gauge: Wallace and Tiernan gauge; reads 0 at atmospheric pressure.

Thermocouple gauge: Bendix, Type GTC-100. The sensor heads for this gauge are mounted at each end of the collector part of the system.

Counter tube: This metal cylinder is fitted with an O-ring valve, beryllium window, and attachment point for a chiller bar. An auxiliary heat reservoir (an aluminum cylinder containing ethanol) is attached to the counter tube while krypton is being condensed in the tube by cooling the chiller bar with liquid helium.

Trapped DP: This watercooled oil diffusion pump, CVC Products, Inc., Type PMCS-2C, has an integral cold trap for liquid N<sub>2</sub>.

Forepump: Welch Duo Seal, Model 1402.

## C. General Comments on the Vacuum Line

All operations are greatly accelerated if the vacuum line is free from sorbed material—especially H<sub>2</sub>O vapor from the atmosphere. The line should be evacuated immediately after use and kept evacuated when not in use. Closing valves that connect sections of the line can prevent contamination of the whole line if an accident or leak occurs in one section. The forepumps should attain a vacuum of  $4 \times 10^{-2}$  torr or less, and the diffusion pumps, a vacuum of  $10^{-5}$  torr or less. A diffusion pump should not be operated at pressures greater than  $10^{-1}$  torr for longer than a few minutes. A liquid N<sub>2</sub> trap should be installed to isolate the pump and prevent pump oil from contaminating the vacuum line. Water should be circulated through a diffusion pump when it is operating. When trap furnaces are hot, the cooling fans should be directed on the glass valves above them.

## D. Auxiliary Vacuum Line

This vacuum line is used to fill the carrier gas bulbs. Important components include a forepump, Hastings vacuum gauge, Baratron gauge, and bottles of compressed xenon and krypton. After pumping down the system and carrier gas bulbs to ~40 torr, zero the Baratron gauge. (This unit is exactly like the one described in the equipment section, except that the head range is 1000 torr.) Close off the forepump and Hastings vacuum gauge, and fill the line with xenon to a pressure of ~50 torr. Record this value, close the lower carrier gas bulb, and pump out the line again. Record the temperature. Repeat the filling process, this time filling the upper bulb with krypton to a pressure of ~100 torr. Record this value; then transfer the carrier gas bulbs to the collector side of the main vacuum line. Pump out the auxiliary vacuum line and turn off the gauges.

## 4. Procedure

### A. Preparation for an Analysis

*Step 1.* Shut the valves to the CuO, the titanium getter, and the MS collector traps and open their by-pass valves. Set the furnace at the CuO trap at 450°C and the one at the titanium getter trap at 900 to 1000°C. Also, set an auxiliary furnace at 450°C.

*Step 2.* Check the system vacuum. Attach the carrier gas bulbs and the high-pressure water bottle to the steel sphere; open all valves from the sphere to the forepump. If the system vacuum is less than  $10^{-1}$  torr as read on gauges No. 1 and 2, turn on the diffusion pump. Close valve H, open G, open I, and make sure that cooling water is circulating through the pump.

*Step 3.* Place coolants on the various traps as indicated:

First water trap: dry ice—*isopropyl alcohol* slush  
MS water-isolation trap: ice water  
Second water trap: dry ice—*isopropyl alcohol* slush  
MS collector trap: liquid N<sub>2</sub>  
DP isolation trap: liquid N<sub>2</sub>

*Step 4.* Isolate the second water trap by closing the appropriate valves. Add 500  $\lambda$  of ionized water to the inlet port and, by opening the valves to the trap, permit the water to enter the trap. Make certain that the valves to all traps and to the titanium getter are open to the line and that all trap by-pass valves are closed.

### B. Separation of Tritium from the Noble Gases

*Step 1.* When the traps (either heated or cooled) have reached their proper operating temperatures and the line vacuum is at  $<10^{-1}$ -torr pressure, close valve B and open the high-pressure water bottle to the sphere. When the sample has been

transferred (and pressure is no longer rising at gauge No. 1), open the valves connecting the carrier gas bulbs to the sphere, thus adding the carrier gases to the water sample.

*Step 2.* Close off valve G to the DP, open the MS collector trap (valve E open; D and F closed), and bleed the sample and carrier gases through valve B with a 20-ss flow rate through the rotometer. Within  $\sim 5$  min, the flow rate will diminish sufficiently so that valves B and C can be opened completely. The sample has been separated into tritium and noble gas fractions when the pressure at gauge No. 1 has fallen to  $\sim 7 \times 10^{-2}$  torr, or after  $\sim 1.5$  h. If the sphere is warmed somewhat, separation may be accelerated, but the pressure at gauge No. 1 will approach  $2 \times 10^{-1}$  torr and much more  $H_2O$  will be collected in the first  $H_2O$  trap than if separation had been effected at room temperature.

### C. Transfer of the Noble Gases to the Separator Part of the System

*Step 1.* Close the inlet to the MS collector trap to isolate the noble gases.

*Step 2.* Close the inlet to the CuO trap, and pump out the titanium getter and CuO traps with the DP (valves D and G are open; H is closed). The pressure on gauge No. 2 should rapidly approach  $2 \times 10^{-3}$  torr, at which point, close off the inlet and outlet valves of the CuO and titanium getter traps, open both by-pass valves, and turn off the CuO and titanium getter trap furnaces. Remove the coolants from the first water trap, the MS water-isolation trap, and the second water trap.

*Step 3.* Open valve K, the cross-over valve to the separator part of the vacuum line, and make certain that the system up to charcoal trap No. 1 is pumped down to a pressure of  $10^{-3}$  torr on gauge No. 2 and thermocouple gauge head No. 1.

*Step 4.* To transfer the collected noble gases, close off valve G to the DP, close the titanium getter

by-pass valve, drop the liquid  $N_2$  coolant from the MS collector trap, and place an auxiliary furnace (maintained at  $450^\circ C$ ) on this trap. Precool the noble gas trap with liquid  $N_2$ , and then place a Dewar that contains liquid helium about three-fourths the way up on the trap. Gauge No. 2 and thermocouple gauge head No. 1 will show the pressure rise and fall as the gas mixture condenses into the trap. When the pressure falls to  $\sim 2 \times 10^{-2}$  torr, move the helium-containing Dewar all the way up on the trap to ensure that the last of the gases is collected; then close the valves on the trap.

*Step 5.* Using the DP, pump out the MS collector trap to a pressure of  $10^{-2}$  torr, close the valves to the trap, and remove the auxiliary furnace. Place the furnace, maintained at  $450^\circ C$ , on the MS water-isolation trap.

### D. Removal of Collected Water

*Step 1.* Isolate the second water trap by closing the by-pass valves of the CuO and titanium getter traps. Remove the valves of the trap; use 5 ml of deionized water in a syringe to rinse both ports. Withdraw the  $H_2O$  to a labeled bottle, rinse the trap with  $\sim 5$  ml of ethanol, discard the rinse, and replace the valves. Open this portion of the vacuum line to the DP. It should pump down quite quickly.

*Step 2.* Open the line to the MS water-isolation trap and begin pumping it out. Connect the heater tapes on the metal tubes next to the first water trap.

*Step 3.* Remove the first water trap, measure the volume of water collected, and transfer it to a labeled bottle. Rinse the trap thoroughly with deionized  $H_2O$ , leave a drop of rinse in the trap, and reattach it to the vacuum line. Attach a plug to the inlet port of the trap, and open valves to connect that trap to the MS  $H_2O$  isolation trap. Momentarily close off the DP (valve G) and pump out the system through the forepump (open valve H). Heat the drop of  $H_2O$  in the first  $H_2O$  trap

to speed evaporation. Resume pumping with the DP. After the pressure in the system drops to  $10^{-2}$  torr, close the valves to the MS water-isolation trap, and remove and turn off the auxiliary furnace. Disconnect the heater tapes on the metal tubes adjacent to the first H<sub>2</sub>O trap.

### E. Cleanup of the Sphere

*Step 1.* Turn on the heater hat under the steel sphere. Remove the carrier gas bulbs and then the high-pressure H<sub>2</sub>O bottle. (This bottle should be rinsed with deionized H<sub>2</sub>O before reuse.) Measure the volume of H<sub>2</sub>O in the sphere and transfer the H<sub>2</sub>O to a labeled bottle. Rinse the sphere thoroughly with deionized H<sub>2</sub>O, and leave  $\sim 1$  l of H<sub>2</sub>O in it. Return the sphere to the heater hat and, while its inlet and outlet valves are closed, heat the sphere until it is quite hot to the touch. Carry the sphere outdoors and open the inlet valve to allow H<sub>2</sub>O and steam to escape. Collect a sample of the H<sub>2</sub>O in a small bottle for measurement of tritium background. When the sphere is empty, return it to the heater hat and attach it to the vacuum line.

*Step 2.* At this point, the vacuum line may be partially by-passed and the sphere may be pumped directly by the forepump. Close valve B and valves H and I at the forepump. Open valve J and close all valves to components not directly in the flow path from the sphere to the auxiliary hose attached at A. (The auxiliary hose connects valves A and J.) Open valve A and begin pumping down the sphere. After the forepump stops gurgling (a few minutes), reopen valve I. The sphere should be kept hot to the touch for at least 1 h. When the pressure of the system approaches  $5 \times 10^{-1}$  torr at gauge No. 1, close valves A and J and begin pumping with the DP. When the gauge reads  $<10^{-1}$  torr, close the sphere outlet valve, then the outlet valve to the first water trap, and, successively, other valves along the vacuum line; this will isolate sections of the collector side.

### F. Separation of Krypton

*Step 1.* Prepare a chloroethene-N<sub>2</sub> slush bath ( $-33^{\circ}\text{C}$ ) and place liquid N<sub>2</sub> coolants on the two charcoal traps. (Chloroethene is 1,1,1 trichloroethane, also known as methyl chloroform.) Turn on the two furnaces set to operate at  $450^{\circ}\text{C}$ , the furnace for the titanium getter trap for 900 to  $1000^{\circ}\text{C}$ , and the cooling fan.

*Step 2.* Make certain that the separator side of the vacuum system has been pumped out (that is,  $<10^{-4}$  torr) with the DP, close the inlet valve to the DP, and turn off the ionization gauge.

*Step 3.* Adjust valves so that helium can flow through charcoal trap No. 1, flow through the TC detector, by-pass charcoal trap No. 2, by-pass the titanium getter, and flow through valves M and P.

*Step 4.* Turn on the helium flow at the tank; be sure that the route of the gas is through the cold trap, the reference side of the TC detector, and then the rotometer. Adjust the flow rate at the rotometer to ss 20, and watch the pressure increase at the W&T gauge. When this gauge reaches 0, open valve Q and allow the helium to vent from the line. Briefly open the inlet to charcoal trap No. 2 and allow it to fill with helium, then close the inlet.

*Step 5.* While the helium is flowing through the rotometer at ss 20, turn on the TC detector power supply (0 to 10 V, 225 mA) and the chart recorder (0.25 in./min).

*Step 6.* Route the flow of helium through the noble gas trap by opening the valves to the trap and closing the by-pass valve. The krypton has now been transferred to charcoal trap No. 1.

*Step 7.* Replace the liquid N<sub>2</sub> on charcoal trap No. 1 with the chloroethene-liquid N<sub>2</sub> slush; mark the time on the chart paper. Argon will be eluted in  $\sim 1$  min; krypton in 4 to 5 min. After the argon has been eluted, but before the krypton appears,

open the inlet and outlet valves to charcoal trap No. 2, and close the by-pass valve. After the krypton is eluted, turn off the chart recorder and the TC detector power supply. Then close valve Q to immediately stop the helium flow at the tank. An elution curve for argon and krypton has the appearance shown in Fig. 2.

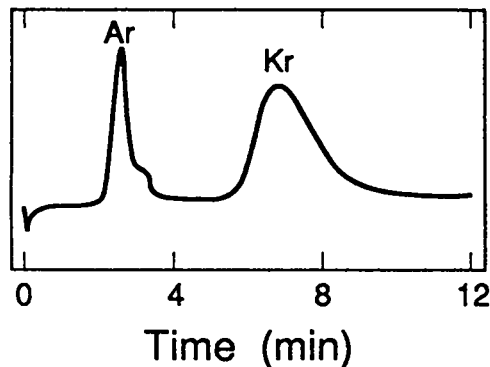


Fig. 2. Elution curve for argon and krypton.

*Step 8.* Close valve L and pump out the line beyond this point by using first the forepump and then the DP. The pressure is indicated on the ionization gauge. (At this stage, replace the slush bath on charcoal trap No. 1 with a furnace at 450°C, and use the DP on the collector side of the vacuum line to pump out the line up to valve L. This procedure speeds up the final pumpdown on the separator side of the line.)

### G. Measurement of Krypton

*Step 1.* Zero the Baratron gauge. Close valve P, open the valves to the titanium getter trap, and close that trap's by-pass valve. Place a furnace set at 450°C on the second charcoal trap. The krypton pressure may be observed on the Baratron gauge.

*Step 2.* Precool the calibrated bulb with a liquid N<sub>2</sub> bath and then immediately position a Dewar with liquid helium about three-fourths of the way up the bulb.

*Step 3.* When the Baratron gauge stops falling, move the Dewar as high as possible, close valve M, open valve P, and pump any remaining helium out of the line. The Baratron gauge should now read 0. Close off the calibrated bulb (valve N), and warm the calibrated bulb with a room-temperature H<sub>2</sub>O bath. Record the temperature and the gauge reading.

*Step 4.* Pump out the counter tube and then close valve P. Check to make sure valve M is closed. Open valve N to the calibrated bulb and record the new reading of the Baratron gauge.

*Step 5.* Place the chiller bar on the counter tube and precool the tube with liquid N<sub>2</sub>. Attach the heat sink and add a little ethanol to it. Quickly place the Dewar with liquid helium on the chiller bar. When the Baratron gauge stops falling, record the reading and close the counter tube. Remove the chiller bar and heat sink, detach the counter tube from the vacuum line, and submit the tube for counting.

*Step 6.* Attach another counter tube to the vacuum line, and pump it down with the DP. Open the titanium getter and charcoal trap No. 2 to the DP. When the pressure falls to <10<sup>-4</sup> torr, these units may be valved shut and their furnaces turned off. When the collector part of the system has been pumped down, turn off the DP, ionization gauge, and thermocouple gauge. Close valves along the collector side of the vacuum line to isolate sections. Check to make sure all furnaces are off; turn off the cooling fan on the titanium getter after it has cooled to <300°C.

(October 1989)

THE SEPARATION OF IODINE  
FOR NEUTRON ACTIVATION  
ANALYSIS OF IODINE-129 IN  
LARGE AQUEOUS SAMPLES

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### 1. Introduction

The following are the major chemical steps in the measurement of trace quantities of  $^{129}\text{I}$  in large aqueous samples. After the addition of  $\text{I}^-$  carrier, the iodine is concentrated and purified before neutron irradiation. The iodine is subjected to another purification cycle after irradiation and before counting is begun.

The iodine, in the presence of  $\text{I}^-$  carrier, is first adsorbed on an anion-exchange resin, from which it is removed as  $\text{IO}_3^-$  by oxidation with  $\text{NaClO}$  in conc  $\text{HNO}_3$ . Any  $\text{Br}_2$  is removed by extraction with  $\text{CCl}_4$ , and  $\text{IO}_3^-$  is reduced to  $\text{I}_2$  by  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . Following a cycle of reduction (to  $\text{I}^-$ ), oxidation (to  $\text{I}_2$ ), and reduction,  $\text{I}^-$  is again adsorbed on an anion-exchange resin. The resin is then irradiated.

Iodide is removed from the irradiated resin by treatment with  $\text{NaClO}$ . The  $\text{IO}_3^-$  formed is reduced to  $\text{I}_2$  by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and then to  $\text{I}^-$  by  $\text{NaHSO}_3$ . Finally, the  $\text{I}^-$  is converted to  $\text{I}_2$  (with acidic  $\text{NaNO}_2$ ), again reduced to  $\text{I}^-$ , and precipitated as the silver salt. The chemical yield is 40 to 60%.

### 2. Reagents

Iodine carrier: 10 mg iodine/ml, added as aqueous KI  
 $\text{HNO}_3$ : conc; 6M  
 $\text{NH}_4\text{OH}$ : 0.3M  
 $\text{NaClO}$ : ordinary bleach solution, fresh or stored cold  
 $\text{NH}_2\text{OH}\cdot\text{HCl}$ : 1M  
 $\text{NaHSO}_3$ : 1M  
 $\text{NaNO}_2$ : 1M  
KBr: 1M  
 $\text{AgNO}_3$ : 1M  
 $\text{CCl}_4$ : cold

Ethanol  
Toluene  
Acetone  
 $\text{SO}_2$ : gas

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh ( $\text{HSO}_4^-$  form)

### 3. Procedure

*Step 1.* To the sample (up to 12  $\ell$ ), add 30 mg of iodine carrier. Wait  $\sim 24$  h and pump the sample through a 1- by 10-cm column of the Bio-Rad AG 1-X8 resin.

*Step 2.* Use  $\sim 10$  ml of distilled  $\text{H}_2\text{O}$  to rinse the resin from the column into a beaker, and add 3 ml of  $\text{NaClO}$ . Heat on a steam bath for 5 min, remove from the bath, and add 3 ml of conc  $\text{HNO}_3$  and 1 ml of  $\text{NaClO}$ . Permit the solution to cool.

*Step 3.* Pass the mixture through a filter and collect the filtrate in a 60-ml separatory funnel. Discard the resin. Add 10 ml of cold  $\text{CCl}_4$  to the solution and extract any  $\text{Br}_2$  present. If the  $\text{CCl}_4$  extract is yellow, repeat the extraction. Discard the  $\text{CCl}_4$  phases.

*Step 4.* To the aqueous phase add 3 ml of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution, extract the  $\text{I}_2$  with 15 ml of toluene, and discard the aqueous phase. Wash the toluene layer twice with 10-ml portions of  $\text{H}_2\text{O}$  and discard the washes.

*Step 5.* Add 10 ml of  $\text{H}_2\text{O}$  to the toluene layer and then 1M  $\text{NaHSO}_3$  dropwise until that layer is colorless. Shake the mixture after each addition of reducing agent. Transfer the aqueous layer to a 125-ml erlenmeyer flask and discard the toluene layer.

*Step 6.* Add 1 ml of 6M  $\text{HNO}_3$  and, with a Meker burner, boil the solution vigorously for 15 to 30 s. Permit the solution to cool.

*Step 7.* Transfer the cooled solution to a clean 60-ml separatory funnel containing 15 ml of toluene. Add a few drops of 1M NaNO<sub>2</sub> to convert I<sup>-</sup> to I<sub>2</sub>. Shake the funnel to extract the I<sub>2</sub> into the toluene and discard the aqueous layer. Wash the toluene with two 10-ml portions of H<sub>2</sub>O and discard the washes.

*Step 8.* Bubble SO<sub>2</sub> through H<sub>2</sub>O; maintain at ice-bath temperature until a saturated solution of the gas is formed. Add the SO<sub>2</sub> solution dropwise to the toluene until the color of I<sub>2</sub> disappears, being certain that the mixture is shaken well after each addition.

*Step 9.* Transfer the aqueous phase to a 125-ml erlenmeyer flask and heat over a Bunsen burner for 30 to 60 s to expel SO<sub>2</sub>.

*Step 10.* Adjust the pH to ~6 with 0.3M NH<sub>4</sub>OH, and pour the solution through a 0.5- by 2-cm column of the Bio-Rad AG 1-X8 resin. Wash the column with distilled H<sub>2</sub>O and then with acetone. Blow air through the resin to expel acetone.

*Step 11.* Heat the column in an oven at 110°C for 60 min. The sample is now ready for neutron irradiation.

*Step 12.* After the irradiation has been completed, place the resin in a beaker containing 10 ml of H<sub>2</sub>O, 1 ml of 1M KBr, and 2 ml of NaClO. Heat on a steam bath for 5 min and then permit the solution to cool.

*Step 13.* Pass the mixture through a filter, collect the filtrate in a clean 60-ml separatory funnel, and discard the resin.

*Step 14.* Extract any Br<sub>2</sub> in solution by shaking with 10 ml of CCl<sub>4</sub>. Discard the CCl<sub>4</sub>. Repeat the extraction if necessary to obtain a colorless extract.

*Step 15.* To the aqueous solution in the separatory funnel, add 3 ml of 1M NH<sub>2</sub>OH•HCl and 15 ml of toluene. Extract I<sub>2</sub> into the toluene and discard the aqueous phase. Wash the toluene layer twice with 10 ml of H<sub>2</sub>O and discard the washes.

*Step 16.* To the toluene add 10 ml of H<sub>2</sub>O, convert I<sub>2</sub> to I<sup>-</sup> as in *Step 5* by the dropwise addition of 1M NaHSO<sub>3</sub>, and transfer the aqueous layer to a clean 125-ml erlenmeyer flask.

*Step 17.* Repeat *Step 6*.

*Step 18.* Repeat *Step 7*.

*Step 19.* Repeat *Step 5*.

*Step 20.* To the H<sub>2</sub>O layer add 1 ml of 6M HNO<sub>3</sub> and boil vigorously for 15 to 30 s. If I<sub>2</sub> appears, reduce it by the dropwise addition of 1M NaHSO<sub>3</sub>.

*Step 21.* Transfer the solution to a clean 40-ml glass centrifuge tube. Keep the solution hot and, while stirring, slowly add 3 ml of 1M AgNO<sub>3</sub>. Stir and heat on a steam bath for 5 min. Cool and centrifuge for 5 min.

*Step 22.* Decant the supernate. Add H<sub>2</sub>O and break up the precipitate. Using a stream of H<sub>2</sub>O, filter the precipitate on a preweighed filter paper. Wash the precipitate three times with 5-ml of H<sub>2</sub>O and then three times with 5-ml amounts of ethanol.

*Step 23.* Dry the precipitate at 110°C for 15 min. Cool for 15 min and weigh. Mount for gamma counting.

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# ANALYSIS OF LEAD AND URANIUM IN GEOLOGIC MATERIALS BY ISOTOPE DILUTION MASS SPECTROMETRY

D. B. Curtis and J. Capps

## 1. Introduction

The procedures described here have been designed to study geochronology and isotope geochemistry. They are used specifically to determine the abundances of isotopes of lead and uranium in earth materials by isotope dilution mass spectrometry. The procedures consist of two parts— isolation of the elements from rock and measurement of the relative isotopic abundances by solid source mass spectrometry. All chemical separations are carried out in a Class 100 clean laboratory. The analyst should wear Vanlab poly gloves during all preparation and implementation steps. In addition, Fashion Seal Disposable coats and hats must be worn during all sample handling procedures.

## 2. Reagents and Materials

Because submicrogram quantities of lead and uranium are to be determined by the procedures, the reagents must be of the highest purity. When possible, reagents were obtained from the National Bureau of Standards (NBS) as "highest purity" substances. All H<sub>2</sub>O was purified by passing "house" deionized H<sub>2</sub>O through a Milli-Q H<sub>2</sub>O purification system.

HF: conc (NBS)

HClO<sub>4</sub>: conc (NBS); 1.2M

HNO<sub>3</sub>: conc (NBS)

Lead spike: lead enriched in <sup>208</sup>Pb; source: Oak Ridge National Laboratory

Uranium spike: <sup>233</sup>U

HCl: conc (NBS); 8M; 1.5M

H<sub>2</sub>SO<sub>4</sub>: 0.1M; made from Suprapur MCB reagent

H<sub>3</sub>PO<sub>4</sub>: 10 g of sublimed high-purity P<sub>4</sub>O<sub>10</sub> dissolved in 250 ml of H<sub>2</sub>O. (This material is

very hygroscopic and appropriate care should be exercised.) To remove lead, the solution is made 1M in HBr and passed through an anion-exchange resin column.

HBr: conc source: Merck high-purity acid; purified by passage through an anion-exchange resin column; 1M

HCl-H<sub>2</sub>SO<sub>4</sub> mixture: 8M in HCl and 3M in H<sub>2</sub>SO<sub>4</sub>

HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> mixture: 2M in HNO<sub>3</sub> and 2% in H<sub>2</sub>O<sub>2</sub>

HCl-NH<sub>4</sub>Cl solution: pH 2.8

NH<sub>4</sub>OH: prepared by bubbling high-purity anhydrous NH<sub>3</sub> through H<sub>2</sub>O

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh (Cl<sup>-</sup> form). Resin and Milli-Q H<sub>2</sub>O are mixed in 1:10 volume proportions and the mixture is shaken for ~1 h. The liquid is decanted, the resin mixed with 4M HCl (1:10 volume proportions), and the mixture shaken for ~1 h. After the resin has settled, the liquid is decanted and the treatment is repeated. Finally, HCl is added to the resin and the resin is stored.

Quartz ion-exchange column: The column is constructed of high-purity, acid-washed quartz. It is 7.5 cm long and of 5-mm diam and has a flared reservoir of 10-ml volume on top and a fritted quartz sintered disk at the bottom.

Teflon electroplating cell: 2-dram threaded vial and cap; Part No. 02.25; source: Savillex Corp. Two holes, each of 0.042-in. diam, are drilled in the cap, one at 12 o'clock and the other at 6 o'clock, and a third hole, of ~0.125-in. diam, at 9 o'clock.

Platinum electrodes: NBS certified wire; SRN 680, 0.03 in. and 99.9% pure platinum wire, 0.01 in.

Teflon-coated magnetic stirring bar: ½ in. by ⅛ in.; source: Bel-Art Products

All laboratory equipment (beakers, columns, pipettes, etc.) is made from FEP Teflon or high-purity quartz obtained from Amersil. Before use, the equipment is carefully cleaned. It is first soaked for a minimum of 1 d in Isoterg green soap and carefully scrubbed with a laboratory brush, without



scratching the Teflon surfaces. This treatment is followed by multiple rinses in Milli-Q H<sub>2</sub>O. The equipment is then placed in a solution of equal volumes of reagent grade HCl and Milli-Q H<sub>2</sub>O for a minimum of 1 d under very low heat. Then the mixture is boiled for 1 h, cooled, and the liquid decanted; the pieces are rinsed with Milli-Q H<sub>2</sub>O. The heating treatment is repeated, first in aqua regia, next in a mixture of equal volumes of analytical reagent HNO<sub>3</sub> and Milli-Q H<sub>2</sub>O, and finally in Milli-Q H<sub>2</sub>O that contains a trace of HNO<sub>3</sub>. After the cleaning processes, the pieces of equipment are covered with Milli-Q H<sub>2</sub>O.

### 3. Preparation of Standards and Spikes

Standards are prepared from lead and uranium metals of high purity. Primary standard solutions are made by dissolving carefully weighed pieces of the metals in conc HNO<sub>3</sub> in a weighed bottle. The resulting solutions are made to volume with Milli-Q H<sub>2</sub>O and then weighed to determine the final concentration (gram of element/grams of solution). By appropriate dilution of a primary solution, desired concentrations of other standard solutions are obtained.

To use the isotope dilution technique, standardized spikes of the elements must be prepared and calibrated. A spike is made by dissolving the isotopically appropriate compound in HNO<sub>3</sub> and diluting with Milli-Q H<sub>2</sub>O to produce a final solution of approximately the desired concentration. Isotopic compositions of spike and standard are determined by direct measurement on a mass spectrometer. Known weights of standard solution are mixed with known weights of spike solution; in these mixtures, the ratio of major spike isotope to major standard isotope is not >10 or <0.1. The isotopic ratio of a mixture is then measured directly on a mass spectrometer. The concentration of spike isotope is calculated by isotope dilution equations, which are given in Sec. 8.C.

### 4. Measurement of Blanks

At the discretion of the analyst, a variety of blanks may be run to assess the quantities and isotopic composition of lead and uranium introduced during the procedure. Rock preparation blanks may be determined by processing high-purity SiO<sub>2</sub> and then spiking and analyzing that substance as though it were a sample. Chemical blanks are routinely measured by analysis of spikes. Corrections for blanks are made on the final results by using the calculations that are discussed in Sec. 8.B.

### 5. Sample Preparation

The analyst must be cognizant of the problem of representative sampling and take precautions to ensure that samples are indeed representative of the proper geological material. Typically, ~10 g of sample is removed from the interior of the material; this is broken into small pieces, pulverized, and screened through a 100-mesh sieve. All the material removed must be included in the final sample. An appropriate portion of this powder is taken for analysis.

### 6. Chemical Separations

#### A. Sample Dissolution and Preparation

It is difficult to write a general procedure because each sample varies in mineralogical composition. (An excellent discussion of dissolution techniques may be found in Dolezal *et al.*) Place a weighed aliquot of the sample solution in conc HF and allow the mixture to stand for a minimum of 12 h. Place the mixture on a hot plate that is maintained at medium heat, and take it to dryness. (The HF treatment converts silicates to volatile SiF<sub>4</sub>.) If silicon has not been effectively removed, repeat the HF treatment.

The following is a procedure that is satisfactory for many rock types after silicates have been decomposed. Add a mixture of conc HF-conc

HClO<sub>4</sub> (1:1 by volume) and again take the sample to dryness. Fume the residue to dryness with conc HClO<sub>4</sub> to remove fluorides. This treatment may have to be repeated. If insoluble carbonaceous material remains, dissolve it by fuming with a conc HClO<sub>4</sub>-conc HNO<sub>3</sub> mixture (1:1 by volume). Convert the residue to nitrates by multiple fumings with conc HNO<sub>3</sub>.

Take up the residue of nitrates in a mixture of equal volumes of conc HNO<sub>3</sub> and H<sub>2</sub>O, and centrifuge the solution to remove any insoluble minerals remaining. Transfer the supernate to a clean, weighed Teflon bottle and make up with H<sub>2</sub>O to a concentration of <10 mg of the original rock/g of solution. The portions of the rock to be analyzed should have been dissolved. Verification can be obtained from such techniques as x-ray diffraction, microscopic and petrographic examination, and electron microscopy.

During the entire dissolution process, keep the volumes of reagents at a minimum to avoid introducing extraneous elements.

## B. Separation of Lead

Use an aliquot of sample solution large enough to provide ~250 ng of lead. Take the solution to dryness on a hot plate at low heat, wet with conc HBr, and dry again. Dissolve in 1M HBr to make a solution that contains ~10 mg of original rock/ml.

An anion-exchange resin column is prepared in the following way. Add 1 ml of Bio-Rad AG 1-X8, 100 to 200 mesh (Cl<sup>-</sup> form) to the quartz column described in Sec. 2. Add 10 ml of conc HCl to the resin and allow to drain. Add a 1- and then a 10-ml portion of H<sub>2</sub>O to rinse the sides of the reservoir; allow to drain. Finally, permit 1 ml of conc HBr to drain through the column. Discard all effluents.

Add the HBr solution of the sample to the resin column and allow to drain. Rinse the sides of the reservoir with 1 and then 2 ml of 1M HBr. Discard

all effluents. Add two 1-ml portions of 1.5M HCl to the resin to rinse the sides of the reservoir and discard the effluents. Add 3 ml of conc HCl; collect the eluate, which contains the lead, in a Teflon electroplating cell. Take the solution to dryness at low heat, add 1 drop of conc HClO<sub>4</sub>, and take the solution to dryness. Repeat the HClO<sub>4</sub> treatment. Add 50 μl of 1.2M HClO<sub>4</sub> and then 7 ml of H<sub>2</sub>O to the cell, cover the cell, carefully place a magnetic stirring bar in the solution, and place the platinum electrodes (0.03-in. wire) into the cell through the cover. Stir the solution magnetically and plate for 12 h at 2 V, using a controlled potential power supply. After plating, add 1 ml of conc NH<sub>4</sub>OH and quickly disassemble the cell. Wash the anode, which has been plated with lead oxide, with ethanol; dissolve the lead oxide in a Teflon beaker in 100 μl of 1.5M HCl that is delivered dropwise on the anode by means of a pipette. Add 10 μl of H<sub>3</sub>PO<sub>4</sub> to the solution to prepare it for mass spectrometric analysis.

Mix another aliquot of sample solution with a weighed aliquot of the <sup>208</sup>Pb spike and repeat the analysis described above.

## C. Separation of Uranium

Use a large enough aliquot of sample solution to provide ~10 ng of uranium, and spike it with an appropriate quantity of <sup>233</sup>U spike. (If only the isotopic composition is of interest, no spike is added.) Dry the sample at low heat and take up in 8M HCl. Prepare an anion-exchange resin column as described in Sec. 6B, but use 8M HCl rather than HBr for the final rinse. Load the sample on the column and add 1 ml of 8M HCl to rinse the sides of the reservoir. Discard the effluent. Add successively to the resin 2 ml of 8M HCl, 1 ml of HCl-H<sub>2</sub>SO<sub>4</sub> mixture (8M in HCl and 3M in H<sub>2</sub>SO<sub>4</sub>), 3 ml of 0.1M H<sub>2</sub>SO<sub>4</sub>, and 3 ml of 8M HCl. Discard all effluents. Then add 1 ml of H<sub>2</sub>O to elute uranium, and collect the eluate in an electroplating cell. Add 2 ml of HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> mixture (2M in HNO<sub>3</sub> and 2% in H<sub>2</sub>O<sub>2</sub>) to the resin and combine the eluate with that in the plating cell.

Take the solution in the cell to dryness at low heat, add 1 drop of conc HCl, and take the solution again to dryness. Repeat the HCl treatment and add 1 ml of HCl-NH<sub>4</sub>Cl solution at pH 2.8. Place a Teflon magnetic stirring bar in the cell, put the lid in place, and introduce the platinum electrodes. The anode is a straight platinum wire (0.030 in.), and the cathode is a platinum wire (0.01 in.) with a loop at the end. Immerse only the loop of the cathode in the electrolytic solution. Plate the uranium at 4 V while stirring gently for 4 h. Rinse the cathode with ethanol. The uranium is now ready for mass spectrometric analysis.

## 7. Mass Spectrometric Analysis

### A. Determination of Lead

All loading is done in a Class 100 air clean hood, and the loading filament is maintained with a heat lamp at  $50 \pm 2^\circ\text{C}$ . Clean Teflon tubes are used for each pickup operation. Standards and samples are dried under a heat lamp until only the relatively nonvolatile H<sub>3</sub>PO<sub>4</sub> remains. Zone-refined, 1.2-mil rhenium ribbon is used as the filament material, and filaments are degassed and baked in a vacuum at 4 A for 30 min under a potential of  $\sim 90$  V. The total sample should contain  $\sim 100$  ng of lead. The loading process is described here.

Rinse a Teflon tube in H<sub>3</sub>PO<sub>4</sub>; draw the acid into the tube farther than the 5- $\mu\text{l}$  sample will reach. Repeat the rinse three times and discard all rinsings. Pick up 5  $\mu\text{l}$  of sample or standard with the clean tube and place on the filament without letting any of it roll under the filament. If it does so, discard the filament. Dry the filament with the heat lamp at 1.3 A for 5 min and then at 1.5 A for an additional 5 min. [The sample (or standard) solution should be reduced to  $\sim 25\%$  its original volume.] Turn off the current. Rinse a new Teflon tube in H<sub>3</sub>PO<sub>4</sub> and use it to load 5  $\mu\text{l}$  of silica gel on the filament. (The silica gel promotes ionization of lead at a reasonable temperature.) Dry the filament at 1 A for 5 min. Hold a 400-ml Teflon beaker over the filament and increase the current until the

H<sub>3</sub>PO<sub>4</sub> begins to fume ( $\sim 2.5$  to 3 A). Hold the mouth of the beaker roughly level with the filament to create a calm air space, which makes the fumes easier to see. When the fuming has stopped, set the beaker down over the filament and dry the filament without changing the current until a full, well-defined white deposit appears. (When there are no gaps in the white deposit, the run is usually successful.) After the drying is completed, hold the beaker slightly above the filament, turn off the heat lamp, and increase the current until the filament is light orange in color. After  $\sim 3$  s, turn off the current. At this point, the deposit on the filament should be a semitransparent or opaque covering.

During the analysis, use the following guidelines: initial temperature, 1100°C; at 5 min elapsed time, 1150°C; at 10 min, 1200°C; at  $\sim 12$  min, scan the mass range 200 to 212 to determine the purity of the spectrum; at 18 min, start the ion beam base line; at 30 min, begin taking data. Because of fractionation on the filament, take symmetrical sets of isotope ratios between 30 and 60 min at consistent intervals:

30 min	208/206
	207/206
	204/206
	204/206
	207/206
60 min	208/206

### B. Determination of Uranium

The procedure described by Rokop *et al.* is used for the analysis of uranium isotopes.

## 8. Calculations

### A. Mass Fractionation

There is a temperature-induced mass-dependent fractionation of isotopes in the mass spectrometer. Correcting the measured data for this mass fractionation is done by an empirically determined mass fractionation factor. The fractionation factor is determined by measuring the isotopic ratio of a standard material of well-known isotopic composition. For lead, this standard is National Bureau of Standards Reference Material-982, and for uranium it is National Bureau of Standards Material-500. The fractionation factor is then calculated by Eq. (1).

fractionation factor = (1)

$$\frac{\frac{(A/B)_{\text{Known}}}{(A/B)_{\text{Meas}}} - 1}{\Delta M}$$

A and B are the isotopes of the element of interest, and  $\Delta M$  is the mass difference between A and B.

Multiple determinations of the standard are made on a regular basis for each element; mean and standard deviations of the fractionation factor are determined from these measurements. The average is used to correct measured ratios in samples; the known ratio in equations becomes the mass fractionation-corrected ratio in the sample. The standard deviation of the fractionation factor may be included in the uncertainty analysis of the final result.

### B. Blank Corrections

All data may be corrected for contributions from blanks by using Eq. (2).

$$(A/B)_x = (A/B)_{\text{Meas}} + B_{\text{Bl}}/B_x[(A/B)_{\text{Meas}} - (A/B)_{\text{Bl}}] \quad (2)$$

$B_{\text{Bl}}$  is the quantity of isotope B in the blank and  $(A/B)_{\text{Bl}}$  is the relevant ratio of isotopes in the blank. These quantities are estimated from multiple determinations of the blank in conjunction with the analysis of the samples.  $(A/B)_{\text{Meas}}$  is the measured ratio corrected for mass fractionation, and  $B_x$  is the abundance of isotope B in the sample as determined by isotope dilution analysis.

### C. Isotope Dilution Analysis

The abundance of isotope A, in units of mols per unit mass, is calculated from Eq. (3).

$$A_x = \frac{\frac{(A/B)_{\text{Meas}} - (A/B)_{\text{Sp}}}{1 - [(A/B)_{\text{Meas}}/(A/B)_x]} B_{\text{Sp}}}{\text{Sample mass}} \quad (3)$$

$(A/B)_{\text{Meas}}$  is the isotope ratio measured in the spiked sample, corrected for mass fractionation and blank. Note that the blank correction and isotope dilution equations often require iterative calculations.  $(A/B)_{\text{Sp}}$  is the isotope ratio in the spike,  $(A/B)_x$  is the corrected isotope ratio in the unspiked sample, and  $B_{\text{Sp}}$  is the known quantity, in units of mols, of isotope B added from the calibrated spike. For lead,  $(A/B)_x$  must be determined by a separate analysis of the unspiked sample. However, the  $^{233}\text{U}$  that is used for a uranium spike is not found in nature; the denominator of Eq. (3) is reduced to a value of unity, and it is only necessary to make a single measurement to obtain the abundance of uranium isotope A (usually  $^{238}\text{U}$ ).

### D. Isotope Ratios in Spiked Samples

To determine the ratio of isotopes in a sample that has been spiked for isotope dilution analysis, calculate the ratio from Eq. (4).

$$(A/B)_x = (A/B)_{\text{Meas}} - B_{\text{Sp}}/B_x[(A/B)_{\text{Meas}} - (A/B)_{\text{Sp}}] \quad (4)$$

$(A/B)_x$  is the unspiked ratio in the sample;  $(A/B)_{Meas}$  is the measured ratio (corrected) in the spiked sample;  $B_{Sp}$  is the quantity of isotope B added in the spike;  $B_x$  is the quantity of isotope B measured in the sample; and  $(A/B)_{Sp}$  is the isotope ratio in the spike solution.

## References

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# DETERMINATION OF FERROUS IRON AND TOTAL IRON IN SILICATE ROCKS

R. J. Prestwood and B. P. Bayhurst

## 1. Introduction

These procedures were adapted from two procedures already reported: one by S. Banerjee on the direct determination of iron(II) in silicate rocks and minerals by ICl, and the other, by K. L. Cheng *et al.*, on the determination of total iron by disodium dihydrogen ethylenediaminetetraacetate titration. Major modifications of the former procedure include the method of preparation of the ICl solution, elimination of the necessity for blanks, and some technique changes. The main modification in the reported method for determining total iron is in the preparation of the sample for analysis. The sample preparation method described here improves the consistency of the analytical results.

### (A) Determination of Ferrous Iron

#### 1. Reagents

HF: conc  
HCl: conc; 9M; 6M  
H<sub>2</sub>SO<sub>4</sub>: 6M  
H<sub>3</sub>BO<sub>3</sub>: solid  
KI: solid; 10% aqueous solution  
KIO<sub>3</sub>: solid;  $2.5 \times 10^{-3}M$ ; standardized  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>•FeSO<sub>4</sub>•6H<sub>2</sub>O: primary standard  
CCl<sub>4</sub>

#### 2. Preparation of ICl reagent

Add 10 g of KI and 6.44 g of KIO<sub>3</sub> to 150 ml of H<sub>2</sub>O in a 1-l bottle that contains a Teflon-coated magnetic stirrer. Stir until the salts have dissolved; then, while stirring, add 450 ml of conc HCl. Add 20 ml of CCl<sub>4</sub> and, while stirring, add 10% KI dropwise until the color of I<sub>2</sub> appears in the CCl<sub>4</sub> (lower) layer. Remove the CCl<sub>4</sub> layer with a transfer pipette and discard. The liter bottle now contains ICl reagent. To 30 ml of this reagent in a

100-ml glass container equipped with a screw cap, add 10 ml of CCl<sub>4</sub> and shake vigorously for 3 h on a wrist-action shaker. Use a transfer pipette to remove the pink CCl<sub>4</sub> layer and discard. Dilute the 30 ml of ICl solution to 100 ml with 9M HCl.

#### 3. Standardization of the $\sim 2.5 \times 10^{-3}M$ KIO<sub>3</sub> solution

In a 1-l volumetric flask, dissolve 7.002 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>•FeSO<sub>4</sub>•6H<sub>2</sub>O (primary standard) and combine with sufficient H<sub>2</sub>SO<sub>4</sub> to make the solution 0.3M in acid. This gives a primary iron(II) standard of 1 mg/ml of solution. For standardization of the KIO<sub>3</sub> solution, proceed as described below for the determination of iron(II), but substitute 3 ml (3 mg) of the iron(II) standard for the iron-containing sample.

#### 4. Procedure

*Step 1.* Weigh out 50 to 70 mg of sample (minus 200 mesh) into a Tefzel 50-ml Nalgene centrifuge tube fitted with a specially machined male Teflon stopper. (A 2-oz. Teflon bottle with cap may be used for holding the sample.) Carefully cover the sample with 3 ml of CCl<sub>4</sub>. To a plastic 50-ml graduated cylinder, add 20 ml of 6M HCl, 3 ml of the diluted ICl reagent, and 2 ml of conc HF. Pour the solution into the mixture of sample and CCl<sub>4</sub> and stopper immediately. Place on a shaker and shake for at least 4 h. As the sample slowly dissolves, the iron(II) is oxidized to the iron(III) state by ICl, which then is reduced to I<sub>2</sub>. The latter dissolves in the CCl<sub>4</sub>.

*Step 2.* To a 125-ml erlenmeyer flask that has a Teflon-coated magnetic stirring bar, add 10 ml of 6M HCl and 1 g of H<sub>3</sub>BO<sub>3</sub>. With the stopper attached to the centrifuge tube, centrifuge the oxidized sample from *Step 1* to remove any trapped CCl<sub>4</sub> around the stopper. Remove the stopper and with a transfer pipette transfer the contents of the tube to the 125-ml erlenmeyer flask containing the HCl and H<sub>3</sub>BO<sub>3</sub>. To prevent loss of I<sub>2</sub> to the air, take great care to ensure that some of the

aqueous phase is on both sides of the  $\text{CCl}_4$  in the transfer pipette. While stirring, titrate the  $\text{I}_2$  with the standardized  $\text{KIO}_3$  solution; disappearance of the pink  $\text{I}_2$  color in the  $\text{CCl}_4$  layer indicates that titration is complete. Calculate the amount of iron(II) present in terms of percent  $\text{FeO}$ .

## (B) Determination of Total Iron

### 1. Reagents

$\text{HClO}_4$ : conc  
HF: conc  
 $\text{HNO}_3$ : conc  
HCl: conc; 6M; 0.1M  
Aqua regia  
 $\text{NH}_4\text{OH}$ : conc  
NaOH: 10M  
 $\text{NaC}_2\text{H}_3\text{O}_2$ : 6M  
 $(\text{NH}_4)_2\text{SO}_4 \bullet \text{FeSO}_4 \bullet 6\text{H}_2\text{O}$ : primary standard  
Iron: National Bureau of Standards (NBS) sample 55e, open-hearth iron (99.8% pure)  
Salicylic acid: 1 g of acid in 100 ml of ethanol  
EDTA reagent: disodium salt of ethylenediamine-tetraacetic acid; 4.0000 g in 1 l of  $\text{H}_2\text{O}$ ; standardized

### 2. Standardization of EDTA reagent

Accurately measure 1.0000 g of NBS sample 55e, open-hearth iron (99.8% pure), and transfer to a 1-l volumetric flask. Add 10 ml of aqua regia and heat the flask on a hot plate until all the iron has dissolved and has been oxidized to iron(III). Add 10 ml of conc HCl and evaporate the solution to a small volume to remove excess  $\text{HNO}_3$ . Repeat the HCl treatment. Make the solution up to 1 l so that it is  $\sim 0.1M$  in HCl.

Dissolve 4.0000 g of the disodium salt of ethylenediaminetetraacetic acid in  $\text{H}_2\text{O}$  and dilute to 1 l (EDTA reagent). Add 3 ml (3 mg) of standard iron(III) solution to a 100-ml beaker that contains a magnetic stirrer; then add 3 to 4 drops of conc HCl. Use a 6M  $\text{NaC}_2\text{H}_3\text{O}_2$  solution to adjust the pH to 2.5 (use pH meter) so that the volume of the

solution is  $\sim 20$  ml. Add 5 drops of salicylic acid indicator solution and titrate immediately with the EDTA reagent.

Analysis showed that 1.62 ml of EDTA solution is equivalent to 1.00 mg of iron(III) or 1.43 mg of  $\text{Fe}_2\text{O}_3$ .

### 3. Procedure

*Step 1.* Weigh out 50 to 100 mg of sample (minus 200 mesh) into a 75-ml Teflon beaker. Add 7 ml of conc  $\text{HClO}_4$ , 2 ml of conc  $\text{HNO}_3$ , and 4 ml of conc HF. Evaporate on a hot plate to  $\text{HClO}_4$  fumes. Cool, carefully add 4 ml of conc HF, and again evaporate to  $\text{HClO}_4$  fumes. Repeat the HF treatment. Fume off all but  $\sim 1$  ml of the  $\text{HClO}_4$ .

*Step 2.* Use 10 to 15 ml of 0.1M HCl to transfer the solution to a 40-ml glass centrifuge tube. Carefully neutralize the solution with conc  $\text{NH}_4\text{OH}$ , then add 4 drops more of the conc  $\text{NH}_4\text{OH}$ . Add 4 drops of 10M NaOH, mix, heat on a steam bath for a few minutes, and centrifuge. Discard the supernate.

*Step 3.* Dissolve the  $\text{Fe}(\text{OH})_3$  precipitate in about 6 drops of conc HCl. Use 0.1M HCl to transfer the solution to a 100-ml beaker that contains a magnetic stirrer. The volume of solution should be  $\sim 20$  ml. Adjust the pH to 2.5 with 6M  $\text{NaC}_2\text{H}_3\text{O}_2$ , add 5 drops of salicylic acid indicator solution, and titrate with standard EDTA reagent. Calculate the total iron present as percent  $\text{Fe}_2\text{O}_3$ .

To determine the original percentage of  $\text{Fe}_2\text{O}_3$ , multiply the percentage of  $\text{FeO}$  [see Sec. (A)] by 1.1115 and subtract from the total  $\text{Fe}_2\text{O}_3$ .

### References

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# A BATCH METHOD FOR DETERMINING SORPTION RATIOS FOR THE PARTITION OF RADIONUCLIDES BETWEEN GROUND- WATERS AND GEOLOGIC MATERIALS

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## 1. Introduction

This procedure provides a method for determining the effect of various parameters on the sorptive properties of geologic material. This work is specifically applied to predicting how groundwater can transport the aqueous radioactive species of various elements through geologic formations. Variables include mineralogy, rock particle size, groundwater composition, oxidation state, element concentration, atmosphere (for example, O<sub>2</sub> and CO<sub>2</sub> fugacity), solution-to-solid ratio, contact time, and temperature.

The procedure has been used in both normal and controlled atmospheres, at room temperature, and 70°C. Depending upon the nature of the radionuclide and the information desired from the experiment, a few variations of the procedure may be used. The procedure has been employed for determination of sorption ratios with a large number of elements, including barium, strontium, cesium, cerium, europium, iodine, nickel, cobalt, sodium, tin, iron, manganese, selenium, technetium, uranium, and the actinides.

The sorption ratio ( $R_d$ ) is defined

$$R_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}}$$

and is the same as the conventional distribution ratio except that equilibrium conditions cannot be guaranteed.

## 2. Special Equipment

Pulverizer: Pulverisette 0 Electromagnetic Micro-pulverizer; source, Tekmar Company

Sieves: ASTM sieves

Shakers: Junior Orbit Shakers; source, Lab-Line Instruments, Inc.

Centrifuge: Sorvall Superspeed Centrifuge SS-3 Automatic

Centrifuge Tubes: Oak Ridge Type (round-bottom tubes with leak-proof screw closures).

These tubes can be obtained in polycarbonate, polyallomer, or polysulfone polymer from the Nalge Company or most chemical laboratory supply houses.

## 3. Procedure

*Step 1.* Crushed rock for the preparation of rock-contacted groundwater and for use in the batch sorption tests is prepared in the following manner. Break up the rock core into pieces small enough to fit in a pulverizer; be careful not to introduce metallic particles. Crush the rock with an agate mortar and ball. Sieve the crushed rock to the desired size; return any particles that are too large to the pulverizer for a second crushing. Sieve the repulverized rock. When the required quantity of crushed rock of the proper size has been obtained, rinse the dust or very light fraction with deionized H<sub>2</sub>O and air dry.

*Step 2.* Shake a mixture of 500 ml of groundwater and 25 g of crushed rock for at least 2 weeks. (The rock may consist of various size particles but should contain no large chunks.) Separate the phases by centrifugation at 7000 rpm for 1 h. Filter the aqueous phase through an 0.05- $\mu$ m Nuclepore polycarbonate membrane. Keep the filtered groundwater and, if it is required for other studies, the solid.

*Step 3.* To prepare the rock sample, weigh ~1 g of dried, crushed solid in a weighed polypropylene or polycarbonate tube that is fitted with a cap. Add 20 ml of groundwater and shake the mixture well.



Place the tube in a shaker and agitate at a rate of  $\sim 200$  rpm for not less than 2 weeks. At the end of the contact period, remove the sample from the shaker and centrifuge for 1 h at  $\sim 12\ 000$  rpm. Remove the liquid phase by decantation and/or pipetting, and reweigh the sample and tube so that the amount of added  $H_2O$  is known. Cap the tube. Begin contact with traced groundwater solution (traced feed solution) within 2 to 24 h.

*Step 4.* Prepare the traced feed solution (Note 1). Evaporate the tracer solution at room temperature in a polypropylene, polycarbonate, or polyethylene container that has been washed with deionized  $H_2O$ . Add a few drops of conc HCl and evaporate to dryness. Remove dried activity from the container by using a vibrator or ultrasonic bath for a minimum of two 1- to 3-min contacts with rock-treated groundwater. After each contact add the aqueous phase to a large polyethylene bottle that has been washed with deionized  $H_2O$ . Repeat the contacts until no tracer is removed from the container in which it was dried. Add sufficient rock-treated groundwater to make up the desired volume. Shake the solution for 1 to 2 d and pass it serially through 0.4- and 0.05- $\mu m$  Nuclepore membranes just before use.

*Step 5.* Add, by pipette or graduated cylinder, 20 ml of traced feed solution to the prepared 1 g sample of groundwater-treated rock; weigh the tube and contents. Mix the two phases, place the tube in a shaker, and shake for a predetermined time. Note the times for the beginning and end of the contact period. Remove the mixture from the shaker and centrifuge for 2 h at 12 000 rpm (28 000 g). Very carefully remove the top 15 ml of the aqueous phase with an automatic pipettor and transfer to a clean polypropylene or polycarbonate tube. The pipette tip is kept as far above the solid phase as possible (Note 2). Cap the tube containing the liquid phase and centrifuge at  $\sim 12\ 000$  rpm for 1 h. After the 15 ml of aqueous phase has been removed from the solid phase, carefully transfer the remaining liquid to a clean tube and save for pH measurement. Recap the tube holding the solid phase and weigh. The solid phase is now ready to be

prepared for counting. When the tube with 15 ml of aqueous phase has been centrifuged, remove the top 12 ml in the same careful manner described above and transfer to a clean polypropylene or polycarbonate tube. Cap the tube and centrifuge for 2 h at 12 000 rpm. Add the remaining 3 ml of liquid to the tube that contains the fraction for pH measurement. After the 12-ml portion has been centrifuged, again carefully remove the top portion of the liquid (this time 9 ml), transfer to a clean polypropylene or polyethylene tube, and cap the tube. The aqueous phase is now ready to be prepared for counting.

*Step 6.* The solid phase of an actinide sample is normally gamma-counted in its container (Note 3). No further preparation of the solid phase is required for actinide samples if they are to be gamma-counted. To prepare the solid phase for the remaining elements (excluding iodine, uranium, and technetium) for counting, remove and weigh a portion of the solid ( $\sim 0.25$  g). Dry in an oven, weigh again, and place in an appropriate container. To prepare the liquid phase for counting, transfer by automatic pipettor an appropriate amount (depending upon the geometry of the detector to be used) to a counting vial and add 1 ml of conc HCl. Mix well and cap the tube with a silicon rubber sealant such as Silastic.

*Step 7.* If desired, start a desorption experiment with the sample. To the solid remaining from *Step 5*, add the appropriate volume of untraced, pretreated groundwater; retain a ratio of  $\sim 20$  ml/g of solid. Cap the tube and weigh the capped tube and its contents. Mix the two phases thoroughly, place the sample in a shaker, and agitate at  $\sim 200$  rpm for a predetermined time. Note the starting time of the desorption experiment. At the end of the desorption period again note the time and treat the sample in exactly the same manner used to separate the solid and liquid phases in the sorption experiment.

*Step 8.* Calculate sorption ratios from data obtained by counting the separated phases.

## Notes

1. Some traced feed solutions cannot be prepared as described in *Step 4*. For example, solutions of technetium cannot be prepared by this method because the element volatilizes from hot acidic solution. Therefore, technetium tracer is delivered in 0.1M alkaline solution. The technetium tracer solution is added in a small volume to the appropriate rock-treated H<sub>2</sub>O. The mixture is then shaken for a few days and passed through a 0.05- $\mu$ m Nuclepore polycarbonate membrane just before use. Uranium-traced feed solutions are prepared by dilution of a stock solution made by dissolving a weighed amount of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O in H<sub>2</sub>O that has been purified with a Millipore deionizing system (Milli-Q system) and filtered through a 0.05- $\mu$ m Nuclepore polycarbonate membrane. An appropriately diluted solution is shaken for a period of up to 1 week and then is filtered through a 0.05- $\mu$ m Nuclepore polycarbonate just before use. The actinide tracers are air-dried but are not evaporated in HCl.

2. The great care taken in removing only the top portion of the liquid phase is necessary to ensure that no fine particulate matter is included in the final aqueous phase. Any such matter present would severely affect measurement of activity in that phase. If a larger volume of liquid phase is taken, the analyst runs the risk of including solid particles in that phase and, thus, obtaining an erroneous sorption value.

3. The tracer activity in the separated phases is determined in several ways. The gamma-emitting actinides, except for uranium, are counted in the following manner. The solid phase is counted moist in its capped polycarbonate container in a NaI(Tl) well detector. Standards are prepared to be counted with the samples and in the same geometry. Aliquots of liquid samples are counted both in a NaI(Tl) well counter and in an automatic gamma scintillation well counter. Alternative methods for counting alpha-emitting plutonium samples include radiochemical analysis of both the liquid

and dissolved solid fractions and liquid scintillation counting of the liquid fraction. The uranium sorption ratio is generally low, so it is necessary to count only the liquid phase. When the tracer used is <sup>237</sup>U, a portion of the liquid phase is placed in a vial and gamma-counted with a Ge(Li) detector. When natural uranium is used, the liquid samples are counted by a delayed neutron-counting method following neutron activation. When crushed-rock samples containing technetium or iodine are prepared for counting, the portion to be counted is air-dried, not oven-dried. The remaining elements are normally gamma-counted on a Ge(Li) detector. A dried fraction of the solid phase is counted in a sealed vial. The liquid samples consist of 10 ml of aqueous phase acidified with 1 ml of conc HCl in a sealed counting vial.

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# A TECHNIQUE FOR MEASURING THE MIGRATION OF RADIOISOTOPES THROUGH COLUMNS OF CRUSHED ROCK

E. N. Treher

## 1. Introduction

One of the major uses of this procedure is to measure the retardation of radioisotope migration through geological materials. This subject is of particular interest in the storage of high-level nuclear waste. In addition, information about multiple oxidation states, particulate transport, and other properties of isotopic species can be obtained. The procedure includes preparation of tracers and pretreated groundwater, treatment of crushed rock for use in the columns, loading of the column with rock, measurement of free column volume, and loading of tracers on the column and their elution.

## 2. The Tracers

The tracers commonly used are  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{133}\text{Ba}$ ,  $^{152}\text{Eu}$ ,  $^{141}\text{Ce}$ ,  $^{95m}\text{Tc}$ ,  $^{131}\text{I}$ , and  $^3\text{H}$  (the  $^3\text{H}$  as tritiated water). All are available commercially and are prepared for use on a column as described here.

For strontium, cesium, and barium, evaporate aliquots of the commercial solutions to dryness, dissolve in  $\sim 2$  ml of conc HCl, and evaporate again. Then add  $\sim 0.5$  ml of pretreated groundwater (see below). Carry out the same treatment for cerium and europium, but use 5 ml of groundwater. Add an aliquot of  $^{95m}\text{Tc}$  (which is obtained in alkaline solution) to  $\sim 0.5$  ml of groundwater. (A  $5\text{-}\mu\text{l}$  aliquot of tracer usually contains between  $10^4$  and  $10^6$  dpm.) Filter and combine the tracer solutions before they are used on a column. Add aliquots of  $^{131}\text{I}$  and tritiated water to  $\sim 5$  ml of groundwater for a final concentration of  $\sim 10^4$  dpm/50  $\lambda$ . (These solutions are used to measure the free column volume.)

## 3. Preparation of Pretreated Groundwater

Add 50 g of crushed rock to 1  $\ell$  of groundwater. For crushed tuff, use the groundwater from Well J-13 in Jackass Flats, Nevada Test Site. For crushed granite and argillite, prepare a synthetic groundwater according to the directions in Refs. 1 and 2, respectively. In each case, shake the mixture for a minimum of 2 weeks. Centrifuge at 7000 rpm and filter through a Nuclepore  $0.05\text{-}\mu\text{m}$  filter.

## 4. Treatment of Rock for Use in a Column

Sieve  $\sim 5$  g of crushed rock to particles of  $< 250$   $\mu\text{m}$  in diameter. Combine with  $\sim 100$  ml of groundwater that has been pretreated with the same kind of rock, and shake for a minimum of 1 week. Decant the fines and wet-sieve the rock with pretreated groundwater. For tuff and granite, the typical particle size used in the column is 38 to 106  $\mu\text{m}$  and for argillite, 180 to 250  $\mu\text{m}$ . Set aside a portion of the rock to dry; use it to characterize the rock (for example, by x-ray diffraction) and to measure the rock density.

## 5. Procedure

Bio-Rad Econo Column polyethylene frits and polypropylene Luer fittings are used in the column. The column itself is made from either Teflon or acrylic tubing; the ends are machined to accommodate the fittings tightly. The width is 0.40 to 0.50 cm, and the length is up to 8 cm.

*Step 1.* Add a Luer fitting that contains a polyethylene frit to boiling  $\text{H}_2\text{O}$  and let stand for several minutes. Place the fitting on one end of the column and a Bio-Rad econo funnel on the other end. Add a small volume of pretreated groundwater to the column and follow that with a slurry of pretreated crushed rock. Let the rock settle; be sure to add enough rock so that some is left in the funnel. Wash and pack the column of crushed rock with a large volume of pretreated groundwater.

*Step 2.* Remove excess rock from above the column, so that the rock is level with the top of the column. Measure the free column volume with either tritiated water or  $^{131}\text{I}$  solution by adding the traced solution to the funnel on top of the column and taking 1-drop samples of effluent with a fraction collector. (If it is not known whether  $^{131}\text{I}$  is sorbed by the rock, measure the free column volume with both tritiated water and  $^{131}\text{I}$  solution.)

*Step 3.* Prepare a beaker of boiling  $\text{H}_2\text{O}$ . Place a Luer fitting that contains a frit in the boiling  $\text{H}_2\text{O}$  for several min. Pipette any excess groundwater from the top of the column and add  $\sim 5 \mu\text{l}$  of tracer solution to the top of the column (Note). Remove the fitting from the boiling  $\text{H}_2\text{O}$ , shake off excess  $\text{H}_2\text{O}$ , and as quickly as possible press the fitting firmly onto the top of the column. (If the fitting cools before being placed onto the column, it will not fit properly, and the column will probably have to be discarded.) Turn the column over and place it directly onto a three-way stopcock at the end of a syringe filled with pretreated groundwater. Use a pump (for example, Sage Model 352) to force groundwater slowly ( $\sim 1 \text{ ml/d}$ ) upward through the column. Run the tubing from the top of the column to a drop sample collector or through the cap of a labeled, weighed collection vial. Weigh each sample as soon as it is collected; use a  $\text{Ge(Li)}$  detector to count the sample if more than one isotope has been loaded, and a  $\text{NaI}$  detector if only one isotope has been loaded.

#### Note

With cerium and europium tracers (and other lanthanides and actinides), the solubilities are such that a larger volume may be needed to load sufficient activity. In those cases, the column should be assembled completely and cerium and europium loaded with the syringe-pump system.

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(October 1989)

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