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*Collected Radiochemical and
Geochemical Procedures*

Fifth Edition

For Reference

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Los Alamos

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*Prepared by Carla E. Lowe, Group INC-11
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LA-1721, 5th Ed.

UC-701 and UC-703
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*Collected Radiochemical and
Geochemical Procedures*

Fifth Edition

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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.

1.

| Representative elements | | d-Block elements | | | | | | | | | | Representative elements | | Noble gases | | | | |
|--|--------------------------------|--|--|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------------------|-----------------------------------|---------------------------------------|---|--|---|--|---|---|----------------------------------|
| I (1) ns^1 | II (2) ns^1 | III (13) $ns^2 np^1$ | IV (14) $ns^2 np^2$ | V (15) $ns^2 np^3$ | VI (16) $ns^2 np^4$ | VII (17) $ns^2 np^5$ | He 2 $1s^2$ 4.00260 | | | | | | | | | | | |
| Period number, highest occupied electron level | Group numbers | 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 | | | | | | | | | | | |
| H 1 $1s^1$ 1.0079 | Li 3 $2s^1$ 6.941 | Be 4 $2s^1$ 9.01218 | Sc 21 $3d^1 4s^2$ 44.9559 | Ti 22 $3d^2 4s^2$ 47.88 | V 23 $3d^3 4s^2$ 50.9415 | Cr 24 $3d^4 4s^2$ 51.996 | Mn 25 $3d^5 4s^2$ 54.9380 | Fe 26 $3d^6 4s^2$ 55.847 | Co 27 $3d^7 4s^2$ 58.9332 | Ni 28 $3d^8 4s^2$ 58.69 | Cu 29 $3d^9 4s^2$ 63.546 | Zn 30 $3d^{10} 4s^2$ 65.38 | Ga 31 $4s^2 3p^1$ 69.72 | Ge 32 $4s^2 3p^2$ 72.59 | As 33 $4s^2 3p^3$ 74.9216 | Se 34 $4s^2 3p^4$ 78.96 | Br 35 $4s^2 3p^5$ 79.904 | Kr 36 $4s^2$ 83.80 |
| Na 11 $2s^1$ 22.98977 | Mg 12 $3s^1$ 24.305 | (3) $(n-1)d^1 ns^2$ | (4) $(n-1)d^2 ns^2$ | (5) $(n-1)d^3 ns^2$ | (6) $(n-1)d^4 ns^2$ | (7) $(n-1)d^5 ns^2$ | (8) $(n-1)d^6 ns^2$ | (9) $(n-1)d^7 ns^2$ | (10) $(n-1)d^8 ns^2$ | (11) $(n-1)d^9 ns^2$ | (12) $(n-1)d^{10} ns^2$ | 3s ² 3p ¹ 26.98154 | 3s ² 3p ² 28.0855 | 3s ² 3p ³ 30.97376 | 3s ² 3p ⁴ 32.06 | 3s ² 3p ⁵ 35.453 | 3s ² 3p ⁶ 39.948 | |
| K 19 $4s^1$ 39.0983 | Ca 20 $4s^2$ 40.08 | Rb 37 $5s^1$ 85.4678 | Sr 38 $5s^2$ 87.62 | Y 39 $4d^1 5s^2$ 88.9059 | Zr 40 $4d^2 5s^2$ 91.22 | Nb 41 $4d^3 5s^1$ 92.9064 | Mo 42 $4d^4 5s^1$ (98) | Tc 43 $4d^5 5s^1$ 101.07 | Ru 44 $4d^6 5s^1$ 102.9055 | Rh 45 $4d^7 5s^1$ 106.42 | Pd 46 $4d^8 5s^1$ 107.868 | Ag 47 $4d^9 5s^1$ 112.41 | Cd 48 $4d^{10} 5s^1$ 114.82 | In 49 $5s^2 5p^1$ 118.69 | Sn 50 $5s^2 5p^2$ 121.75 | Sb 51 $5s^2 5p^3$ 127.60 | Te 52 $5s^2 5p^4$ 126.9045 | I 53 $5s^2 5p^5$ 131.29 |
| Cs 55 $6s^1$ 132.9054 | Ba 56 $6s^2$ 137.33 | La ^a 57 $5d^1 6s^2$ 138.9055 | Hf 72 $4f^1 5d^2 6s^2$ 178.49 | Ta 73 $5d^3 6s^2$ 183.85 | W 74 $5d^4 6s^2$ 186.207 | Re 75 $5d^5 6s^2$ 190.2 | Os 76 $5d^6 6s^2$ 192.22 | Ir 77 $5d^7 6s^2$ 195.09 | Pt 78 $5d^8 6s^2$ 196.9665 | Au 79 $5d^9 6s^2$ 200.59 | Hg 80 $5d^{10} 6s^2$ 204.383 | Tl 81 $6s^2 6p^1$ 207.2 | Pb 82 $6s^2 6p^2$ 208.9804 | Bi 83 $6s^2 6p^3$ (209) | Po 84 $6s^2 6p^4$ (210) | At 85 $6s^2 6p^5$ (222) | Rn 86 $6s^2$ 6s ² 6p ⁶ | |
| Fr 87 $7s^1$ (223) | Ra 88 $7s^1$ 226.0254 | Ac ^b 89 $6d^1 7s^2$ (261) | Unq 104 $6d^2 7s^2$ (262) | Unp 105 $6d^3 7s^2$ (263) | Unh 106 $6d^4 7s^2$ (262) | Uns 107 $6d^5 7s^2$ (265) | Uno 108 $6d^6 7s^2$ (266) | Une 109 $6d^7 7s^2$ (266) | | | | | | | | | | |

f-Block elements

| | | | | | | | | | | | | | | |
|--------|--|--|---|--|--|--|--|--|--|---|---|---|---|--|
| Symbol | * Lanthanides ~ $4f^n 5d^0 - 16s^2$ | | | | | | | | | | | | | |
| | Ce 58 $4f^1 5d^1 6s^2$ 140.12 | Pr 59 $4f^2 5d^0 6s^2$ 140.9077 | Nd 60 $4f^3 5d^0 6s^2$ 144.24 | Pm 61 $4f^4 5d^0 6s^2$ (145) | Sm 62 $4f^5 5d^0 6s^2$ 150.36 | Eu 63 $4f^6 5d^0 6s^2$ 151.96 | Gd 64 $4f^7 5d^1 6s^2$ 157.25 | Tb 65 $4f^8 5d^0 6s^2$ 158.9254 | Dy 66 $4f^9 5d^0 6s^2$ 162.50 | Ho 67 $4f^{10} 5d^0 6s^2$ 164.9304 | Er 68 $4f^{11} 5d^0 6s^2$ 167.26 | Tm 69 $4f^{12} 5d^0 6s^2$ 168.9342 | Yb 70 $4f^{13} 5d^0 6s^2$ 173.04 | Lu 71 $4f^{14} 5d^1 6s^2$ 174.967 |
| Symbol | * Actinides ~ $5f^n 6d^0 - 17s^2$ | | | | | | | | | | | | | |
| | Th 90 $5f^1 6d^1 7s^2$ 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 $5f^5 6d^1 7s^2$ (244) | Am 95 $5f^6 6d^1 7s^2$ (243) | Cm 96 $5f^7 6d^1 7s^2$ (247) | Bk 97 $5f^8 6d^1 7s^2$ (247) | Cf 98 $5f^9 6d^0 7s^2$ (247) | Es 99 $5f^{10} 6d^0 7s^2$ (251) | Fm 100 $5f^{11} 6d^0 7s^2$ (252) | Md 101 $5f^{12} 6d^0 7s^2$ (257) | No 102 $5f^{13} 6d^0 7s^2$ (258) | Lr 103 $5f^{14} 6d^0 7s^2$ (260) |

H
1
 $1s^1$
Atomic number
1.0079
Outer configuration
1s¹
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
- Separation of Element 105 from Fission Products
- 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
- $^{230}\text{Th}(\text{ionum})$

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, $Sb_2O_5 \bullet XH_2O$ (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}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 $K_2TeO_4 \bullet 2H_2O$ in 6M HCl

Copper carrier: 5 mg copper/ml, added as $CuCl_2 \bullet 2H_2O$ in 6M HCl

HCl: conc; 6M

HI: conc (47%)

4-methyl-2-pentanone (hexone)

H_2S ; gas

HAP: $Sb_2O_5 \bullet XH_2O$; 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 $SbCl_5$ are diluted to 2 l with H_2O , 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 H_2O . The material is dried under reduced pressure for several hours, powdered, and dried in an oven at 270°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 H_2O . (The HCl concentration should be ~1M.) Saturate the solution with H_2S , 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 H_2O (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 ~2 min on a steam bath, and transfer the solution to a 60-ml separatory funnel. Add 20 ml of hexone, shake for ~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 H₂O, and saturate the solution with H₂S. 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 ~2 ml of butanol-HCl reagent. Permit the mixture to stand for ~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 (~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 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 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 1*M* 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 $\text{FeCl}_3 \bullet 6\text{H}_2\text{O}$ in 1*M* HCl

HCl: 1*M*; conc

HClO_4 : conc

HNO_3 : 3*M*; 6*M*; conc

Aqua regia: 3:1 V/V conc HCl: conc HNO_3

NH_4OH : conc

NaOH : 6*M*

H_2S : gas

Ethanol: absolute

9-molybdochosphoric acid solution: 5 g of 12-molybdochosphoric acid, gently heated to ~400 to 450°C (color will change through orange to green). Cool. Leach with ~10 ml H_2O . Filter, oxidize greenish solution to yellow

solution with bromine water. Make up to ~20 ml with 6*M* HNO_3 .

TPT exchanger: To 180 ml of a 0.0015*M* TlNO_3 solution in 0.4*M* 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 0.4*M* HNO_3 . Evaporate the mixture containing precipitated thallium(I) phospho-12-tungstate until the volume is ~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 6*M* 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 HNO_3 , and 8 ml of conc HClO_4 . Heat until dense 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 ~15 min in an ice bath. Centrifuge and discard the supernate. Add 20 ml of absolute ethanol to the 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 H_2O in 1 drop of conc HCl and stir to effect solution. Neglect any residue. Add 5 drops of iron carrier and then conc NH_4OH 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 3*M* HNO_3 , and transfer to a clean centrifuge tube. Wash the erlenmeyer flask twice with 10-ml portions of 3*M* 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 HNO₃. Discard the washing.

Step 5. Dissolve the precipitate in a minimum amount of 6M NaOH, heating if necessary. Dilute to 20 ml with H₂O and make barely acidic with 6M HNO₃ and then barely alkaline with 6M NaOH. Saturate the solution with H₂S, heat to boiling, add 1 drop of conc HNO₃, and heat to coagulate the MoS₃ 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 HNO₃ 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 HNO₃ under pressure (6 to 8 drops per min) until the effluent is clear. Wash the erlenmeyer flask with two 2-ml portions of 3M HNO₃ 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 HNO₃ 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 HNO₃ and 8 ml of conc HClO₄, and evaporate until dense HClO₄ 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 RbClO₄ 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 TlNO₃.

(October 1989)

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 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 CsClO_4 precipitated from 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 CsCl in H_2O ; 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 HNO_3

HCl : 6*M*; conc

HNO_3 : conc

HClO_4 : 70%

NaOH : 6*M*; pellets

NH_4OH : 6*M*

Silicotungstic acid: solid

Ethanol: absolute

Phenolphthalein indicator solution: 1% in 90% ethanol

3. Preparation and Standardization of Carrier

Dissolve 12.7 g of CsCl in H_2O and dilute to 1 ℓ with H_2O .

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

HNO_3 and 5 mL of 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°C for 15 min, cool, and weigh as 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 6*M* in HCl . [If the active solution contains HNO_3 , evaporate (with carrier) to dryness and take up with 40 mL of 6*M* HCl .]

Step 2. Add ~2 g of silicotungstic acid dissolved in 2 mL of H_2O and let stand for at least 1 h (preferably overnight). Centrifuge, discard the supernate, and wash the precipitate twice with 10- mL portions of 6*M* HCl .

Step 3. Dissolve the cesium precipitate by boiling with 2 mL of H_2O and adding two pellets of NaOH (~0.24 g). Add H_2O , if necessary, to prevent boiling to dryness. Pour into 20 mL of hot HCl in a 125- mL erlenmeyer flask and boil. Add 0.5 mL of conc HNO_3 and continue to boil. Add 10 mL of HClO_4 and boil until white fumes appear. Cool and add 10 mL of H_2O , 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 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 H₂O, heat to boiling, add 0.5 ml of iron carrier, 2 drops of phenolphthalein indicator, and 6M NH₄OH 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)₃. Centrifuge and pour the supernate into a 50-ml erlenmeyer flask.

Step 7. Boil and remove NH₃ by adding 2 drops of 6M NaOH.

Step 8. Add 0.5 ml of conc HNO₃ and 5 ml of HClO₄. 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 H₂O, heating if necessary, and transfer to a 50-ml erlenmeyer flask. Wash the centrifuge tube with 2 ml of H₂O and transfer washing to the 50-ml erlenmeyer flask. Heat to boiling to remove ethanol (1 min). Repeat *Step 8*, making sure to remove HClO₄ 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 CsClO₄. Silica and tungstic oxide (WO₃) remain behind.

2. The CsClO₄ must be washed thoroughly with absolute ethanol to remove NaClO₄ that has coprecipitated.

3. If 13.7-d ¹³⁶Cs is to be determined in the presence of 33-y ¹³⁷Cs, gamma-counting with a scintillation counter is advantageous because there are 2 γ 's per disintegration for ¹³⁶Cs and only one for ¹³⁷Cs. A 400-mg Al/cm² absorber will stop most of the betas that are emitted by both isotopes of cesium. The most practicable way of resolving the two components, ¹³⁶Cs and ¹³⁷Cs, 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 2*M* 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 H_2O ; 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 HNO_3

HClO_4 : 3*M*; conc

HCl : 2*M*; 6*M*; conc

HNO_3 : conc

NaOH : pellets

Silicotungstic acid: 1 g/ ml H_2O

Sodium dipicrylaminate solution: Stir 25 g of dipicrylamine with 500 ml of H_2O and add 6*M* 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 0.1*M* NaOH and dilute to 100 ml with H_2O .

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 HNO_3 and 5 ml of conc 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 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 6*M* 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 6*M* HCl.

Step 2. Add 2 ml of H_2O 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 3*M* 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 dipicrylaminate 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 HNO₃ and evaporate the solution to ~10 ml. Add 5 ml of conc HClO₄ 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 CsClO₄ 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 CCl_4 of the beryllium-acetylacetone 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 BaBeF_4 . The chemical yield is $\sim 90\%$. Beryllium run on 10^{14} fissions 4 d old gave less than 1 β count/min. Another sample, consisting of a mixture of ^7Be , 10^{14} old fission products, and 2×10^{14} fresh fission products in 100 ml of 4M HCl, resulted in pure ^7Be .

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 Na_2TeO_4 in H_2O

HCl: conc, 6M

HNO_3 : conc

HF: conc

NH_4OH : conc

NaOH : 10M

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

Acetylacetone (3,4-pentanedione): solution made by shaking 15 ml with 100 ml H_2O

Wash solution: The wash solution for the extraction is made up as follows: 15 ml acetylacetone, 100 ml 0.2M EDTA, and 300 ml H_2O ; NH_4OH added until the pH

reaches 7.7. Kept in tightly closed plastic bottle

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 acetylacetone solution. Mix thoroughly. Add conc NH_4OH until the pH equals 7.7 ± 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 CCl_4 and shake 1 min. Transfer the CCl_4 layer to 60-ml separatory funnel. Extract twice more with 8 ml of CCl_4 ; add each portion to the same 60-ml separatory funnel. Discard the H_2O layer. To the 24 ml of CCl_4 add 20 ml of wash solution (see Reagents). Shake 1 min and let stand several minutes. Transfer the CCl_4 to a clean separatory funnel.

Step 3. Add 10 ml of 6M HCl to the CCl_4 and shake for ~ 30 s. Drain the 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 CCl_4 in the separatory funnel, shake 30 s and discard the 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 HNO_3 if the solution starts to turn dark because of the organic material present. Add ~ 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 ~ 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 H₂O. Add excess NH₄OH and put in an ice bath for ~30 min or until all the beryllium has precipitated as Be(OH)₂. 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)₂ in 10 drops of conc HCl and add 1 drop of zirconium carrier. Make the volume ~15 ml with H₂O and add 3 to 4 ml 10M NaOH. Mix thoroughly and centrifuge the Zr(OH)₄. Transfer the supernate to a clean plastic centrifuge cone and discard the Zr(OH)₄.

Step 6. To the supernate add 2 drops of methyl red solution and conc HCl until the solution is acidic. Precipitate Be(OH)₂ by adding NH₄OH. Centrifuge and discard the supernate. Dissolve the Be(OH)₂ with 10 drops of conc HCl and dilute to 15 ml with H₂O. 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 NH₄OH 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 ScF₃.

Step 8. Put sample in a steam bath until hot and add 1.5 ml of 1M BaCl₂. 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 H₂O, centrifuge, and discard the wash. Transfer the precipitate with H₂O to the Millipore filter system (Note 3). Filter

the sample, wash with H₂O, 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 ¹³²Te-¹³²I and ⁹⁵Zr-⁹⁵Nb. 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°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-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 TMPolypropylene columns; source: Bio-Rad Laboratories, Richmond, California. Column dimensions: ~10 cm long; reservoir volume: ~9 ml; resin bed volume: ~2 ml; bed dimensions: ~4 cm by ~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°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 ~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 ~20 ml with H_2O , and make alkaline with 10M $NaOH$. Add ~1 ml of excess $NaOII$ 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 NH₄OH. (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 NH₄OH. (Two precipitations are necessary to minimize the presence of 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 H₂O content would change drastically the concentration of the H₂C₂O₄-HCl solution that is used to dissolve it.) Add 8 ml of the 0.25M H₂C₂O₄-0.1M 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 H₂C₂O₄-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 H₂C₂O₄-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 NH₄OH in slight excess to precipitate Be(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 Be(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 H₂O and carefully neutralize the solution with conc NH₄OH to precipitate Be(OH)₂ (Note 2). Centrifuge and discard the supernate.

Dissolve the precipitate in a minimum of conc HCl, dilute the solution to ~5 ml with H₂O, add paper pulp, and precipitate Be(OH)₂ with conc NH₄OH. Filter and ignite to BeO at 1000°C in a furnace for 30 min.

Notes

1. It is perfectly safe to fume to dryness a solution containing H₂SO₄ and HClO₄ if both acids are initially dilute. Do not add conc H₂SO₄ to conc HClO₄ 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 ⁷Be. If the Be(OH)₂ contains relatively large amounts of impurities, repeat the double NaOH scavenge as described in *Step 3*. Then carry out two double NH₄OH precipitations before igniting Be(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}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 3×10^{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 HNO_3

Scandium carrier: 10 mg scandium/ml, added as 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 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 HNO_3

Barium carrier: 1M BaCl_2

Strontium carrier: 10 mg strontium/ml, added as $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in H_2O

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

H_2SO_4 : conc

NH_4OH : conc; 0.1M

NaOH : 10M

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

NH_4Cl : 3M

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

H_2S : gas

Ethanol: absolute

Dowex AG 50-X4, 100 to 200 mesh cation-exchange resin; slurry in H_2O

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 NH_4Cl and dilute to 20 ml with H_2O .

Step 2. Add 2 drops each of iron, lanthanum, scandium, and zirconium carriers and then an excess of conc NH_4OH 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 H_2S 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 H_2S .

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 H_2SO_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 $Mg(OH)_2$. 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 H_2O , add 2 drops of palladium carrier, and bubble in H_2S 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 H_2S 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 H_2O to 20 ml, add 3 ml of 1.5M $(NH_4)_2HPO_4$, and then add an excess of conc NH_4OH dropwise to precipitate $MgNH_4PO_4 \cdot 6H_2O$. Centrifuge and discard the supernate. Wash the precipitate with H_2O containing a few drops of NH_4OH and discard the washings.

Step 12. Dissolve the precipitate in 1 to 2 drops of conc HCl and dilute to 10 ml with H_2O . 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 H_2O 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 H_2O . Centrifuge and transfer the supernate to a clean centrifuge tube. To the supernate add 3 ml of 1.5M $(NH_4)_2HPO_4$ and heat on a steam bath for 2 min. Add conc NH_4OH dropwise until $MgNH_4PO_4 \cdot 6H_2O$ precipitates. Filter the precipitate onto a weighed filter paper, wash the precipitate with 0.1M NH_4OH 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 $NH_4^+-NH_4OH$ solution; most of the magnesium is left in the supernate and is recovered by precipitation with NaOH. The precipitate from the NH_4OH treatment is dissolved and reprecipitated until no detectable magnesium is found in the supernate after addition of NaOH. All $Mg(OH)_2$ precipitates are dissolved in conc HCl and combined. The solution is then treated with $NH_2OH \cdot HCl$ as described in *Step 1* before *Step 2* is taken.

(October 1989)

CALCIUM

W. H. Burgus

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 HNO_3 . The 40-h ^{140}La , which has grown in from 12.5-d ^{140}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 $\sim 30\%$.

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 HNO_3 ; standardized

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 $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ in very dilute HCl

Copper carrier: 10 mg copper/ mL , added as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in H_2O

Nickel carrier: 10 mg nickel/ mL , added as $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in very dilute 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 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 HNO_3

Barium carrier: 10 mg barium/ mL , added as $\text{Ba}(\text{NO}_3)_2$ in H_2O

Lanthanum carrier: 10 mg lanthanum/ mL , added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

HCl : 6*M*

HNO_3 : conc; white fuming

NH_4OH : conc

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

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

NaBrO_3 : 1*M*

H_2S : 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 H_2O . Add 1 mL of HNO_3 , and dilute to 1 L with H_2O .

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 H_2O and once with ethanol. Suck dry for several minutes. Dry to constant weight in an oven at no more than 100°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 H_2O 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 NH_4OH . Centrifuge and discard the precipitate, transferring the supernate to 40- mL centrifuge tube.

Step 2. Acidify the solution with conc HNO_3 , add 6 drops of iron carrier, heat to boiling, and precipitate $\text{Fe}(\text{OH})_3$ by the dropwise addition of conc NH_4OH . 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, 0.1*M* in HCl , and add 4 drops of palladium and 8 drops of copper carriers. Heat to boiling and pass in H_2S 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 NH_4OH until the solution is alkaline to litmus, then add an additional 0.5 ml of NH_4OH . Pass in H_2S 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 H_2O .

Step 7. Dissolve the precipitate in 5 ml of H_2O and 1 ml of conc 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 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 H_2O , 1 ml each of barium and strontium carriers, and 30 ml of fuming 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 H_2O . Transfer to a 40-ml centrifuge tube and make ammoniacal with conc NH_4OH . 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 HNO_3 and 2 ml of 1*M* NaBrO_3 (Note 1). Boil down to ~1 ml. Add 30 ml of H_2O , make strongly ammoniacal, and add 4 ml of saturated $(\text{NH}_4)_2\text{CO}_3$ solution. Centrifuge the CaCO_3 and discard the supernate.

Step 12. Dissolve the CaCO_3 in 1 to 2 ml of conc HNO_3 . Dilute to 30 ml, and add 1 ml of lanthanum carrier. Precipitate $\text{La}(\text{OH})_3$ by the addition of conc NH_4OH . 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 H_2O and then with ethanol. Suck dry. Dry in oven at 100°C for 5 min. Weigh, mount, and count (Note 2).

Notes

1. 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}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}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 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}Sr . Yttrium carrier is added and separated with the ^{90}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 HNO_3 ; standardized

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

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

Barium carrier: 10 mg barium/ mL , added as $\text{Ba}(\text{NO}_3)_2$ in H_2O

HCl : 1*M*; conc

HNO_3 : fuming; conc

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

NH_4OH : conc

Na_2CO_3 : saturated aqueous solution

Na_2CrO_4 : 10% aqueous solution

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

KClO_3 : solid

Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 241.5 g of $\text{Sr}(\text{NO}_3)_2$ in H_2O , add 10 mL of conc HNO_3 , and dilute to 1 L with H_2O . Into a 40- mL centrifuge tube, pipette 5.0 mL of the

carrier solution and add 15 mL of saturated Na_2CO_3 solution. Stir and allow to stand for at least 15 min. Filter the SrCO_3 precipitate through a weighed 15- mL sintered glass crucible of fine porosity. Wash the precipitate with 10 mL of H_2O and again with 5 mL of 95% ethanol. Dry in oven at 110°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 $\sim 5\text{ mL}$ with H_2O . Add 30 mL of cold, fuming HNO_3 (Note 1) and permit the mixture to stand in an ice bath for ~ 10 min. Centrifuge and discard the supernate.

Step 2. Dissolve the $\text{Sr}(\text{NO}_3)_2$ precipitate in 10 mL of H_2O and add 5 drops of iron carrier. Make the solution alkaline by the dropwise addition of conc NH_4OH 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% Na_2CrO_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 H_2O and stirring. Centrifuge and discard the wash.

Step 5. Add 2 mL of conc HNO_3 and 5 mL of H_2O , stir, and then add 30 mL of fuming HNO_3 . Allow to stand in an ice bath for ~ 10 min. Centrifuge and discard the supernate.

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

Step 7. To the precipitate of SrC_2O_4 add 2 ml of conc HNO_3 and ~ 200 mg of KClO_3 . Carefully bring the solution to a boil and then boil vigorously for ~ 2 min.

Step 8. Adjust the volume to ~ 15 ml with H_2O and add 5 drops of iron carrier. Make the solution alkaline by the dropwise addition of conc NH_4OH 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 BaCrO_4 precipitate through a 2-in. 60° funnel. Collect the filtrate in a clean 40-ml centrifuge tube.

Step 10. To the filtrate add conc NH_4OH until the solution is barely alkaline. Then add 5 ml of saturated Na_2CO_3 solution to precipitate SrCO_3 . Centrifuge and discard the supernate. Wash the precipitate with a mixture of 10 ml of H_2O and 2 ml of saturated Na_2CO_3 . Centrifuge and discard the wash. Slurry the precipitate and filter onto a weighed filter circle. Wash the precipitate with 5 ml of H_2O and 5 ml of 95% ethanol, dry in an oven at 110°C , and weigh (Note 2). Transfer the precipitate into a clean 40-ml centrifuge tube and permit ^{90}Y to grow into equilibrium with the ^{90}Sr . (This process requires ~ 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 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 HCl and remove it.

Step 12. Add conc NH_4OH dropwise until Y(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 Y(OH)_3 in a minimum of conc HCl and add 15 ml of H_2O . Add 20 mg of strontium holdback carrier and precipitate Y(OH)_3 with excess conc NH_4OH . Centrifuge and discard the supernate.

Step 14. Repeat *Step 13*.

Step 15. Wash the precipitate with H_2O , dissolve in a minimum of conc HCl , and add 15 ml of H_2O . Again precipitate Y(OH)_3 with conc NH_4OH , 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 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 H_2O and place in a porcelain crucible. Ignite at 900°C for 30 min. Grind the Y_2O_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°C , cool, weigh, and mount.

Notes

1. Using refrigerated fuming HNO_3 reduces the time required for cooling in an ice bath.
2. The SrCO_3 formed in this step may be mounted and counted for ^{89}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}Y is separated from ^{90}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}Y . The procedure for the analysis assumes that the yttrium has been separated from all other elements.

2. Reagents

Strontium carrier: 50 mg SrCO_3 /2 ml, standardized

Yttrium carrier: 10 mg yttrium/ml, added as Y_2O_3 in dilute HCl

HCl: conc

HNO_3 : fuming; conc

NH_4OH : 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 Na_2CO_3 was employed to precipitate SrCO_3 .

4. Procedure

Step 1. Following the procedure for the decontamination of yttrium (see the YTTRIUM procedures), weigh the Y_2O_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 Y_2O_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}Sr is ~ 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 ~ 15 ml.

Step 2. To the solution add 3 drops of methyl red solution; add conc NH_4OH 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 H_2O to 10 ml, add 3 drops of methyl red solution and an excess of 3 drops of conc NH_4OH . Centrifuge and add the supernate to the one from the first precipitation of $\text{Y}(\text{OH})_3$. The total volume should now be ~ 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 NH_4OH 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 NH_4OH and 5 ml of 10% $(\text{NH}_4)_2\text{CO}_3$. Place on a steam bath until SrCO_3 precipitates. Centrifuge and discard the supernate.

Step 6. Dissolve the precipitate in 1 to 3 drops of conc HNO_3 and 1 ml of H_2O . Add 30 ml of ice-cold fuming 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 H_2O , 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 SrCO₃ precipitate add ~5 ml of H₂O and with the aid of a stirring rod suspend the solid. Filter onto a weighed filter circle. Wash the precipitate thoroughly with H₂O and then with absolute ethanol. Dry at 110°C for 5 min, weigh as SrCO₃, 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, BaCrO_4 . Three precipitations of the chloride are carried out; the first and second are followed by Fe(OH)_3 scavenging steps. The final precipitation of barium as the chromate is preceded by a La(OH)_3 scavenging step to remove lanthanum and other fission products that were not removed by Fe(OH)_3 scavenging and form insoluble hydroxides. The chemical yield is ~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

NH_4OH : 1*M*; 6*M*

HCl: 6*M*

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

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$: 3*M*

Na_2CrO_4 : 1.5*M*

Phenolphthalein indicator solution

Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 19.0 g of $\text{Ba}(\text{NO}_3)_2$ in H_2O and dilute to 1 *l*. Pipette 5.0 ml of carrier solution into a 250-ml beaker and dilute to ~100 ml. Add 10 ml each of 6*M* $\text{H}_2\text{C}_3\text{O}_2$ and 3*M* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Place on a hot plate and bring to a boil. Add 5 ml

of 1.5*M* Na_2CrO_4 dropwise with stirring, boil for 1 min with stirring, cool to room temperature, and filter the Ba_2CrO_4 into a sintered glass crucible of fine porosity that has been washed with H_2O and ethanol, dried at 110°C for 15 min, and weighed. Wash the precipitate three times with 5-ml portions of H_2O and three times with 5-ml portions of ethanol. Dry at 110°C, cool, and weigh.

Four standardizations of the carrier solution are performed. The spread in results is ~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 H_2O and add 1 drop of phenolphthalein solution and 3 drops of iron carrier. Neutralize with 6*M* NH_4OH 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 H_2O , and add 1 drop of phenolphthalein solution and 10 drops of lanthanum carrier. Neutralize with 6*M* NH_4OH 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 6*M* HCl, and then add 10 ml of the 6*M* $\text{HC}_2\text{H}_3\text{O}_2$ -3*M* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. Heat to boiling and dropwise add 2 ml of 1.5*M* Na_2CrO_4 . Boil for 1 min with constant stirring, centrifuge, and discard

the supernate. Wash the precipitate by stirring with 20 ml of H₂O, centrifuge, and discard the supernate. Slurry the precipitate with 20 ml of H₂O and filter the BaCrO₄ on a previously washed, dried, and weighed filter paper. Wash the precipitate three times with 5-ml portions of H₂O 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 BaCl₂•H₂O, 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 BaCl₂•H₂O is precipitated. To the mixture of sample and carrier in a 40-ml centrifuge tube add 2 to 4 drops of conc H₂SO₄ to precipitate BaSO₄. Wash the precipitate by stirring with 10 ml of H₂O, centrifuge, and discard the supernate. Add 5 ml of saturated K₂CO₃ solution and boil for 2 min, adding H₂O if necessary. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H₂O 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 H₂O and cool in an ice bath. Proceed with the precipitation of BaCl₂•H₂O.
3. The BaCrO₄ precipitates are set aside for 134 h before counting is begun. This permits ¹⁴⁰Ba and ¹⁴⁰La 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 ¹⁴⁰Ba and ¹⁴⁰La.

(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 π^+ ions of high energy and ^{238}U . The main steps of the analysis are the extraction of gallium into isopropyl ether from an aqueous solution 8*M* in HCl, PdS scavenges from dilute acid solutions, and a final precipitation of gallium as the 8-quinolinate (8-hydroxyquinolate). The chemical yield is ~80%.

2. Reagents

Gallium carrier: added as GaCl_3 in 0.1*M* HCl; ~5 mg Ga^{3+}/mL ; the carrier was standardized by precipitation of the metal as the 8-quinolinate; 1 mL of carrier gave 36 mg of the quinolinate.

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

HClO_4 : conc

HCl: conc; 8*M*; 0.2*M*

NH_4OH : conc

H_2S : gas

NH_4Cl : 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 2*M* $\text{HC}_2\text{H}_3\text{O}_2$

Isopropyl ether

Methyl red indicator solution: 0.1% solution in ethanol

3. Procedure

Step 1. To the sample (3*M* in HCl) in a 60-mL separatory funnel, add sufficient conc HCl to make the acid concentration 8*M*. 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 8*M* HCl and discard the washes. Remove the gallium from the ether layer by extraction with two 10-mL portions of distilled H_2O and drain the H_2O layers into a clean 40-mL centrifuge tube. Discard the ether layer.

Step 3. Add ~2 g of NH_4Cl and 2 drops of methyl red indicator solution, and neutralize the solution with conc NH_4OH , adding 1 drop in excess. Centrifuge the $\text{Ga}(\text{OH})_3$ precipitate and discard the supernate. Wash the precipitate with 10 mL of H_2O and discard the wash.

Step 4. Dissolve the precipitate in 10 mL of 0.2*M* HCl. Add 2 drops of palladium carrier, place the solution on a steam bath, and bubble in H_2S until the 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 0.2*M* HCl, add 2 drops of palladium carrier, and repeat the PdS scavenge and filtration.

Step 5. Boil the filtrate to remove excess H_2S . Add 2 drops of methyl red indicator solution and neutralize with conc NH_4OH , adding 1 drop in excess. Centrifuge the $\text{Ga}(\text{OH})_3$ precipitate and discard the supernate.

Step 6. Add 1 mL of conc HClO_4 to the precipitate and heat to fumes over a burner. (The fuming process removes any ruthenium present as the volatile RuO_4 .) Cool the solution and add 10 mL of H_2O and ~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-quinolinate onto a previously washed, dried, and weighed filter circle. Wash the precipitate thoroughly with 5-mL portions of H_2O and permit it to dry under suction. Finally, dry the precipitate in an oven at 110°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 NH_4OH ; 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 1*M* HCl and is then precipitated as the hydroxide and converted to the bromide by means of 4.5*M* 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 InCl_3 in 1.5*M* HCl; standardized

Antimony carrier: 10 mg antimony/*mL*, added as SbCl_3 in 1*M* HCl

Cadmium carrier: 10 mg cadmium/*mL*, added as CdCl_2 in 1*M* HCl

HCl: 1*M*; 1.5*M*

HBr: 4.5*M*

NH_4OH : conc

H_2S : gas

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

Sulfosalicylic acid: 5% in H_2O

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

Ethyl ether: saturated with 4.5*M* 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 1.5*M* HCl.

Pipette 2.00 *mL* of the above solution into a 100-*mL* beaker, and add 20 *mL* of H_2O , 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 H_2O 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 NH_4OH . Centrifuge the precipitate and discard the supernate.

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

Step 3. Dissolve the precipitate in 10 *mL* of 1*M* 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 H_2S , 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 1*M* HCl and digest just at boiling for 1 min. Centrifuge and transfer the supernate to a clean 40-*mL* centrifuge tube. Discard the precipitate.

Step 6. Dilute the solution to 10 *mL* with H_2O and repeat *Steps 3* through *5* three times.

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

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

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

Note

This procedure has been used for the determination of 4.5-h ^{115}In , daughter product of 58-h ^{115}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 SO_2 and N_2H_4 in HCl medium. This is followed by a series of TlI and La(OH)_3 precipitations. The 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 TlCl_3 in dilute HCl ; standardized

Tellurium carrier: 10 mg tellurium/ mL , added as Na_2TeO_3 in dilute HCl

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

HCl : 3M

HNO_3 : 6M

NH_4OH : 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 H_2O

KHSO_3 : solid

SO_2 : saturated aqueous solution

NaI : solid

Methanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 11.17 g of Tl_2O_3 in dilute 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 KHSO_3 . Boil off excess SO_2 and make the solution

alkaline with conc NH_4OH . Add 5 mL of 10% $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ solution to precipitate Tl_2CrO_4 . Bring to a boil, permit the precipitate to stand for ~ 12 h, and filter onto a weighed 30- mL sintered glass crucible of fine porosity. Wash the precipitate with 10 mL of H_2O and then with 10 mL of 95% ethanol. Dry at 110°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 HCl and again evaporate to dryness. Repeat evaporation once again with 5 mL of HCl . Add 20 mL of 3M 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° 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 H_2O to make the total volume ~ 75 mL and then add ~ 2 g of solid 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 HNO_3 . Heat over open flame until all I_2 color has disappeared. Dilute with H_2O 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 NH_4OH . Add 1 mL of NH_4OH in excess.

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

Step 4. To the supernate add ~ 1 g of NaI , centrifuge the precipitated TlI , and discard the supernate. To the precipitate add 1 ml of 6M HNO_3 and heat over open flame until 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% $\text{Na}_2\text{CrO}_4 \bullet 4\text{H}_2\text{O}$ solution. Allow to stand 5 to 10 min to permit the Tl_2CrO_4 precipitate to coagulate. Filter on a weighed filter circle. Wash the precipitate with 5 ml of H_2O , and then with two 5-ml portions of absolute methanol. Dry at 110°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 $TlCl_3$ in dilute HCl; standardized (see THALLIUM procedure)

Arsenic carrier: 10 mg arsenic/ml, added as $Na_3AsO_4 \cdot 12H_2O$ in H_2O ; standardized (see ARSENIC procedure)

Scandium carrier: 10 mg scandium/ml, added as $ScCl_3$ in dilute HCl; standardized; (see SCANDIUM I procedure)

Tellurium carrier: 10 mg tellurium/ml, added as Na_2TeO_4 in H_2O

HNO_3 : 6M

$HClO_4$: conc

HCl: conc; 3M

NH_4OH : conc

$N_2H_4 \cdot H_2SO_4$: solid

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 H_2O . Add a few drops of saturated aqueous 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 HNO_3 to the TlI precipitate and heat over an open flame until all I_2

color has disappeared. Add 1 ml each of tellurium carrier and conc $HClO_4$ 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 $N_2H_4 \cdot H_2SO_4$ and heat to boiling. Add 1 ml of saturated aqueous SO_2 and continue to boil while making three or four successive additions of $SO_2 \cdot H_2O$. 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 $SO_2 \cdot H_2O$ 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 H_2S until precipitation of As_2S_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 H_2S and excess HCl. Precipitate $Sc(OH)_3$ by making the solution alkaline by the dropwise addition of conc NH_4OH . 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, LaF_3 , and BaSO_4 scavengings are performed in the presence of the F^- ion, which keeps germanium in solution as the 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 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 H_2O

Barium carrier: 10 mg barium/ml, added as $\text{Ba}(\text{NO}_3)_2$ in H_2O

Lanthanum carrier: 10 mg lanthanum/ml, added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

Copper carrier: 10 mg copper/ml, added as $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in H_2O

Zirconium carrier: 10 mg zirconium/ml, added as $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1M HNO_3

HCl: 4.5 to 5.5M; conc

HI: 47% aqueous solution

H_2SO_4 : conc

HF: conc

H_3BO_3 : saturated solution

NH_4OH : conc

H_2S : gas

CH_3OH : anhydrous

3. Preparation of Carrier

Fuse 14.4092 g of reagent grade GeO_2 with 30.0 g of Na_2CO_3 . Dissolve the melt in H_2O 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 NH_4OH , add 10 to 20 drops of conc H_2SO_4 , place on a steam bath, and saturate with H_2S 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 H_2O . Discard the precipitate.

Step 3. To the filtrate add 10 drops of lanthanum carrier and 1 ml of copper carrier and saturate with H_2S 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 H_2S 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 H_3BO_3 ; saturate with H_2S . Transfer to 40-ml conical centrifuge tube, centrifuge the GeS_2 precipitate, and discard the supernate (Note 1).

Step 7. Dissolve the GeS_2 in 1 ml of conc NH_4OH and dilute to 15 to 20 ml with H_2O . Add 4 drops of zirconium carrier, centrifuge, and discard the precipitate. Make the supernate 3M with HCl, saturate with H_2S , centrifuge, and discard the supernate.

Step 8. Slurry the GeS_2 with 4.5 to 5.5M HCl (Note 2) and transfer the solution to the special still

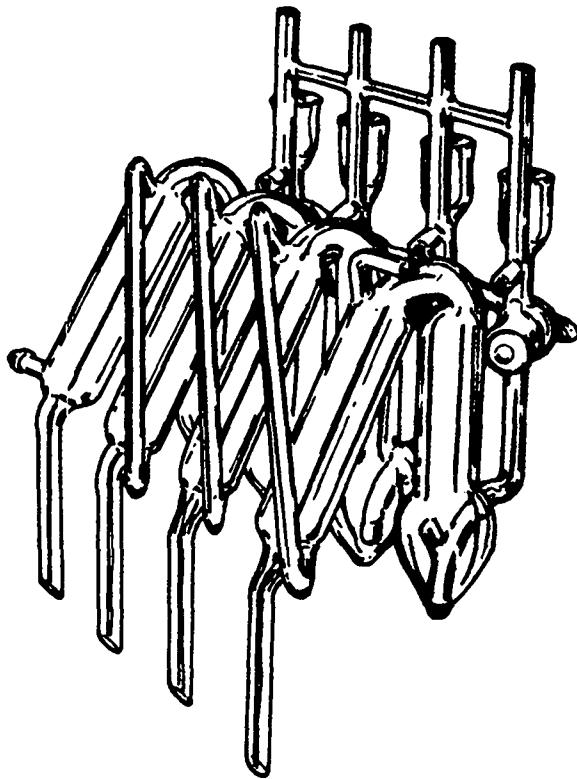


Fig. 1. Special distilling flask.

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

Step 9. Distill the GeCl_4 on an oil bath at 120°C into a 50-ml beaker containing 5 ml of 4.5 to 5.5M HCl that has been saturated at room temperature with H_2S and kept in an ice bath (Note 3). 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 H_2S and filter the precipitate onto a weighed filter circle. Wash the precipitate with anhydrous CH_3OH and dry in an oven at 110 to 120°C for 10 min. Cool, weigh as GeS_2 , and mount.

Notes

1. A water-clear supernate is not ordinarily obtained upon centrifugation of the 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 GeS_2 precipitation.

2. The concentration of HCl must not exceed that of the constant boiling mixture, or 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 H_2O and no GeCl_4 is distilled. As soon as the composition of the still reaches that of the constant boiling mixture, all the GeCl_4 distills rapidly. At higher HCl concentrations, the GeCl_4 is immediately swept out with HCl gas.

3. The H_2S is present in the receiver to show (by the formation of white GeS_2) when GeCl_4 begins to distill.

(October 1989)

SEPARATION OF GERMANIUM AND ARSENIC FROM A FISSION-PRODUCT SOLUTION

R. J. Prestwood

1. Introduction

Arsenic(III) is separated from germanium(IV) by precipitation as the sulfide in a HCl medium containing the F^- ion; the latter strongly complexes germanium(IV) as 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: 6*M*

HF: conc

H_3BO_3 : saturated solution

H_2S : gas

NaI: solid

Aerosol: 0.1% in H_2O

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 5*M* 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 H_2S until the As_2S_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 As_2S_3 precipitate is then treated as described, beginning with *Step 2* of the ARSENIC procedure.

Step 2. To the filtrate containing the germanium, add 5 to 6 ml of saturated H_3BO_3 and saturate with H_2S . Centrifuge the GeS_2 precipitate and discard the supernate. Then carry out *Steps 7* through *11* of the GERMANIUM procedure.

(October 1989)

TIN I

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

1. Introduction

This procedure for separating tin from fission products is performed ~ 2 d after irradiation; this interval is necessary to allow 2-h ^{127}Sn to decay to 93-h ^{127}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 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 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 F^- ion with H_3BO_3 , the tin is again precipitated as the sulfide, dissolved, adsorbed on an anion-exchange column, and eluted. After a final SnS_2 precipitation, the tin is dissolved and reduced to the metal by 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 Na_2TeO_3 in 3M HCl

Tellurium(VI) carrier: 10 mg tellurium/ml, added as Na_2TeO_4 in 3M HCl

Molybdenum carrier: 10 mg molybdenum/ml, added as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\bullet 4\text{H}_2\text{O}$ in 6M HCl

Antimony carrier: 10 mg antimony/ml, added as SbCl_3 in 6M HCl

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

HCl: 0.9M; conc

HF: conc

HClO_4 : 1.8M

H_3BO_3 : saturated aqueous solution

H_2S : gas

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

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 H_2O

Ethanol: absolute

Rubber cement: 6% in benzene

3. Preparation and Standardization of Carrier

Accurately weigh ~ 2.5 g of tin metal and dissolve it quantitatively in ~ 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 H_2O . Add 10 ml of a saturated aqueous solution of phenylarsonic acid, and heat at 110°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°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 Br_2 is gone; dilute with H_2O until the solution is 1M in HCl. Place in an ice bath and saturate with H_2S . 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 H₂S. 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 Br₂-H₂O and heat until the Br₂ is gone.

Step 3. Dilute the sample to 12 ml with H₂O. (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 HClO₄ and collect the eluate in a 40-ml centrifuge tube. Add 4 drops of molybdenum carrier and saturate with H₂S. 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 MoS₃ present will not dissolve) and boil for 3 min to remove H₂S. Add 1 drop each of the following carriers: tellurium(VI), tellurium(IV), and antimony. Add 0.5 ml each of Br₂-H₂O and conc HF. Dilute the sample to 6 ml with H₂O and boil. Saturate the *hot* solution with H₂S, 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 Br₂-H₂O and boil. Again saturate the *hot* solution with H₂S, 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 H₂O. Add 10 ml of saturated H₃BO₃ solution and cool in an ice bath. Bubble in H₂S. 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 H₂S. Add 1 drop each of tellurium(VI), tellurium(IV), and antimony carriers and 0.5 ml of Br₂-H₂O. Heat until all the Br₂ has been expelled. If a precipitate (MoS₃) is still present, centrifuge, and pipette the supernate into a clean centrifuge tube.

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

Step 10. Dissolve the precipitate in 2 ml of conc HCl with heat and boil the solution for 3 min to remove H₂S. Dilute the solution to ~8 ml with H₂O, cool, and add an equal volume of *cold* CrCl₂ 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 H₂O, 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 ¹²¹Sn and 9.625-d ¹²⁵Sn can be performed. Small amounts of 129.0-d ¹²³Sn and 2.8-y ¹²⁵Sb (daughter of ¹²⁵Sn) can also be observed at later times. (The half-life values quoted here are those reported by Lawrence *et al.*) If ¹²¹Sn is to be determined, a least squares analysis of the data is performed with the half-lives fixed. If only ¹²⁵Sn is to be determined, beta-counting is begun ~12 d after bombardment, when the contribution of ¹²¹Sn is small, and a correction is applied for the small amount of ¹²³Sn in the sample. A least squares analysis of the

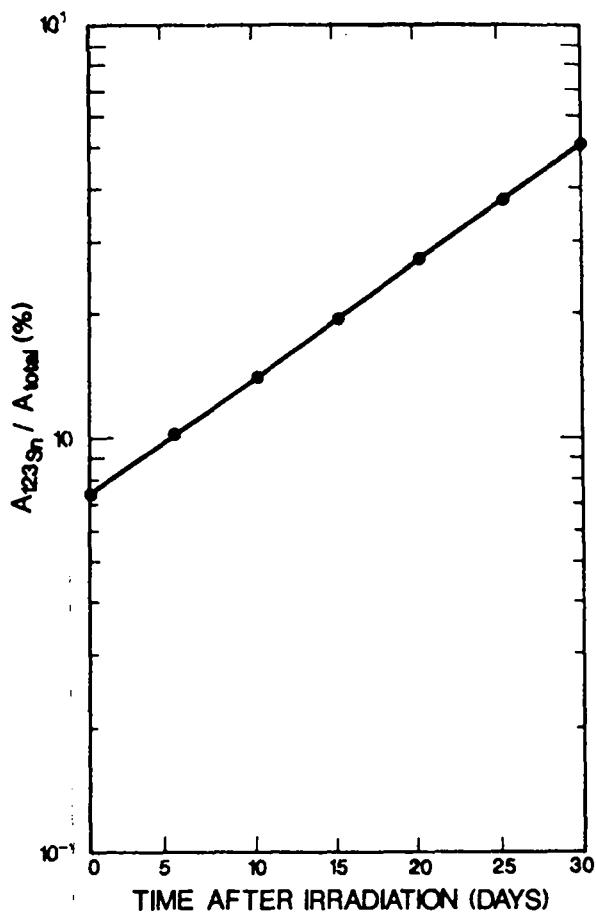


Fig. 1. Contribution of ^{123}Sn to total beta count.

decay data for several samples showed that the contribution of ^{123}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-mg/cm² aluminum windows. The proportion of ^{123}Sn activity may, of course, be different for different counting conditions.) For ease of calculation, a graph showing the contribution of ^{123}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}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 H_2SO_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 H_2SO_4 -KI. Following two cycles of the process, an Sb_2S_3 scavenge is performed; after SnS_2 precipitation, the tin is reduced to the elemental state, in which form it is counted.

The procedure requires ~ 15 min per sample and gives chemical yields of 40 to 60% with a decontamination factor of at least 10^5 for all ^{235}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 H_2O

Antimony carrier: 4 mg antimony/ml, added as $SbCl_3$ in 12M HCl

HCl: conc

NH_4OH : conc

$NH_2OH \cdot HCl$: 1M aqueous solution

$NaBrO_3$: 1M aqueous solution

H_2SO_4 -NaCl solution: 0.6M in H_2SO_4 and 0.4M in NaCl

KI: 1.2M aqueous solution

KI-I₂ solution: 1.2M KI-4 mg I₂/ml

$CrCl_2$: $\sim 1.6M$ aqueous solution

$[(CH_3)_4N]Cl$: 4M aqueous solution

4-methyl-2-pentanone (hexone)

Ethanol: 95%

H_2S : gas

N₂: 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 $NaBrO_3$, and then an excess of 1M $NH_2OH \cdot HCl$. Dilute to 40 ml with H_2O (the solution should be $<1M$ in HCl) and saturate with H_2S . Heat to digest the SnS_2 and when the precipitate has coagulated, centrifuge, and discard the supernate.

Step 2. Dissolve the SnS_2 in ~ 0.6 ml of conc HCl and add 1 ml of 4M $[(CH_3)_4N]Cl$ and 17 ml of 95% ethanol to precipitate $[(CH_3)_4N]_2SnCl_6$. Digest on a steam bath for 1 min, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate in 10 ml of 0.6M H_2SO_4 -0.4M NaCl and add the solution to 10 ml of 1.2M KI solution that has been flushed with oxygen-free N₂ in the upper extraction vessel of the extraction apparatus (Fig. 1). Continuing the N₂ flow, start the stirrer, add 2 ml of $\sim 1.6M$ $CrCl_2$ 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 H_2SO_4 -0.4M NaCl solution and 10 ml of KI-I₂ 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 I₂ and is extracted into the aqueous phase.]

Step 5. Run the aqueous phase into the lower extraction vessel, add 3 ml of $\sim 1.6M$ $CrCl_2$ 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

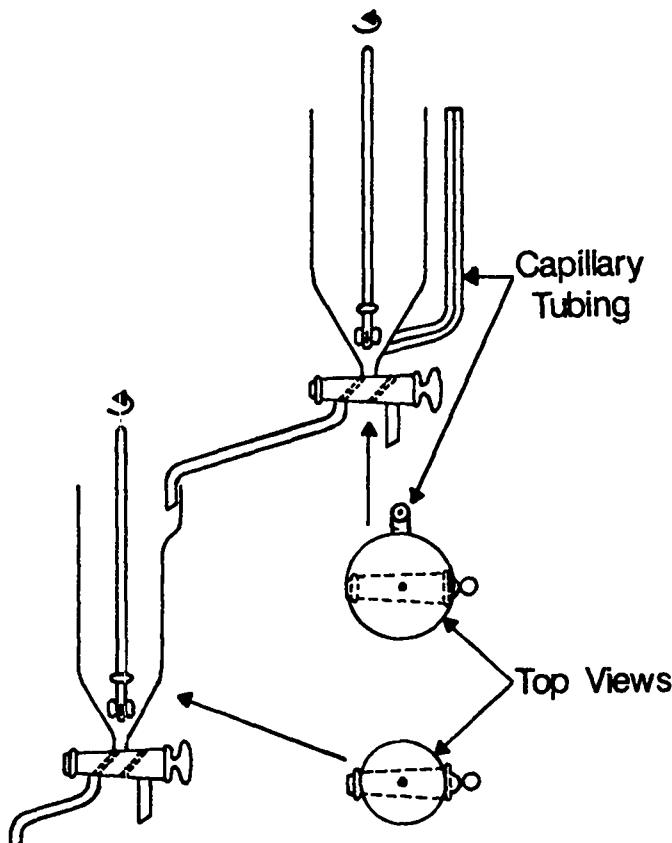


Fig. 1. Extraction vessels.

in a dry ice-isopropanol bath for 45 s, saturate with a very rapid stream of H_2S for 30 s, and centrifuge for 45 s. Filter through a Millipore HA, 0.45- μm pore filter paper with absorbent pad, and collect the filtrate in a clean centrifuge tube. Discard the precipitate.

Step 8. Add $\sim 8\text{ ml}$ of conc NH_4OH to the filtrate, saturate with H_2S , and digest on a steam bath until the precipitate coagulates. Centrifuge and discard the supernate.

Step 9. Dissolve the SnS_2 in 2 ml of hot conc HCl , add 40 ml of H_2O previously saturated with H_2S , 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 HCl , dilute to

40 ml with H_2O , and saturate with H_2S . Digest the precipitate on a steam bath, centrifuge, and discard the supernate.

Step 12. Dissolve the SnS_2 in 0.5 ml of hot conc HCl , add 8 ml of H_2O , and then add 3 ml of $\sim 1.6\text{M}$ CrCl_2 to precipitate elemental tin. Filter through a weighed, 10- μm -pore polypropylene filter paper, wash the precipitate with 95% ethanol, and air dry under suction for ~ 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) PbCl_2 , (3) $\text{Fe}(\text{OH})_3$, and (4) 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 0.01*M* HNO_3 ; standardized

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

HCl : conc

HNO_3 : conc; fuming (sp gr 1.5)

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

NH_4OH : 1*M*; conc

NaOH : 12*M*

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

Na_2CrO_4 : 1.5*M*

NH_4Cl : solid

H_2S : 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 H_2O . Pipette 5.0 mL of the solution into a 250- mL beaker, add 3 mL of 6*M* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and 2 mL of 6*M* $\text{HC}_2\text{H}_3\text{O}_2$, and dilute to 30 mL with H_2O . Heat to boiling and add 5 mL of 1.5*M* Na_2CrO_4 dropwise. Digest on a steam bath for 30 min and filter onto a weighed 15- mL sintered glass crucible. Wash the precipitate with H_2O 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 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 HNO_3 , and evaporate nearly to dryness.

Step 2. Dissolve the residue in a minimum amount of H_2O , add 30 mL of fuming 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 H_2O . Add 1 mL of conc HNO_3 , 25 mL of 95% ethanol, and 4 drops of conc HCl . Chill in an ice bath. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate in 20 mL of H_2O , add ~2 g of solid NH_4Cl , 4 drops of iron carrier, and heat to boiling. Add 2 drops of bromophenol blue indicator solution and neutralize to an alkaline endpoint with 1*M* NH_4OH . Centrifuge while hot and transfer the supernate to a clean centrifuge tube; discard the precipitate.

Step 5. Saturate the supernate with H_2S . Centrifuge and discard the supernate.

Step 6. Dissolve the precipitate in 2 mL of conc HCl and evaporate to dryness. Add 1 mL of conc HNO_3 and evaporate nearly to dryness.

Step 7. Repeat *Steps 2* and *3*.

Step 8. Add 20 mL of H_2O and 4 drops of iron carrier to the precipitate and heat to boiling. Add 12*M* 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 12*M* 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 $\text{HC}_2\text{H}_3\text{O}_2$ and 3 ml of 6M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, dilute to 20 ml with H_2O , heat to boiling, and add 3 ml of 1.5M Na_2CrO_4 while the solution is at the boiling point. Filter onto a weighed filter circle. Wash the PbCrO_4 precipitate with H_2O 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 $(NH_4)_3PO_4 \bullet 12MoO_3 \bullet 3H_2O$ (?). Arsenic is removed by precipitation of the pentasulfide. Lanthanum fluoride scavenging is included. Phosphorus is finally precipitated as $MgNH_4PO_4 \bullet 6H_2O$, in which form it is counted. The chemical yield is 70 to 80%. A sample containing 1.5×10^{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 ~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 $ZrO(NO_3)_2 \bullet 2H_2O$ in 1*M* HNO_3

Arsenic carrier: 10 mg arsenic/ml, added as $Na_2HAsO_4 \bullet 7H_2O$ in H_2O

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

HCl: 3*M*; conc

HNO_3 : 6*M*; 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 $(NH_4)_6Mo_7O_24 \bullet 4H_2O$, 800 ml H_2O , and 160 ml conc NH_4OH

"Magnesia" mixture: 50 g $MgCl_2 \bullet 6H_2O$, 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 ~10 min and then allow the precipitate to stand in the balance case for ~30 min. Weigh as $MgNH_4PO_4 \bullet 6H_2O$.

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 6*M* 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 6*M* 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_2O_2 (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_2O 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_2S 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_2O containing a few drops of aerosol solution. While the precipitate is being washed, pass H_2S 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_2S_5 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_3 precipitate.

Step 6. To the supernate, add 4 ml of conc HNO_3 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_2O 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_4OH and add 2 ml of citric acid solution (0.5 g/ml). Add 10 ml of "magnesia" mixture and conc NH_4OH (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_4OH . After precipitation begins, swirl the mixture for at least 1 min and then add 4 ml of conc NH_4OH . 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_4OH . Dissolve the precipitate in a few drops of conc HCl and a few ml of H_2O . Collect the filtrate in a 100-ml beaker.

Step 9. Add 10 ml of "magnesia" mixture and just enough conc NH_4OH to neutralize the HCl in the mixture. (One drop of NH_4OH in excess should cause the precipitate of $MgNH_4PO_4 \cdot 6H_2O$ to start forming.) Swirl for ~1 min and then add 3 ml of conc NH_4OH . 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_4OH , 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_4^{2-} 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_4NO_3 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_2O , ammonium phosphomolybdate reprecipitates.
4. The 14.1-d ^{32}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 HNO_3 , HCl , and HClO_4 removes germanium, which volatilizes as the tetrachloride; arsenic is oxidized to H_3AsO_4 . The arsenic is then converted to the triiodide by treatment with 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 H_2SO_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 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 H_2O ; standardized
 HCl : 3*M*; 6*M*; conc
 HNO_3 : conc
 H_2SO_4 : 1*M*
 HClO_4 : conc
 HI : 47%
 NaI : solid
 CrCl_2 : $\sim 1.6\text{M}$ solution
 H_2S : gas
Aerosol: 0.1% aqueous solution
Benzene
Ethanol: absolute

3. Preparation and Standardization of Carrier

Prepare an aqueous solution containing 56.6 g of $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}/\text{L}$. Pipette exactly 5 mL of the carrier solution into a 40- mL glass centrifuge tube, add 10 mL of 6*M* HCl , and heat. To the hot solution add 10 to 15 mL of 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 H_2O and once with 5 mL of absolute ethanol. Dry at 110°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 HCl and ~ 20 mg of solid NaI . Pass H_2S into the solution, which is maintained at room temperature. Centrifuge the sulfide precipitate and discard the supernate.

Step 2. To the As_2S_3 precipitate add 0.5 mL each of conc HNO_3 and HCl and 1 mL of conc HClO_4 . Heat the solution gently and then to fumes of 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 3*M* HCl into a 125- mL separatory funnel. Add 5 mL of 47% HI and 30 mL of C_6H_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 C_6H_6 phase containing AsI_3 with 5 mL of 3*M* HCl and 2 mL of 47% HI . Drain and discard the wash solution.

Step 5. Add 10 ml of 1M H₂SO₄ to the C₆H₆ 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 C₆H₆ layer.

Step 6. To the aqueous phase add 10 ml of 6M HCl, 8 ml of 47% HI, and 30 ml of C₆H₆. 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 H₂SO₄ to the C₆H₆ 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 H₂S. Centrifuge the As₂S₃ 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 CrCl₂ solution and stir continuously for 1 min, while keeping the solution hot. Again add 5 ml of CrCl₂ 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 H₂O 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 ⁷⁷As 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 ⁷⁶As (26.5 h). The thermal neutron capture cross section for arsenic is quite high and ⁷⁶As 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 $\sim 125^\circ\text{C}$. Allow the bomb to cool and then open it.

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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.

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 1*M* HCl; ~5 mg gallium/ml. (One milliliter of carrier solution is equivalent to ~36 mg of gallium 8-quinolinolate)

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

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

HNO_3 : conc

$HClO_4$: conc

HCl : 4*M*; 3*M*

HF : conc

H_3BO_3 : saturated aqueous solution

$H_2C_4H_4O_6$ (tartaric acid): saturated aqueous solution

$HC_2H_3O_2$: 2*M*

H_2S : gas

NH_4OH : conc

NaI : solid

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

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 4*M* 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 2*M* $HC_2H_3O_2$. Transfer to a clean 40-ml centrifuge tube, centrifuge, and discard the supernate. Dissolve the precipitate in ~3*M* HCl by heating. Centrifuge and transfer the supernate to a clean centrifuge tube (Note 3). Neutralize and precipitate the 8-quinolinolate as above.

Filter while hot onto a weighed filter circle. Wash the precipitate with H_2O and then with ether. Dry in oven at $110^\circ C$, cool, weigh as the 8-quinolinate, mount, and count.

Notes

1. This procedure was developed primarily for (n,p) and (n,α) 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_2 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 MoS_3 precipitation in the presence of 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 Sb_2S_3 in the presence of tin carrier and F^- ion; the latter keeps the tin in solution as a fluoro complex. Tellurium, which precipitates along with antimony, is removed by precipitation with H_2S 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 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 SbCl_3 in 6M HCl; standardized

Molybdenum carrier: 10 mg molybdenum/ml, added as Na_2MoO_4 in H_2O

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 Na_2TeO_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

H_2SO_4 : conc

H_2S : gas

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

NH_4OH : conc

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 H_2O

Methanol: absolute

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

3. Preparation and Standardization of Carrier

Dissolve 18.7 g of 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 CrCl_2 solution. After conversion to antimony metal is complete, filter and wash the precipitate with small portions of H_2O 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 Br_2 and make the solution ~1.5M in HCl. Add 1 ml each of conc HF and conc H_2SO_4 per 25 ml of solution. Bring to a boil, saturate with H_2S to precipitate 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 H_2O . Saturate with H_2S to precipitate Sb_2S_3 , add a few drops of aerosol solution, and centrifuge. Discard the

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

Step 3. Dissolve the precipitate in 4 *ml* of conc HCl, boil off H₂S, and remove any undissolved MoS₃ 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 1*M* HCl, add a few drops of aerosol solution, and saturate with H₂S to precipitate Sb₂S₃. 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 H₂S, 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 H₂S, 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 H₂S, filter into a 40-*ml* centrifuge tube, and discard the precipitate.

Step 6. Boil off the H₂S, evaporate the solution to about half of its original volume (it will now be ~6*M* in HCl), and dilute with H₂O to make the solution 0.9*M* in HCl. Add 6 *ml* of H₂O for every 1 *ml* of solution. Measure volumes accurately and do the dilution carefully. The 0.9*M* value is critical because the distribution coefficient for molybdenum rises steeply both above and below 0.9*M* 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 0.9*M* 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 0.9*M* HCl, discarding the washings. Elute the antimony with 20 *ml* of 20% NaKC₄H₄O₆ that has been made alkaline with 12 drops (~1 *ml*) of conc NH₄OH. 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 H₂S, centrifuge, and discard the supernate.

Step 9. Dissolve the precipitate in 5 to 10 *ml* of conc HCl and boil off the H₂S. Make the solution 3 to 5*M* in HCl and filter through a 60-*ml* sintered glass crucible of fine porosity into a 40-*ml* centrifuge tube.

Step 10. Add sufficient CrCl₂ 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 H₂O 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 H₂S 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 H₂O until a white precipitate forms, dilute to 10 *ml* with 0.9*M* 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 ¹²⁷Te to grow into equilibrium with 93-h ¹²⁷Sb.

(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, SbH_3 , and the collection of this volatile compound in a Br_2 -HCl solution. A TeS_2 scavenger is then performed and the antimony is reduced to the elemental state for counting and chemical yield purposes.

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

2. Reagents

Antimony carrier: 10 mg antimony/ mL , added as $SbCl_3$ in 6*M* HCl. The solution is standardized by precipitation of antimony metal with $\sim 1.6M$ $CrCl_2$ (ANTIMONY I procedure)

Tellurium(VI) carrier: 10 mg tellurium/ mL , added as $Na_2H_4TeO_6$ in 6*M* HCl

HCl: conc; 6*M*

Br_2

NH_4OH : conc

Drierite ($CaSO_4$)

N_2 : gas

H_2S : gas

Zinc: dust

$NH_4OH \bullet HCl$: solid

Ethanol: absolute

$CrCl_2$: $\sim 1.6M$ aqueous solution

3. Procedure

Step 1. Assemble the separation apparatus as shown in Fig. 1. Fill the \cup -tube with Drierite ($CaSO_4$) and cover each side with glass wool. Place 10 mL of 6*M* HCl and 10 drops of Br_2 in each of the traps. Add 20 g of zinc dust to the round-bottomed

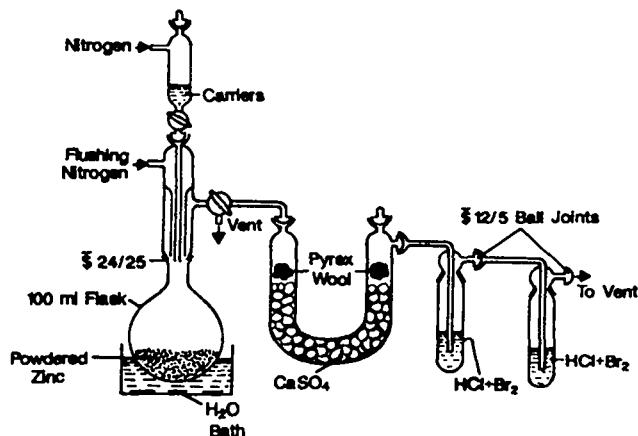


Fig. 1. Separation apparatus.

flask and bring the water bath to a boil. Flush the entire system well with 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 ~ 5 mL with 6*M* HCl. Drop the solution onto the zinc in one batch, collect the gas (SbH_3 and H_2) for 10 to 15 s, and then open the vent.

Step 3. Transfer the 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 $NH_4OH \bullet HCl$, and saturate with H_2S . 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 NH₄OH (the resulting solution should be ~2M in HCl), saturate with H₂S, and digest in a steam bath for a few minutes. Filter the Sb₂S₃ precipitate onto a glass frit of medium porosity. Wash the Sb₂S₃ with H₂O, discontinue suction, and discard the filtrate. Dissolve the Sb₂S₃ 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 H₂S, add 10 ml of absolute ethanol, mix, and then add 5 ml of ~1.6M CrCl₂. Swirl for 15 s and filter the metal precipitate onto a weighed Gelman VF-6 filter paper (0.45- μ m pore). Wash the precipitate with a 50/50 mixture of 6M HCl and ethanol, then with H₂O, and finally with ethanol alone. Dry under suction for a few minutes, weigh, and mount.

Note

The first Br₂-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}Sb . It was developed primarily for samples containing large amounts of zirconium, niobium, uranium, and HF and HClO_4 . The simplification of the chemistry results from using a Ge(Li) detector to measure ^{127}Sb and ^{125}Sb (spike) gamma rays in an imperfectly purified sample. Major interference in the measurements is caused by the ^{132}I daughter of ^{132}Te .

The chemical separation consists of a series of Sb_2S_3 and TeI_2 (by-product) precipitations. Exchange with antimony(V) carrier is effected in the presence of aqueous Br_2 at elevated temperatures. Recovery is measured by means of the ^{125}Sb tracer-carrier; yields are high.

2. Reagents

^{125}Sb tracer-carrier: sufficient activity for measurement on the available detector + 10 mg antimony(V)/mL, added as SbCl_5 in dilute HCl.

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

Tellurium(IV) carrier: 10 mg tellurium/mL, added as Na_2TeO_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

H_3BO_3 : saturated aqueous solution

H_2S : gas

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

3. Procedure

Step 1. Pipette 1 mL of ^{125}Sb tracer-carrier solution into a 40-mL glass centrifuge tube. Add 10 mL of saturated H_3BO_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 Nb_2O_5 , which carries down antimony.)

Step 2. Dilute by a factor of 2 with H_2O and saturate with H_2S . (If an orange precipitate of Sb_2S_3 does not form, it will be necessary to dilute the solution further and to use more H_3BO_3 to remove 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 H_2O and saturate with H_2S . 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 MoS_3 and TeS_2 . Boil the supernate for 30 s.

Step 5. Add 5 mL of H_2O 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 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 TeI_2 precipitate.

Step 6. Dilute to 20 mL with H_2O , saturate with H_2S , 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}Te full-energy peak should be no > 50 times larger than the counts in the 473-keV ^{127}Sb full-energy peak. If this ratio is exceeded, repeat *Steps 5* and *6*. When adequate decontamination has been attained, measure the ^{125}Sb activity by means of its 176-, 428-, 464-, and 635-keV gamma rays and that of ^{127}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 BiOCl , (b) extraction of BiI_3 into hexone, (c) AgCl scavenging, and (d) precipitation of Bi_2S_3 from 1.5M 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 HCl; standardized

Rhodium carrier: 10 mg rhodium/ml, added as $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ in 0.01M HCl

Ruthenium carrier: 10 mg ruthenium/ml, added as RuCl_3 in 0.01M HCl

Silver carrier: 10 mg silver/ml, added as AgNO_3 in H_2O

Tellurium(IV) carrier: 10 mg tellurium/ml, added as Na_2TeO_3 in dilute HCl

HCl: conc; 1M; 3M; 6M;

HClO_4 : conc

NH_4OH : conc

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

NaI: solid

NaNO_2 : solid

H_2S : gas

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 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 H_2O , and digest overnight on a steam bath. Filter into a weighed 15-ml sintered glass crucible of medium porosity. Wash the BiOCl precipitate with H_2O and then

with methanol. Dry at 110°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 HCl and again evaporate to dryness. (Evaporation is necessary to ensure tellurium exchange and also to remove NO_3^- , which inhibits reduction of tellurium to metal.) Add 15 ml of 3M HCl and ~ 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 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 ~ 2 -min intervals.) Filter and collect the filtrate in a 40-ml conical centrifuge tube. Rinse the erlenmeyer flask with hot 3M 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 NH_4OH to precipitate $\text{Bi}(\text{OH})_3$. Centrifuge and discard the supernate (Note 2).

Step 3. To the precipitate add 10 drops of 6M HCl and 5 drops of rhodium carrier; stir to dissolve. Wash the sides of the centrifuge tube with 2 to 4 ml of H_2O and heat on a steam bath. (The solution at this point should be clear.) Add 30 ml of boiling H_2O and digest for 5 min. Centrifuge the BiOCl precipitate and discard the supernate.

Step 4. To the precipitate add 2 ml of conc HClO_4 and 5 drops of ruthenium carrier, and with vigorous stirring heat to fumes. Fume until all the 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 H₂O, 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 NH₄OH. Centrifuge and discard the supernate.

Step 6. Add 5 ml of 6M HCl to the Bi(OH)₃ 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 H₂O layer into a clean separatory funnel. Add 10 ml of hexone and 1 to 2 g of solid NaI, shake, and discard the H₂O layer. Add 10 ml of 6M HCl (containing ~1 g of NaI) to the hexone layer. Shake and discard the H₂O layer. To the hexone phase add 10 ml of 6M HCl and ~0.5 g of solid NaNO₂ 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 H₂O layer into a clean 40-ml centrifuge tube containing 5 ml of conc NH₄OH. Centrifuge and discard the supernate.

Step 7. To the Bi(OH)₃ precipitate add 10 ml of 3M HCl and 10 ml of H₂O. Place on a steam bath and saturate with H₂S for at least 2 min. Centrifuge and discard the supernate. Dissolve the Bi₂S₃ precipitate by boiling in 5 ml of 6M HCl.

Step 8. Precipitate Bi(OH)₃ as in *Step 2*.

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

Step 10. Transfer the Bi(OH)₃ 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 H₂O layer. Add 10 ml of 6M HCl containing ~1 g of NaI to the hexone layer. Shake and discard the H₂O layer. To the hexone phase add 10 ml of 6M HCl and ~0.5 g of solid NaNO₂ and swirl. Place the stopper in the separatory funnel and shake vigorously. Drain the H₂O layer into a clean 40-ml centrifuge tube

containing 5 ml of conc NH₄OH. 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 H₂O 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(NO₃)₃•5H₂O 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)₃ precipitate add 5 drops of lead carrier and 2 ml of 12M NaOH; boil with vigorous stirring. Add 20 ml of H₂O 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 μg of bismuth from up to 25 g of underground nuclear debris. The separation process prepares ^{205}Bi , ^{206}Bi , $^{207}\text{Bi}(?)$, and ^{210}Bi for radiochemical determination and ^{207}Bi and ^{208}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 0.1*M* in each H_2SO_4 and KBr , (2) back-extraction with 0.5*M* HClO_4 , (3) adsorption of the element on a cation-exchange resin column, (4) elution from the resin by means of 1*M* HCl , (5) adsorption as a chloro complex on an anion-exchange resin column, and (6) elution with 2*M* 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

H_2SO_4 : 0.1*M*; conc

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

HClO_4 : 0.5*M*

HNO_3 : 0.1*M*, 4*M*

HF : 2*M*

KBr : solid

H_2SO_4 - KBr solution: 0.1*M* in each

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

mesh; stored in 4*M* HCl

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

3. Procedure

Step 1. Mix 200 ml of tri-*n*-octylamine solution with 200 ml of the 0.1*M* H_2SO_4 -0.1*M* 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 H_2SO_4 to a sample of ~5 g of the debris in 3*M* HCl and fume to dryness. Dissolve the residue in 0.1*M* H_2SO_4 and, by appropriate addition of solid KBr and 0.1*M* H_2SO_4 , make up 1 ℓ of sample solution that is 0.1*M* in each acid and salt. Warm the solution to ~35°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 0.1*M* H_2SO_4 -0.1*M* KBr solution and discard the washes.

Step 4. To the amine solution (now containing the bismuth), add 100 ml of 0.5*M* HClO_4 , shake the mixture for 2 min, and remove the aqueous phase. Repeat the extraction with 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-cm³ 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 7*M* HCl and then with 10 ml of 0.5*M* HClO_4 . Pass the combined aqueous phases from *Step 4* through the column. Wash the column with 5 ml of 0.01*M* HCl . (For tantalum-rich samples, wash with 10 or 15 ml of 0.01*M* HCl to remove that element.) Wash the tip of the column with H_2O and elute the bismuth with 10 ml of 1*M* 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 HNO₃. Wash the tip of the column with H₂O.

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 HNO₃, and evaporate to dryness. Dissolve the residue in 0.1M HNO₃ 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 PbO₂ 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 HClO₄ 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 HNO₃ 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 HNO₃. 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

H₂SO₄: conc

HCl: 7M

HClO₄: 0.5M

H₂SO₄-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).

HNO₃: 10M; 4M

HClO₄: 0.5M

HCl-HNO₃: 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 H₂SO₄ 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 H₂SO₄-0.1M 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 H₂SO₄-0.1M 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 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 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 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 ~ 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 HNO_3 and then with 0.5 ml of 10M HNO_3 .

Step 16. Elute the bismuth with 5 ml of 10M HNO_3 and collect the eluate in a counting vial.

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

Step 18. Take an aliquot containing an estimated 1 to 2 μg 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 HNO_3 .

Step 24. Elute bismuth with 2.5 ml of 10M 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 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}Bi , ^{208}Bi , ^{207}Bi , and ^{206}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 HClO₄ 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 HClO₄ 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}Bi content of the ore is important because the isotope is the final decay product of ^{237}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 H_2SO_4 . This procedure was checked with carrier-free ^{207}Bi and a chemical yield of 99% was obtained.

2. Reagents

HCl: conc; 0.5M

H_2SO_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 H_2SO_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 H_2SO_4 in a 10-ml volumetric flask and make up to exactly 10 ml with H_2O . 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 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 BaSO_4 separated from a fission-product solution 6 d old and containing 3×10^{13} fissions. The chemical yield is $\sim 75\%$.

2. Reagents

SO_4^{2-} carrier: equivalent to 10 mg BaSO_4/mL , prepared by diluting 2.4 mL of conc H_2SO_4 to 1 L and standardized by conversion to 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 HNO_3

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

NH_4OH : 1M

NaOH: 0.5M

BaCl_2 : 1M

K_2CO_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 H_2O

3. Procedure

Step 1. Add the sample (in dilute acid medium) to 3 mL of SO_4^{2-} carrier in a 40-mL glass centrifuge tube. Then add 2 mL of 1M BaCl_2 , centrifuge, and discard the supernate. Wash the BaSO_4 precipitate with H_2O and discard the washings.

Step 2. With the aid of a minimum amount of H_2O , transfer the precipitate to a 125-mL erlenmeyer flask. Add 10 drops of 50% K_2CO_3

solution and heat to dryness. Add 20 mL of H_2O , boil, and transfer the mixture to a clean centrifuge tube. Centrifuge and transfer the supernate containing the SO_4^{2-} ion to a clean centrifuge tube. (The K_2CO_3 treatment should have converted the BaSO_4 completely to BaCO_3 . The precipitate should be treated with 6M HCl, and if it does not dissolve completely, the K_2CO_3 treatment should be repeated on the remaining 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 ~ 2.5 . Add 5 mL of benzidine reagent, centrifuge, and discard the supernate. Wash the precipitate with 15 mL of H_2O 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 H_2O and dilute NaOH. Wash the column first with 10 mL of a mixture of equal volumes of acetone and H_2O and then with 10 mL of a mixture of equal volumes of 1M NH_4OH and acetone. Discard both washes. To elute the 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 BaCl_2 , precipitate 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 H₂O. (Warming speeds dissolution.) Add 2 ml of 1M BaCl₂, centrifuge, and discard the supernate. Wash the precipitate with H₂O that contains a few drops of BaCl₂ solution and HCl. Centrifuge and discard the wash. Slurry the precipitate in H₂O and filter through a weighed Millipore (0.8-μm) filter. Wash the precipitate with H₂O 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 6*M* HCl on an anion-exchange resin column. Tellurium in the +4 state is adsorbed on AG 1-X4 resin, eluted with 0.2*M* HCl, reduced to the metal, and then oxidized to the +6 state with NaBiO₃ in HNO₃. The bismuthate is removed on an anion-exchange column, and the tellurium(VI) is made 6*M* 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 Na₂TeO₄•2H₂O and 8.7 g Na₂TeO₃ in 1 l of 4*M* HCl; standardized

HBr: conc

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

HNO₃: conc; 3*M*

SO₂: gas

NaBiO₃: solid

Dowex AG 1-X4 anion-exchange resin column;
slurry in 6*M* 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 3*M* HCl, saturate the solution with SO₂, and let it stand for ~20 min. Saturate again with SO₂ and filter the elemental tellurium onto a weighed, fritted filter funnel of fine porosity. Wash

the tellurium first with H₂O 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 6*M* 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 6*M* HCl. When the solution reaches the resin, wash the erlenmeyer flask with 3 ml of 6*M* HCl and transfer the washings to the column. Discard the effluents.

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

Step 4. Wash the column with two 5-ml portions of 0.2*M* 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 SO₂. Let stand for ~20 min, centrifuge, and discard the supernate. Wash the precipitate with 5 ml of H₂O.

Step 6. To the precipitate add 3 drops of conc HNO₃, warm with stirring, and then add 3 ml of 3*M* HNO₃. Add ~50 mg of NaBiO₃, 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 H₂O rather than with 6*M* HCl. Wash the centrifuge tube with 1 ml of 3*M* HNO₃ and add the washings to the column. Wash the column with 5 ml of 0.2*M* HCl and then with 5 ml of 6*M* 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 SO₂, let stand for 10 min, centrifuge, and discard the supernate. Wash the precipitate with H₂O 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 Fe(OH)_3 scavenging and by precipitation of AgI from ammoniacal medium. Precipitation of 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, AgCl is formed and the chlorine is removed as HCl by treatment with conc H_2SO_4 . Chlorine is finally precipitated as the mercury(I) compound, in which form it is counted. The chemical yield is $\sim 75\%$.

2. Reagents

Cl^- ion carrier: 10 mg Cl^-/mL ; NaCl is used as a primary standard

I^- ion carrier: 10 mg I^-/mL , added as KI in H_2O

Iron carrier: 10 mg iron/ mL , added as $\text{Fe(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in very dilute HNO_3

HNO_3 : conc

H_2SO_4 : conc

HCHO : 37% aqueous solution

NH_4OH : conc

KOH : 10M

AgNO_3 : 0.1M

$\text{Hg}_2(\text{NO}_3)_2$: 0.1M solution in dilute HNO_3

KNO_2 : solid

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

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 NaCl carrier. Then add 4 to 6 drops of iron carrier and precipitate Fe(OH)_3 by the addition of a slight excess of conc NH_4OH . Centrifuge, transfer the supernate containing Cl^- ion to a clean centrifuge tube, and discard the precipitate (Note 1).

Step 2. To the supernate add 5 mL of conc NH_4OH and 4 drops of KI carrier solution. Precipitate AgI by the addition of a slight excess of 0.1M 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 KI carrier and remove a AgI by-product precipitate as in the previous step. This time, however, filter the supernate through filter paper in a 2-in. 60° funnel to ensure complete removal of AgI .

Step 4. To the filtrate add 5 mL of EDTA reagent and slowly acidify with conc HNO_3 to precipitate AgCl . Boil to coagulate the precipitate, centrifuge, and wash the AgCl with 30 to 40 mL of H_2O containing 2 drops of conc HNO_3 . Discard the supernate and washings.

Step 5. Dissolve the AgCl precipitate in 3 mL of conc NH_4OH , add 5 mL of EDTA reagent, dilute to 30 mL , and reprecipitate AgCl by the addition of conc HNO_3 . Boil to coagulate the AgCl and wash as in the previous step.

Step 6. Dissolve the AgCl in 40 drops of conc NH_4OH ; add 15 mL of H_2O , 10 drops of 10M KOH , and 10 drops of 37% HCHO . Heat to boiling to coagulate the metallic silver precipitate. Add 4 drops of 0.1M AgNO_3 and again remove a silver precipitate. Filter both silver precipitates together through filter paper in a 2-in. 60° funnel, and collect the filtrate in a 125- mL erlenmeyer flask.

Step 7. Acidify the filtrate with conc HNO₃, 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 CCl₄, and a few crystals of KNO₂. Extract I₂ into the CCl₄ layer and discard. Add three separate additional 10-ml portions of CCl₄, extract I₂, and discard the CCl₄ layer after each extraction.

Step 8. To the remaining aqueous layer add 2 to 3 ml of conc HNO₃, transfer to a 40-ml glass centrifuge tube, and heat to boiling to remove excess NO₂⁻ ion. Add 4 drops of iron carrier and precipitate Fe(OH)₃ with conc NH₄OH. 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 Fe(OH)₃ scavenger precipitate as in the previous step.

Step 10. To the Cl⁻-containing supernate add 0.1M AgNO₃ to precipitate AgCl. Centrifuge and wash the precipitate as in *Step 4*.

Step 11. Dissolve the AgCl precipitate in 2 ml of conc NH₄OH. Wash with several milliliters of H₂O into a special distilling flask (see GERMANIUM procedure). Bubble air through the solution to remove most of the NH₄OH. Cautiously add 6 ml of conc H₂SO₄ (Note 3) and heat until all the HCl has distilled over into a 50-ml beaker containing 20 ml of H₂O.

Step 12. After adding 1 to 2 ml of conc HNO₃, precipitate Hg₂Cl₂ from the solution of HCl distillate by the dropwise addition of 0.1M Hg₂(NO₃)₂ solution. Wash the precipitate with H₂O after filtering on a weighed filter circle. Wash with absolute ethanol and dry in an oven for 20 min at 110°C. Cool, weigh, mount, and count (Note 4).

Notes

1. If the radiochlorine is originally in a form other than Cl⁻ ion or Cl₂, 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 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 HCHO.

3. Addition of conc H₂SO₄ precipitates Ag₂SO₄. During distillation continue bubbling air through the solution.

4. Hg₂Cl₂ is used as the compound mounted in preference to AgCl because it does not form agglomerates as AgCl does. PbCl₂ is too soluble and therefore not suitable. For counting 4 × 10⁵-y ³⁶Cl, a self-absorption curve should be constructed and corrections applied for a 0.72-MeV β^- .

(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}Zr and ^{97}Zr is effected by formation of the fluorozirconate complex $[\text{ZrF}_6]^{2-}$. Lanthanide and alkaline-earth activities are removed by LaF_3 scavenging, and then zirconium is separated by three $\text{Ba}[\text{ZrF}_6]$ precipitations. Zirconium is finally precipitated with mandelic acid from HCl medium and ignited to the oxide, 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}Zr or ^{97}Zr separately or to determine them together. To assay for ^{95}Zr , the chemistry is not begun until the 17-h ^{97}Zr has decayed. After completion of the chemical procedure, the ZrO_2 is counted on the top shelf of a beta-proportional counter before too much ^{95}Nb has grown in. To analyze for ^{97}Zr , the ZrO_2 is counted through a 112-mg Al/cm^2 absorber.

To determine both ^{95}Zr and ^{97}Zr in the sample, the 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}Zr), 35-d (^{95}Nb), and 65-d (^{95}Zr) components. The decay curve may be analyzed by least squares.

2. Reagents

Zirconium carrier: 10 mg zirconium/ mL , added as $\text{ZrO}(\text{NO}_3)_2 \bullet 2\text{H}_2\text{O}$ in 1*M* HNO_3 ; standardized
Lanthanum carrier: 10 mg lanthanum/ mL , added as $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O
Niobium hold-back carrier: solution of $\text{K}_8\text{Nb}_6\text{O}_{19}$ 10 g per 100 mL of solution.
 HCl : 1*M*; 8*M*; conc
 HNO_3 : 1*M*; conc
 H_2SO_4 : conc
 HF : conc
 H_3BO_3 : saturated aqueous solution

NH_4OH : conc

$\text{NH}_2\text{OH} \bullet \text{HCl}$: 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 $\text{ZrO}(\text{NO}_3)_2 \bullet 2\text{H}_2\text{O}$ in H_2O and add sufficient conc HNO_3 to make the solution 1*M* in HNO_3 . Filter and make the filtrate up to 1 L with 1*M* HNO_3 .

Pipette 10.0 mL of the solution into a 100- mL beaker, make the solution 2*M* in HCl , and cool in an ice bath. Add a slight excess of 6% cupferron solution and filter. Wash the precipitate with 1*M* 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 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 5*M* in HNO_3 and to a volume of $\sim 12\text{ mL}$ (Note 1). Add solid $\text{NH}_2\text{OH} \bullet \text{HCl}$ so that the solution is 2 to 3% in NH_2OH (Note 2). Add 3 drops of niobium carrier and make the solution 5*M* in 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 LaF_3 scavengings, add 1 $\text{m}\ell$ of $\text{Ba}(\text{NO}_3)_2$ solution per 5 $\text{m}\ell$ of the supernate. Let stand for 1 min and centrifuge. Discard the supernate.

Step 5. To the precipitate add 4 $\text{m}\ell$ of saturated H_3BO_3 (Note 3) and slurry. Add 2 $\text{m}\ell$ of conc HNO_3 and slurry again. Add 10 to 12 $\text{m}\ell$ of H_2O 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 H_3BO_3 , the HNO_3 , and the H_2O on a steam bath before they are used.)

Step 6. Precipitate $\text{Ba}[\text{ZrF}_6]$ by the addition of 2 $\text{m}\ell$ of $\text{Ba}(\text{NO}_3)_2$ solution and 2 $\text{m}\ell$ 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 $\text{m}\ell$ of saturated H_3BO_3 , 4 $\text{m}\ell$ of conc HCl , and 10 $\text{m}\ell$ of H_2O . Add 3 drops of conc H_2SO_4 diluted with 5 $\text{m}\ell$ of H_2O and let stand for 15 min. Add 1 to 2 drops of aerosol solution and centrifuge. Transfer the supernate to a 40- $\text{m}\ell$ glass centrifuge tube and discard the BaSO_4 precipitate.

Step 8. To the supernate add conc NH_4OH until the solution is alkaline. Centrifuge down the $\text{Zr}(\text{OH})_4$ and discard the supernate. Dissolve the precipitate in 2 $\text{m}\ell$ of conc HCl , 4 $\text{m}\ell$ of saturated H_3BO_3 , and 10 $\text{m}\ell$ of H_2O . Centrifuge and, if a precipitate forms, transfer the supernate to a 40- $\text{m}\ell$ centrifuge tube; discard the precipitate. Reprecipitate $\text{Zr}(\text{OH})_4$ with conc NH_4OH . Centrifuge and dissolve the precipitate in 15 $\text{m}\ell$ of 8*M* HCl . Heat to boiling, add 10 $\text{m}\ell$ 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 $\text{m}\ell$ of H_2O and 8 drops of conc NH_4OH . (The dissolution of the precipitate takes 2 to 3 min and may be hastened by the addition of another 1 to 2 drops of NH_4OH .) Add 3 $\text{m}\ell$ of conc HCl , heat to boiling, and add 10 $\text{m}\ell$ 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 $\text{m}\ell$ of ethanol and filter onto a filter circle. Transfer the paper and precipitate to a porcelain crucible and ignite for 1 h at 800°C. Powder the ZrO_2 with the fire-polished end of a stirring rod. Add 2 drops of ethanol, slurry, and grind again. Add 10 $\text{m}\ell$ of ethanol, stir, and filter onto a washed, dried, and weighed filter circle. Wash the ZrO_2 with 5 $\text{m}\ell$ of ethanol. Dry at 110°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 LaF_3 scavengings is small.

2. NH_2OH reduces neptunium(VI) and plutonium(VI) so that they will be carried on the LaF_3 and thus not interfere in the zirconium separation. NH_2OH may decompose on the addition of HF, which causes the solution to effervesce.

3. H_3BO_3 removes F^- ion by conversion to BF_4^- , and thus aids in the dissolution of $\text{Ba}[\text{ZrF}_6]$ by 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 6*M* 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 ZrO₂ 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 ZrO₂/mℓ, added as ZrOCl₂•8H₂O in H₂O; standardized

Lanthanum carrier: 10 mg lanthanum/mℓ, added as La(NO₃)₃•6H₂O in H₂O

Yttrium carrier: 10 mg yttrium/mℓ, prepared by dissolving Y₂O₃ in dilute HCl

Scandium carrier: 10 mg scandium/mℓ, added as ScCl₃ in 1*M* HCl

HNO₃: conc

HCl: conc; 6*M*

H₂SO₄: conc

HNO₃-HF solution: 4*M* in HNO₃ and 2.5*M* in HF

NH₄OH: conc

NH₄HF₂ solution: 4*M* in NH₄HF₂ and 1*M* in HF

NH₄H₂PO₄: 1.5*M* aqueous solution

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

BaCl₂: 1*M* aqueous solution

Methyl red indicator solution

Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 52.31 g of ZrOCl₂•8H₂O in H₂O and dilute to 1 ℥ with 0.1*M* 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 ZrO₂.

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 6*M* HCl to an extraction vessel of appropriate size and add 50 mℓ of 0.5*M* 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 6*M* 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 4*M* in HNO₃ and 2.5*M* 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 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 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 H_2SO_4 , stir, and place on a steam bath for a few minutes. Dilute to 20 ml with H_2O and allow to stand until 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 NH_4OH 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 HCl and dilute to 20 ml with H_2O . (At this point there may be a small amount of 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 NH_4OH , centrifuge, and discard the supernate. The $\text{Zr}(\text{OH})_4$ precipitate may be used for milking experiments or may be converted to ZrO_2 for counting as described below.

Step 7. Dissolve the $\text{Zr}(\text{OH})_4$ in conc HCl , add 5 ml of filter paper pulp slurry, make ammoniacal with conc NH_4OH , and filter onto a 9-cm filter paper. Transfer to a porcelain crucible and ignite at 900°C for 5 to 10 min. With a polished stirring rod or the ultrasonic technique, powder the ZrO_2 and, using absolute ethanol, transfer to a weighed filter circle. Dry at 110°C, weigh as 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 ~4M in either HNO_3 or 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 NH_4HF_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 H_2O , and neutralize to a methyl red end point with conc NH_4OH . 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 HCl , and heat on a steam bath until ScF_3 coagulates. Centrifuge, transfer the supernate to a clean plastic tube, and discard the precipitate.

Step 5. Add 1.5 ml of 1M 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 H_2SO_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 H_2O and let stand until 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 NH_4OH . 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 NH_4OH to precipitate $\text{Zr}(\text{OH})_4$, centrifuge, and discard the supernate.

Step 10. Dissolve the $\text{Zr}(\text{OH})_4$ in conc HCl , centrifuge out any BaSO_4 , and reprecipitate $\text{Zr}(\text{OH})_4$ with conc NH_4OH . The $\text{Zr}(\text{OH})_4$ may be milked for other experiments or may be converted to 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}Ta is precipitated as the oxide by heating with conc HNO_3 . The oxide is discarded. Aluminum, calcium, and magnesium are removed from solution by appropriate treatment with NH_4OH and NaOH . The lanthanide elements are then removed by 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 $\sim 60\%$.

For the separation of zirconium in the absence of tantalum, the procedure begins with LaF_3 scavenges and proceeds as described above. The chemical yield is $\sim 75\%$.

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

(a) After tantalum removal in Sec. 3.A.

(b) After adding $\text{NH}_2\text{OH} \bullet \text{HCl}$, niobium hold-back carrier, and HF, but before the LaF_3 scavenge. Interruption at this point permits good exchange for any niobium that grows in (for example, overnight).

(c) After 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 $\text{ZrO}(\text{NO}_3)_2 \bullet 2\text{H}_2\text{O}$ in 1M HNO_3 or $\text{ZrOCl}_2 \bullet 8\text{H}_2\text{O}$ in 1M 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 HNO_3 . The final solution is made up so that it contains the equivalent of ~ 10 to 12 mg of Ta_2O_5 /ml in 0.5M HF/0.5M 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 $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O

Barium carrier: 50 mg barium/ml, added as BaCl_2 in H_2O

HF: conc

HClO_4 : conc

HNO_3 : conc

HCl: 6M; conc

HCl-HF solution: 9M in HCl and 0.004M in HF

H_3BO_3 : saturated aqueous solution

H_2SO_4 : conc

NaOH : 10M

NH_4OH : conc

Mandelic acid solutions: 15 g of the racemic acid in 100 ml of H_2O ; 2 g of acid in 100 ml of 1M HCl.

$\text{NH}_2\text{OH} \bullet \text{HCl}$: 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 HClO₄ to dissolve any tantalum that has precipitated.

Step 2. Take the solution to near dryness and transfer it to an erlenmeyer flask with conc HNO₃. Add conc HNO₃ 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 Ta₂O₅ precipitate with 6M HCl, centrifuge for 15 min, and add the supernate to the previous supernate. Wash the precipitate with H₂O, 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 NH₄OH 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 NH₄OH. 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 NH₂OH•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[ZrF₆] precipitate add 2 ml of saturated H₃BO₃ solution and slurry. Add 2 ml of conc HNO₃, stir, and heat on a steam bath for 10 to 15 min. Add 12 ml of H₂O 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 H₃BO₃ 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 H₃BO₃ and 4 ml of conc HCl. Add 10 ml of H₂O.

Step 16. Add 3 drops of conc H₂SO₄. Stir and let stand for 10 min. Centrifuge and discard the BaSO₄ precipitate.

Step 17. Add conc NH₄OH, stir, centrifuge, and discard the supernate. Wash the precipitate in 5 ml of H₂O.

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 H₂O, and precipitate the hydroxide with conc NH₄OH. 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 H₂O) 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_{sep}*). 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 NH₂OH•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 ²⁰⁵Ta 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.

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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 CHCl_3 . This step gives an effective separation from uranium(VI). The cupferron complex is destroyed and the niobium precipitated as the hydrous oxide, $\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$, by means of NH_3 water; molybdenum remains in solution as a molybdate. The oxide is dissolved in H_2SO_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 $\text{ZrO}(\text{NO}_3)_2 \bullet 2\text{H}_2\text{O}$ in 1*M* HNO_3

Copper carrier: 10 mg copper/ mL , added as $\text{CuCl}_2 \bullet 2\text{H}_2\text{O}$ in H_2O

HCl : 6*M*; conc

HNO_3 : 6*M*; conc

H_2SO_4 : conc

HF : conc

Tartaric acid: 25% aqueous solution

H_3BO_3 : saturated aqueous solution

$\text{H}_2\text{C}_2\text{O}_4$: saturated aqueous solution

NH_4OH : 6*M*; conc

$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$: saturated aqueous solution

NH_4NO_3 : 2% aqueous solution

BaCl_2 : 50 mg/ mL

KClO_3 : solid

H_2S : 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, $\text{K}_8\text{Nb}_6\text{O}_{19} \bullet 16\text{H}_2\text{O}$, in $\sim 200 \text{ mL}$ of H_2O , heat the solution nearly to boiling, and add 15 mL of conc 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% NH_4NO_3 solution. Add 200 mL of saturated $\text{H}_2\text{C}_2\text{O}_4$, and heat with stirring until Nb_2O_5 dissolves. Cool and dilute with H_2O 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 6*M* HNO_3 and ~ 1 g of KClO_3 and carefully heat the solution to boiling. Boil gently with occasional stirring for ~ 5 min. Cool the mixture and add $\sim 15 \text{ mL}$ conc NH_4OH 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 H_2O . Ignite in a porcelain crucible at $\sim 800^\circ\text{C}$ for 15 to 20 min and weigh as Nb_2O_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 4*M* HCl , 1 mL of zirconium carrier, and 4 mL of 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

$\text{Ba}[\text{ZrF}_6]$ 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_3BO_3 to decompose the niobium-fluoride complex and make the solution 1*M* 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_3 and transfer the CHCl_3 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_3 , and combine the extract with the previous one. Wash the aqueous phase with 10 ml of CHCl_3 and combine the washings with the previous extracts.

Step 4. Heat the CHCl_3 extract with 3 ml of conc H_2SO_4 and ~20 ml of HNO_3 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_4OH . Centrifuge and discard the supernate. Dissolve the precipitate ($\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$) in 3.3 ml of conc H_2SO_4 and dilute the solution to 20 ml with H_2O . Add 1 ml of copper carrier and saturate the solution with H_2S . Centrifuge and filter into a clean 40-ml centrifuge tube.

Step 6. Make the supernate alkaline by adding conc NH_4OH to precipitate $\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$. Centrifuge, discard the supernate, and wash the precipitate with a mixture of 5 ml of 6*M* NH_4OH , 3 ml of 6*M* HNO_3 , and 5 ml of H_2O (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_3 to the supernate and heat the mixture on a steam bath for ~15 min. Centrifuge, discard the supernate,

and dissolve the $\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$ precipitate in 1 ml of conc HF and 3 drops of 6*M* HCl.

Step 8. Transfer the solution to a 125-ml separatory funnel, add 10 ml of saturated H_3BO_3 , and make the solution 1*M* in HCl. Add 4 ml of cold cupferron reagent and extract the solution with 20 ml of CHCl_3 . Transfer the CHCl_3 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 $\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$ precipitate formed in *Step 7* in 5 ml of saturated $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ solution and sufficient conc NH_4OH to make the solution alkaline.

Step 11. Cool the solution in an ice bath and add 4 ml of cupferron reagent. Add 6*M* 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_2O_5 , mount, and beta-count (Note 2).

Notes

1. The $\text{Nb}_2\text{O}_5 \bullet \text{XH}_2\text{O}$ precipitate is washed with NH_4NO_3 solution to prevent peptization.
2. The isotopes counted are 72-min ^{97}Nb , 23.3-h ^{96}Nb , and 35-d ^{95}Nb .

(October 1989)

TANTALUM
B. P. Bayhurst

1. Introduction

In the separation of tantalum from niobium and other fission products, decontamination is effected by LaF_3 and Sb_2S_3 scavenges, $\text{Ba}[\text{ZrF}_6]$ precipitation, and extraction of tantalum into hexone from a solution 2.88M in HNO_3 and 1.1M in HF. The tantalum is back-extracted from hexone by means of a 1.5% H_2O_2 solution and precipitated as the hydrous oxide, $\text{Ta}_2\text{O}_5 \bullet \text{XH}_2\text{O}$, 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 HNO_3 and HF and diluting to the appropriate volume with H_2O .

Antimony(III) carrier: 10 mg antimony(III)/ml, added as SbCl_3 in 1M HCl

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

Zirconium carrier: 10 mg zirconium/ml, added as purified $\text{ZrOCl}_2 \bullet 8\text{H}_2\text{O}$ in 0.1M HCl

HNO_3 : conc; fuming

HF: conc

H_3BO_3 : saturated aqueous solution

H_2S : gas

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

HNO_3 -HF solution: 2.88M in HNO_3 and 1.1M in HF

NH_4OH : dilute; conc

BaCl_2 : 1M

NH_4NO_3 : saturated aqueous solution

Hexone (4-methyl-2-pentanone)

H_2O_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 NH_4NO_3 and H_3BO_3 . Make the solution alkaline to phenolphthalein with conc NH_4OH , centrifuge, and discard the supernate. Wash the precipitate with 30 ml of dilute NH_4OH (1 ml of conc NH_4OH and 29 ml of H_2O) and 2 ml of saturated NH_4NO_3 , centrifuge, and discard the wash.

Step 2. Add 10 ml of fuming HNO_3 , place on a steam bath, and permit the $\text{Ta}_2\text{O}_5 \bullet \text{XH}_2\text{O}$ to coagulate. Centrifuge, and discard the supernate. Dissolve the precipitate in 7 drops of conc HF, dilute to 10 ml with H_2O , and add 100 mg of $\text{NH}_2\text{OH} \bullet \text{HCl}$. 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 LaF_3 scavenge twice.

Step 3. To the supernate from the final LaF_3 scavenge, add 4 drops of antimony(III) carrier and saturate with H_2S on a steam bath. Remove the tube from the bath, cap it, and permit the Sb_2S_3 to coagulate. Centrifuge, transfer the supernate to a clean plastic tube, and repeat the Sb_2S_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 H_2S . Add 6 drops of conc HF and 2.75 ml of conc HNO_3 and bring the volume to 15 ml with H_2O . Add 2 drops of zirconium holdback carrier and 4 drops of 1M 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 HNO_3 -HF solution (2.88M in 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% H₂O₂. Repeat the extraction three times, combining all extracts in a Teflon beaker and discarding the hexone layer.

Step 7. Add 5 ml of conc HNO₃ and boil the solution to a volume of 2 to 3 ml. Repeat. Add 5 ml of conc HNO₃, boil down the solution to ~2 to 3 ml, and use conc HNO₃ to transfer the mixture to a 40-ml plastic centrifuge tube. Centrifuge and discard the supernate. Wash the precipitate twice with conc HNO₃, 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 Ta₂O₅ 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

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 BaCrO_4 , which is then converted to the blue peroxy compound, CrO_5 , by treatment with H_2O_2 in HCl medium in the presence of ethyl ether. The peroxy compound is extracted into the ether layer (effecting further decontamination), then back-extracted into aqueous NH_3 , and 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 BaSO_4 , chromium is finally precipitated and counted as 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 $\text{PdCl}_2 \bullet 2\text{H}_2\text{O}$ in very dilute HCl
Copper carrier: 10 mg copper/ml, added as $\text{CuCl}_2 \bullet 2\text{H}_2\text{O}$ in H_2O
Iron carrier: 10 mg iron/ml, added as $\text{FeCl}_3 \bullet 6\text{H}_2\text{O}$ in very dilute HCl
 HCl : conc; dilute (3 ml conc HCl/ℓ)
 H_2SO_4 : 3M
 HNO_3 : 6M
 $\text{HC}_2\text{H}_3\text{O}_2$: 1M
 NH_4OH : conc
 H_2S : gas
 H_2O_2 : 30%
 $\text{Ba}(\text{NO}_3)_2$: saturated solution
 NaBrO_3 : 1M
 $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$: 1M
Aqueous SO_2 solution: saturated

Ethanol: 95%

Ethyl ether

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 SO_2 solution dropwise until all of the $\text{Cr}_2\text{O}_7^{2-}$ has been reduced to Cr^{3+} ion. Boil off the excess SO_2 .

Step 2. To the hot solution add conc NH_4OH dropwise to precipitate $\text{Cr}(\text{OH})_3$. Caution: Do not use a great excess of NH_4OH (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 NH_4OH . 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 H_2S for 5 min. Filter and discard the sulfide scavenger precipitate, retaining the Cr^{3+} -containing filtrate in a 40-ml centrifuge tube.

Step 5. Precipitate $\text{Cr}(\text{OH})_3$ from the filtrate (*Step 4*), centrifuge, and discard the supernate.

Step 6. Dissolve the $\text{Cr}(\text{OH})_3$ in 8 drops of conc HCl , boil out remaining H_2S , 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 H_2S , and reprecipitate $\text{Cr}(\text{OH})_3$ with conc NH_4OH . 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 H_2O and ~6 ml of 1M NaBrO_3 . Transfer to a 125-ml erlenmeyer flask and heat over a flame until all the Cr^{3+} ion is oxidized to $\text{Cr}_2\text{O}_7^{2-}$. If the oxidation does not appear to be complete, additional 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 BaCrO_4 . If precipitation appears to be incomplete, 1 drop of conc NH_4OH should be added. Transfer to a 40-ml centrifuge tube centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O , centrifuge, and discard the washings.

Step 11. Dissolve the BaCrO_4 in ~6 drops of conc HCl and 10 ml of H_2O . (Heating may be required.) Dilute to ~30 ml and reprecipitate 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 H_2O , centrifuge, and discard the washings.

Step 12. Dissolve the BaCrO_4 in 10 ml of H_2O and 5 drops of conc HCl. Cool to 0 to 5°C in an ice bath. Transfer to a 125-ml separatory funnel to which 90 to 100 ml of cold (below 5°C) ethyl ether has been added. Add 3 drops of cold (below 5°C) 30% H_2O_2 and immediately extract the blue peroxy compound 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 (~5°C) H_2O that contains 3 ml of conc HCl/l. Discard the washings.

Step 14. Back-extract into H_2O by shaking the ether with ~15 ml of H_2O that contains 3 to 4 drops of conc NH_4OH . 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 BaCrO_4 . Centrifuge and wash with 30 ml of H_2O ; discard the supernate and washings.

Step 16. Dissolve the BaCrO_4 in 15 ml of H_2O and 8 drops of conc HCl. Heat to boiling and add 3 drops of 3M H_2SO_4 . Centrifuge and discard the 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 NH_4OH . Centrifuge and discard the $\text{Fe}(\text{OH})_3$; transfer the supernate to a 40-ml centrifuge tube. Acidify the supernate with HNO_3 .

Step 18. Repeat *Step 17* and heat the supernate to boiling.

Step 19. Add ~3 ml of saturated $\text{Ba}(\text{NO}_3)_2$ solution to remove SO_4^{2-} ion. Centrifuge the BaSO_4 , discard the precipitate, and transfer the supernate to a 40-ml centrifuge tube.

Step 20. Precipitate BaCrO_4 from the supernate by the addition of conc NH_4OH . 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 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 BaCrO_4 . Filter onto a weighed filter circle. Wash the precipitate three times with 15- to 20-ml portions of hot H_2O and then with ethanol. Dry for 10 min at 110°C. Weigh, mount, and count immediately.

Notes

1. It is important to avoid using a large excess of conc NH_4OH to precipitate $\text{Cr}(\text{OH})_3$ because some of the $\text{Cr}(\text{OH})_3$ will complex with NH_3 and go into solution.

2. The Cl^- and 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 Cr^{3+} ion with BrO_3^- .

3. It is possible to visually determine whether oxidation of Cr^{3+} ion to $\text{Cr}_2\text{O}_7^{2-}$ is complete.

4. The formation and ether extraction of the blue peroxy compound, CrO_5 , must be carried out in the cold; otherwise the $\text{Cr}_2\text{O}_7^{2-}$ will merely oxidize the H_2O_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 NH₄OH remove most of the interfering ions. Molybdenum is eluted from the column with 6M NH₄C₂H₃O₂, precipitated with alpha-benzoinoxime, and converted by ignition to MoO₃, in which form it is weighed and counted. The chemical yield is ~75%.

2. Reagents

Molybdenum carrier: 10 mg molybdenum/ml (NH₄)₆Mo₇O₂₄•4H₂O solution; standardized

Iron carrier: 10 mg iron/ml, added as aqueous FeCl₃•6H₂O

Copper carrier: 10 mg copper/ml, added as aqueous CuSO₄•5H₂O

H₂SO₄: conc

H₂C₂O₄: saturated aqueous solution

• NH₄Cl: 3M

NaBrO₃: 0.5M

HNO₃: 1M; conc

HCl: 6M; conc

HClO₄: conc

HCl-HF: 0.1M in HCl and 0.05M in HF

NH₄OH: 3M; conc

NH₄C₂H₃O₂: 6M

Alpha-benzoinoxime: 2% in ethanol

H₂S: gas

Br₂-H₂O

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 (NH₄)₆Mo₇O₂₄•4H₂O in H₂O, add 1 ml of 0.5M NaBrO₃, 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 HNO₃ and 0.5 ml of conc HClO₄. 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 MoO₃.

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 Br₂-H₂O, 4 drops of copper carrier, and 1 to 5 ml of conc H₂SO₄, 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 H₂O, and warm to dissolve the residue. While the solution is kept warm, saturate with H₂S. 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 NH₄Cl and 10 ml of H₂O. Centrifuge and discard the washings. Dissolve the precipitate in 1 ml of conc HCl and a few drops of conc HNO₃. Add 10 ml of H₂O, boil to remove excess H₂S, and then add 3 to 4 drops of iron carrier. Precipitate Fe₂O₃•xH₂O by adding 2 to 3 ml of conc NH₄OH. 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 Br₂-H₂O.

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 NH₄OH.

Step 5. As soon as the level of the NH₄OH 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 NH₄C₂H₃O₂ 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 NH₄OH, 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 HNO₃, 1 ml of Br₂-H₂O, and 1 ml of saturated H₂C₂O₄ 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 HNO₃.

Step 8. Place the filter paper and contents in a porcelain crucible and ignite to MoO₃ at 550°C for ~1 h (Note 4).

Step 9. After ignition, allow the crucible to cool and grind the MoO₃ 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 H₂SO₄ and 1 ml of Br₂-H₂O. Fume to dryness, cool, add 10 ml of H₂O and 3 drops of iron carrier, and precipitate Fe₂O₃•xH₂O 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 MoO₃.

5. The sample is permitted to stand for 18 h before counting to allow the 6-h ⁹⁹Tc 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}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 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 $>1\ell$, 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 Fe(OH)_3 scavenger. The molybdenum is finally precipitated as the 8-quinolinate, in which form it is counted. The chemical yield is 60 to 70%.

2. Reagents

Molybdenum carrier: 10 mg molybdenum/ $\text{m}\ell$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$; standardized as described in the MOLYBDENUM I procedure.

Iron carrier: 10 mg iron/ $\text{m}\ell$, 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

HNO_3 : conc

HClO_4 : conc

H_2SO_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

NH_4OH : 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 $\text{m}\ell$ of molybdenum carrier (Note 1). Boil the solution briefly and dilute with ice and H_2O to 750 $\text{m}\ell$ (Note 2). Transfer the solution to a 1- ℓ pear-shaped separatory funnel and precipitate molybdenum with 25 $\text{m}\ell$ of alpha-benzoinoxime reagent.

Step 2. Add 50 $\text{m}\ell$ 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- $\text{m}\ell$ pear-shaped separatory funnel. Extract the aqueous phase with 10 $\text{m}\ell$ of alpha-benzoinoxime and 30 $\text{m}\ell$ 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 $\text{m}\ell$ of 1M HCl and 20 $\text{m}\ell$ of ethanol; discard the washings. Transfer the chloroform layer to a 125- $\text{m}\ell$ separatory funnel. Add 25 $\text{m}\ell$ of 0.6M NaOH and shake vigorously to remove the molybdenum. Discard the chloroform and transfer the aqueous layer to a 250- $\text{m}\ell$ Vycor or quartz erlenmeyer flask.

Step 4. Boil the solution briefly to expel any chloroform present. Add 10 $\text{m}\ell$ of conc HNO_3 and boil the solution to half its original volume. Add 4 $\text{m}\ell$ of conc HClO_4 and 2 $\text{m}\ell$ of conc H_2SO_4 , and boil carefully until the exothermic reaction subsides. Then boil until strong fumes of 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 NH₄OH.

Step 6. Elute the molybdenum from the column with 15 ml of 6M NH₄C₂H₃O₂ solution. To the eluate add 3 ml of conc NH₄OH 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 HC₂H₃O₂, 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 H₂O and then with acetone.

Step 8. Dry the molybdenum quinolinate 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 H₂O 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 H₂O 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 ⁹⁹Nb and ⁹⁹Mo before the molybdenum has grown in.

4. The Fe(OH)₃ scavenge removes niobium, which otherwise contaminates the final sample.

5. The 8-quinolinate 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"), $\text{WO}_3 \bullet \text{XH}_2\text{O}$. 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 HCl medium by extraction into 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 $\sim 50\%$.

2. Reagents

Tungsten carrier: 10 mg tungsten/ mL , added as $\text{Na}_2\text{WO}_4 \bullet 2\text{H}_2\text{O}$ in H_2O ; standardized

Bismuth carrier: 10 mg bismuth/ mL , added as $\text{Bi}(\text{NO}_3)_3 \bullet 5\text{H}_2\text{O}$ in very dilute HNO_3

Iron carrier: 10 mg iron/ mL , added as $\text{FeCl}_3 \bullet 6\text{H}_2\text{O}$ in very dilute HNO_3

Molybdenum carrier: 10 mg molybdenum/ mL , added as $(\text{NH}_4)_6\text{Mo}_7\text{O}_24 \bullet 4\text{H}_2\text{O}$ in H_2O

Niobium carrier: 10 mg niobium/ mL , added as Nb_2O_5 in $\text{H}_2\text{C}_2\text{O}_4$ solution

HCl: conc

HNO_3 : conc

H_2SO_4 : conc

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

Tartaric acid: 50% aqueous solution

NH_4OH : 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 $\text{NaC}_2\text{H}_3\text{O}_2$

H_2S : 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 H_2O

Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 17.94 g of $\text{Na}_2\text{WO}_4 \bullet 2\text{H}_2\text{O}$ in H_2O 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 $\sim 80^\circ\text{C}$. 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 H_2O 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 HNO_3 for 12 h. The $\text{WO}_3 \bullet \text{XH}_2\text{O}$ 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 WO_3 begins to volatilize.) It is then cooled and weighed as WO_3 .

Four standardizations were run, and results agreed within $\sim 1\%$. 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 HNO₃ and digest on a steam bath for 10 min. Remove, centrifuge, and discard the supernate.

Step 2. To the WO₃•XH₂O residue add 6 drops of conc NH₄OH and dilute to 15 ml with H₂O. 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 H₂SO₄, and 5 drops each of bismuth and molybdenum carriers. Place on steam bath and bubble in H₂S rather vigorously for at least 2 min (Note 2). (Some time is required for MoS₃ to coagulate, but coagulation is aided by the precipitation of Bi₂S₃.) 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 H₂O and pour the washings through the filter funnel. To the filtrate add 10 ml of conc HNO₃ 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 WO₃•XH₂O precipitate in 6 drops of conc NH₄OH and add 15 drops of 50% tartaric acid solution. With 10 ml H₂O, 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 H₂O 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 HNO₃.

Step 7. To the WO₃•XH₂O precipitate obtained in *Step 6*, add 6 drops of conc NH₄OH. Using H₂O 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 HC₂H₃O₂ 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 HNO₃ 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 CHCl_3 extraction has been eliminated; fuming with conc H_2SO_4 has been introduced; and the final weighing form of the tungsten is 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 H_2O ; standardized

Iron carrier: 10 mg iron/ mL , added as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in very dilute 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 H_2O

Palladium carrier: 10 mg palladium/ mL , added as PdCl_2 in 1*M* HCl

Lanthanum carrier: 10 mg lanthanum/ mL , added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

HCl : conc

HNO_3 : conc

H_2SO_4 : conc

Tartaric acid: 50% aqueous solution

NH_4OH : conc

NaOH : 10*M*

H_2S : 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 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 4*M* in 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 H_2SO_4 and, while stirring, fume until 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 H_2O . When cool, carefully add 20 mL of H_2O , 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 10*M* NaOH , dilute to 15 mL with H_2O , 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 H_2SO_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 H_2S 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 H_2S 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 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 NH_4OH rather than $NaOH$.

Step 10. To the supernate add 10 drops of tartaric acid, 10 drops of conc H_2SO_4 , and 5 drops of palladium carrier. Saturate with H_2S 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 HNO_3 , digest for 10 min on a steam bath, centrifuge, and discard the supernate. To the precipitate add 3 ml of conc H_2SO_4 and fume as in *Step 2*. Cool, add 20 ml of H_2O , and heat on a steam bath for 10 min. Centrifuge and discard the supernate.

Step 12. Dissolve the precipitate in 1 ml of conc NH_4OH 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 HCl . Digest for 10 min on a steam bath. Filter the hot mixture onto a Millipore filter (pore size $\leq 1.2 \mu m$). Do not wash the precipitate. Transfer the precipitate and filter paper to a porcelain crucible and ignite for 5 to 10 min at $800^\circ C$. Cool and powder gently with a polished glass rod. Using absolute ethanol, transfer the powdered material onto a weighed filter circle. Weigh as WO_3 .

Notes

1. This treatment seems to ensure subsequent decontamination from niobium.

2. The presence of Fe^{3+} delays the reduction of molybdenum by H_2S 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 H_2O in a Waring blender and macerating for ~ 5 min. The pulp mixture is transferred to a Pyrex container and made slightly acidic with 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 3*M* in HCl. After dissolution of the precipitate in 10*M* NaOH, $La(OH)_3$ scavenges are carried out, and the tungsten is then precipitated as the 8-quinolinolate in the presence of EDTA. The precipitate is wet ashed, the WO_3 formed is dissolved in 10*M* 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, $WO_3 \bullet XH_2O$, 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 $Na_2WO_4 \bullet 2H_2O$ in H_2O ; standardized

Molybdenum carrier: 10 mg molybdenum/ml, added as $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$ in H_2O

Palladium carrier: 10 mg palladium/ml, added as $PdCl_2$ in 1*M* HCl

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

EDTA solution: 0.2*M* solution of disodium ethylenediamine tetraacetate

Cinchonine ($C_{19}H_{22}N_2O$) solution: 125 g diluted to 1 *l* with 6*M* 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 2*M* $HC_2H_3O_2$

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 3*M* 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 10*M* 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 0.2*M* 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 $\text{WO}_3 \bullet \text{XH}_2\text{O}$ precipitate in 10 drops of 10*M* NaOH and dilute to 15 ml with H_2O . 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 CHCl_3 and shake vigorously for ~1 min. Add 5 ml of 6% cupferron reagent, shake for 1 min, and discard the CHCl_3 (lower) layer. To the aqueous layer add 10 ml of CHCl_3 and 3 ml of cupferron reagent, shake for 1 min, and discard the CHCl_3 layer. Wash the aqueous layer with 5 ml of 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 H_2SO_4 , 5 drops of palladium carrier, and 1 drop of molybdenum carrier; saturate the solution with H_2S . 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 H_2S 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 HNO_3 , and then heat on a steam bath to coagulate the $\text{WO}_3 \bullet \text{XH}_2\text{O}$ 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- μm) and ignite for 15 min at 800°C. Weigh and mount the 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 $\text{MnNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$ after standard decontamination steps. No detectable contamination was found in the manganese separated from 2.5×10^{14} fissions 1-h old.

2. Reagents

Manganese carrier: 10 mg manganese/ml, added as MnCl_2 in H_2O ; standardized

Tungsten carrier: 10 mg tungsten/ml, added as $\text{Na}_2\text{WO}_4 \bullet 2\text{H}_2\text{O}$ in H_2O

Iron carrier: 10 mg iron/ml, added as FeCl_3 in 1*M* HCl

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

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

HCl: conc; 6*M*

HNO₃: conc

HC₂H₃O₂: glacial

NH₄OH: conc; 0.1*M*

NaOH: 10*M*

H₂S: gas

NaBrO₃: saturated solution

(NH₄)₂S: 20% solution

(NH₄)₂HPO₄: 1.5*M*

Aerosol: 0.1% in H_2O

Dowex AG 50-X4, 100 to 200 mesh, cation-exchange resin; slurry in H_2O

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

Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 22.9 g of MnCl_2 in H_2O 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 1.5*M* $(\text{NH}_4)_2\text{HPO}_4$, and make alkaline with conc NH₄OH. Heat to boiling, let stand for 10 min, and filter the precipitate into a weighed sintered glass crucible. Wash the precipitate first with 0.1*M* NH₄OH and then with ethanol. Dry at 110°C, cool, and weigh as $\text{MnNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$.

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 HNO₃.

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 NaBrO₃ and heat on a steam bath. (MnO₂ begins to precipitate and the solution fizzes.) Carefully add another 3 ml of NaBrO₃ and heat on a steam bath until the total time of heating is ~10 min. Cool the solution, add H_2O to fill the tube, and centrifuge. Discard the supernate, wash the precipitate twice with H_2O , 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 H_2O , add conc NH₄OH 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% (NH₄)₂S, heat for 1 to 2 min on a steam bath, and centrifuge. Discard the supernate. The precipitate is 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 H_2O , place on a steam bath, and bubble in H_2S . 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 NH_4OH dropwise until $\text{MnNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$ 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 H_2O , 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 H_2O , 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 H_2O and add the rinsings to the resin. Wash the resin with several 2- to 3-ml portions of H_2O 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 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 NH_4OH dropwise until $\text{MnNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$ 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 H_2O , add a few drops of aerosol, and centrifuge. Transfer the supernate to a clean centrifuge tube and reprecipitate $\text{MnNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$. Filter onto a weighed filter circle. Wash the precipitate first with 0.1M NH_4OH and then with ethanol. Dry at 110°C, cool, weigh, and mount.

(October 1989)

RHENIUM

B. P. Bayhurst

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) LaF_3 and $\text{La}(\text{OH})_3$ scavenges, (2) Re_2S_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-quinolinolate 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: KReO_4 in H_2O , 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 $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O

Copper(II) carrier: 10 mg copper/ml, added as $\text{CuCl}_2 \bullet 2\text{H}_2\text{O}$ in H_2O

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

Ruthenium(III) carrier: 10 mg ruthenium/ml, added as RuCl_3 in 0.1M HCl; probably contains some ruthenium(IV)

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

NH_4OH : conc

NaOH : 10M

H_2S : gas

H_2O_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 (H^+ form)

Ethanol: absolute

Methyl red indicator solution

3. Procedure

Step 1. Dissolve ~2 g of sample in a Teflon beaker by the successive addition of fuming HNO_3 , conc HCl, and conc HF. The process is aided by heating, but the mixture is never taken to dryness (the Re_2O_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 H_2O .

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 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 H_2S for ~15 min. Stopper the tube and permit it to stand until the Re_2S_7 formed has coagulated. Centrifuge and discard the supernate. Add 30 ml of HF-HCl solution to the Re_2S_7 and saturate with H_2S on a steam bath. Centrifuge and discard the supernate. Add 30 ml of 6M HCl to the Re_2S_7 , saturate again with H_2S , centrifuge, and discard the supernate.

Step 5. To the precipitate, add 1 ml of 10M NaOH and 5 to 6 drops of 30% H_2O_2 . Heat on a steam bath until a clear solution (ReO_4^-) is formed. Dilute with H_2O 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 $\sim 2 \text{ ml}$ 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 (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 $\sim 2 \text{ ml}$ and dilute to 15 ml with H_2O . 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-quinolinate 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-quinolinate 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-quinolinate carries down molybdenum activity.] Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate. Repeat the iron(III)-8-quinolinate 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 H_2S for 15 min. Stopper the centrifuge tube and permit the Re_2S_7 to coagulate. Treat the precipitate with HF-HCl solution and $6M$ HCl as described in *Step 4*.

Step 10. Dissolve the Re_2S_7 with $10M$ NaOH and 30% H_2O_2 as in *Step 5*. Use H_2O to transfer the perrhenate solution to a 125-ml erlenmeyer flask. Boil the solution until all the H_2O_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 $\sim 2 \text{ ml}$, 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 H_2S for 15 min, centrifuge, and discard the supernate. Wash the Re_2S_7 precipitate with 20 ml of $6M$ HCl and discard the wash.

Step 12. Add 1 ml of conc NH_4OH and 5 to 6 drops of 30% H_2O_2 to the sulfide. Heat on a steam bath until the solution is completely clear and dilute it to 15 ml with H_2O . 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 H_2O and then with cold absolute ethanol. Dry in an oven at 110°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 Re_2S_7 from a medium that is $\sim 5M$ in both HCl and HF. The chemical yield is $\sim 80\%$.

2. Reagents

Rhenium carrier: KReO_4 in H_2O , corresponding to ~ 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 H_2O

Lanthanum carrier: 10 mg lanthanum/ mL , added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

HCl: conc; 6M

HF: conc

HF-HCl: 5M in each

H_2S : gas

NH_4OH : conc

H_2O_2 : 30%

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 KReO_4 in H_2O 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 H_2O , and make the solution 0.5M in 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°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 $\sim 10\text{ mL}$ 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 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 HF and HCl. Add 2 mL of tungsten carrier and saturate with H_2S for at least 10 min while heating the solution on a steam bath. Centrifuge and discard the supernate. To the Re_2S_7 precipitate add 30 mL of HF-HCl mixture, saturate with H_2S , centrifuge, and discard the supernate.

Step 4. To the precipitate add 1 mL of conc NH_4OH and 5 to 6 drops of 30% H_2O_2 . Let the mixture stand on a steam bath, while stirring, until solution is complete. Add 30 mL of the 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 H_2S . Centrifuge and discard the supernate. Wash the precipitate with 20 to 30 mL of 6M HCl and discard the washings.

Step 6. To the precipitate add 1 mL of conc NH_4OH and 5 to 6 drops of 30% H_2O_2 . Heat on a steam bath to dissolve the Re_2S_7 and transfer the solution to a clean 40-mL glass centrifuge tube. Make the solution acidic with HCl and boil over a burner for a few min to ensure complete removal of H_2O_2 .

Step 7. Add 4 drops of lanthanum carrier, make the solution alkaline with conc NH_4OH , 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 H_2O and a small amount of absolute ethanol. Dry in an oven at 110°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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1*M* HCl; standardized

Antimony(III) carrier: 100 mg antimony/ml, added as SbCl_3 in 3*M* HCl

Tin(II) carrier: 100 mg tin/ml, added as SnCl_2 in 3*M* HCl

Tellurium(IV) carrier: 10 mg tellurium/ml, added as TeCl_4 in 3*M* HCl

Thallium(III) carrier: 10 mg thallium/ml, added as TlCl_3 in H_2O

I^- carrier: 100 mg I^- /ml, added as KI in H_2O

HCl: 0.2*M*; 8*M*; conc

HNO_3 : conc

Tartaric acid: saturated aqueous solution

NH_4OH : conc

$(\text{NH}_4)_2\text{S}$: saturated solution

$(\text{NH}_4)_2\text{CO}_3$ reagent: 392.5 g of $(\text{NH}_4)_2\text{CO}_3$ in 175 ml of conc NH_4OH ; diluted to 1 *l*

$\text{NH}_4\text{H}_2\text{PO}_4$ reagent: 230 g $\text{NH}_4\text{H}_2\text{PO}_4$ /l

Br_2 : liquid

Aerosol: 0.1% aqueous solution

Isopropyl ether (alcohol-free)

Ethanol: 95%

3. Preparation and Standardization of Carrier

Weigh out 48.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and make up to 1 *l* in 1*M* HCl. Pipette 5.0 ml into an electroplating cell and add conc NH_4OH dropwise until $\text{Fe}(\text{OH})_3$ begins to precipitate. Add 1 ml of $\text{NH}_4\text{H}_2\text{PO}_4$ reagent and 10 ml of $(\text{NH}_4)_2\text{CO}_3$ reagent. Plate onto a weighed 1-in. platinum disk at 2 A and 70°C for 90 min. Wash the plate with H_2O 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_4OH and add 5 ml of $(\text{NH}_4)_2\text{S}$ 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_2S . Add 1 ml of tellurium(IV) carrier, 1 drop each of tin(II) and antimony(III) carriers, and 20 ml of 0.2*M* HCl. Add 1 drop of aerosol solution and saturate with H_2S . 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 $(\text{NH}_4)_2\text{S}$ solution. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate in 3 to 4 drops of conc HCl and oxidize the Fe^{2+} ion with 1 to 2 drops of conc HNO_3 . Evaporate the solution to dryness; add 3 to 4 drops of conc HCl, and again evaporate to dryness. Use 10 ml of 8*M* HCl to transfer the FeCl_3 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_2O 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 $(NH_4)_2S$ 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_2S . Add 1 drop of antimony(III) carrier and 3 to 4 drops of liquid Br_2 . Boil off excess Br_2 , and add 1 ml of thallium(III) carrier and 1 ml of I^- 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_2S . 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_2S . 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 $Fe(OH)_3$ with conc NH_4OH . Centrifuge and discard the supernate.

Step 12. To the precipitate add 1 ml of $NH_4H_2PO_4$ reagent and 10 ml of $(NH_4)_2CO_3$ reagent; warm to dissolve the $Fe(OH)_3$. 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_2O 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_2 , and the pentapositive antimony is then reduced by I^- ion. In the next operation, H_2S 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, RuO_4 , and distillation of this volatile oxide. The oxidation is effected by means of a mixture of HClO_4 and NaBiO_3 in the presence of red fuming HNO_3 . The bismuthate converts the halogens to their nonvolatile oxoacids. The RuO_4 is distilled into NaOH solution and the ruthenium is precipitated as a mixture of oxides, Ru_2O_3 and RuO_2 , by reduction with ethanol. These oxides are dissolved in 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 RuCl_3 and RuCl_4 in 0.1*M* HCl ; standardized

I^- carrier: 10 mg I^-/ml , added as KI in H_2O

HCl : 0.1*M*; 1*M*; 6*M*; conc

HNO_3 : red fuming

HClO_4 : 70%

H_3PO_4 : 85%

NaOH : 6*M*

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 0.1*M* HCl .

Pipette 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask and add ~ 0.4 g of powdered magnesium metal in portions; shake after each addition. Dissolve the excess magnesium metal in conc HCl and decant the resulting supernate carefully. Add 20 ml of 1*M* 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 H_2O and twice with 5-ml portions of 95% ethanol. Dry for 15 min at 110°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 I^- holdback carrier, 6 ml of red fuming HNO_3 , 0.4 g of NaBiO_3 , 1 ml of 85% H_3PO_4 (Note 1), and 10 ml of 70% HClO_4 . Keep the flask in a hot H_2O bath until the solution is a light amber color.

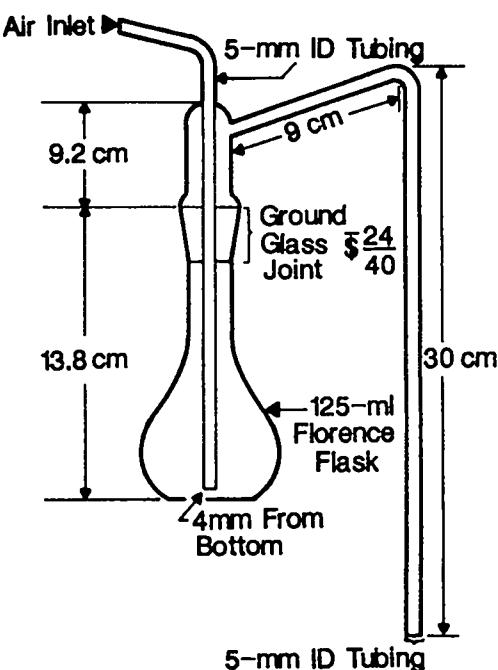


Fig. 1. Ruthenium distilling flask.

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 6*M* 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 RuO₄ 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 H₂O.

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 H₃PO₄ is added to the distilling flask to prevent the slight volatilization of molybdenum by HClO₄.

2. Technetium is volatilized, probably as Tc₂O₇. 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 ⁹⁹Tc (daughter of 67-h ⁹⁹Mo) is the longest-lived technetium isotope prominent in fission.

3. The 42-d ¹⁰³Ru activity can be separated conveniently from 1-y ¹⁰⁶Ru because the ¹⁰³Ru activity is ~43 times as abundant as ¹⁰⁶Ru as a result of half-life and fission-yield factors. Ruthenium-103 also has about three times as many gamma rays as ¹⁰⁶Ru does. By using a scintillation counter and a 2000-mg aluminum absorber to

eliminate the 3.55-MeV beta from ¹⁰⁶Ru, it is possible to determine ¹⁰³Ru. 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 ¹⁰³Ru. The 0.55-MeV gamma from ¹⁰³Ru is counted also, and must be corrected for by counting through a series of heavy aluminum absorbers (1600 to 2500 mg/cm²) 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 $\text{HC}_2\text{H}_3\text{O}_2$. Dilute to 25 ml with H_2O and cool to room temperature.

Step 3. Precipitate $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ by the addition of a reagent made by saturating 6 ml of 3M $\text{HC}_2\text{H}_3\text{O}_2$ with KNO_2 . Allow ~ 3 min for complete precipitation. Centrifuge, discard the supernate, wash the precipitate once with 30 ml of H_2O , and discard the washings.

Step 4. Dissolve the $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ 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_2O .

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 $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ 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_2O and make $\sim 0.1\text{M}$ in HCl. Heat to boiling and pass in H_2S 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_2S from the filtrate. Add 2 drops of palladium and 4 drops of copper carriers and dilute to 20 ml with H_2O . Make 0.1M in HCl, heat to boiling, and pass in H_2S for 5 min. Again remove sulfides by filtration (*Step 7*).

Step 9. Boil out H_2S from the filtrate. This will require concentration almost to dryness (Note 2). Dilute to 25 ml with H_2O and transfer quantitatively to 40-ml centrifuge tube. Add 4 drops of iron carrier and precipitate $\text{Fe}(\text{OH})_3$ by addition of conc NH_4OH ; add ~ 0.5 ml of NH_4OH in excess. Centrifuge and discard the $\text{Fe}(\text{OH})_3$ scavenger; retain the supernate.

Step 10. Acidify the supernate with HCl. Add 4 drops of iron carrier and remove $\text{Fe}(\text{OH})_3$ again by the addition of conc NH_4OH (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_4SCN 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_4SCN solution. Discard washings.

Step 13. Back-extract the cobalt into 20 ml of H_2O to which 4 to 6 ml of conc NH_4OH 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_2S for 1 min. Centrifuge and discard the supernate.

Step 15. Transfer the CoS precipitate with 5 to 10 ml of H_2O to a 125-ml erlenmeyer flask. Add 10 ml of conc HNO_3 . Boil nearly to dryness (1 to 2 ml). Add 3 ml of conc H_2SO_4 and heat to SO_3 fumes. Cool and slowly add 5 to 10 ml of H_2O . Cool again. Neutralize with conc NH_4OH and add 1 ml in excess. Add 2 g of $(\text{NH}_4)_2\text{SO}_4$, transfer to a plating cell, and electroplate cobalt on a weighed platinum foil. (For a circular foil of $\sim \frac{7}{8}$ -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 RuO_4 , (b) extraction of iridium and platinum chlorides into TBP(tributyl phosphate) solution in *n*-hexane, (c) precipitation of Rhl_3 , and (d) Fe(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 H_2SO_4 solution after destruction of the complex. The chemical yield is $\sim 60\%$.

2. Reagents

Rhodium carrier: 10 mg rhodium/ml, added as $\text{RhCl}_3 \bullet 4\text{H}_2\text{O}$; standardized

Platinum carrier: 10 mg platinum/ml, added as H_2PtCl_6 in dilute HCl

Cobalt carrier: 10 mg cobalt/ml, added as $\text{CoCl}_2 \bullet 6\text{H}_2\text{O}$ in H_2O

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

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

Barium carrier: 10 mg barium/ml, added as $\text{BaCl}_2 \bullet 2\text{H}_2\text{O}$ in H_2O

Antimony(III) carrier: 10 mg antimony/ml, added as SbCl_3 in 1*M* HCl

Tellurium(IV) carrier: 10 mg tellurium/ml, added as Na_2TeO_3 in 1*M* HCl

HCl: 3*M*; 6*M*; conc

HNO_3 : conc

H_2SO_4 : conc

HClO_4 : conc

NaOH : 6*M*

NH_4OH : conc

KCN: 3*M*

NaNO_2 : 5*M*

Na_2CO_3 : 0.5*M*

KCl: solid

$\text{Cu}(\text{NO}_3)_2$ solution: 100 mg copper/ml

KI: solid

H_2S : 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 $\text{RhCl}_3 \bullet 4\text{H}_2\text{O}$ and make up to 1 *l* in 0.01*M* HCl. Pipette 3 ml of the solution into a 125-ml erlenmeyer flask and add 3 ml of conc H_2SO_4 , 2 ml of conc HClO_4 , and 1 ml of conc HNO_3 . Heat until SO_3 fumes appear. Transfer the solution with 20 ml of H_2O 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 H_2O 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 HClO_4 , 1 ml of conc HNO_3 , and heat to near dryness. Add 30 ml of 6*M* HCl.

Step 3. Add 1 to 2 g of solid KI and boil for 20 min; add 3*M* 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 Rhl_3 precipitate with 20 ml of warm 3*M* HCl and discard the supernate.

Step 4. To the precipitate add 3 ml of 3*M* KCN, and heat until solution occurs. Add 1 ml of tellurium(IV) carrier and 2 ml of 6*M* HCl; heat to boiling. While heating, add 5*M* NaNO_2 dropwise until I_2 fumes are no longer visible.

Step 5. Dilute to 20 ml with H₂O, add 3 drops of iron carrier, then add conc NH₄OH 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 NH₄OH, 1 ml of barium carrier, and 3 ml of 0.5M Na₂CO₃; 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 H₂S. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 8. Boil the solution for ~30 s to remove H₂S. Add 7 ml of conc HCl and 2 ml of Cu(NO₃)₂ solution; cool in an ice bath. (The rhodium is precipitated, presumably as the compound Cu₃[Rh(CN)₆]₂.) Centrifuge and discard the supernate.

Step 9. To the precipitate add 20 ml of H₂O, 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 H₂SO₄ and evaporate the solution to near dryness to destroy the rhodium-cyanide complex.

Step 11. Use 20 ml of H₂O to transfer the solution to a 40-ml glass centrifuge tube. Add 6M NaOH dropwise to precipitate Rh(OH)₃ (pH~8). Centrifuge and discard the supernate.

Step 12. Add 3 drops of platinum carrier, 40 mg of KCl, 3 drops of conc HNO₃, 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 9* through *9*.

Step 14. Repeat *Steps 6* through *10*.

Step 15. Add 2 ml of conc HClO₄ and 1 ml of conc HNO₃; heat until SO₃ fumes evolve. Transfer to the plating cell with 20 ml of H₂O. Electroplate at room temperature and 0.1 A for 16 h on a weighed platinum cathode disk. Wash the cathode with H₂O 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.

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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 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 SO_2 and ruthenium is distilled as RuO_4 . Iridium is oxidized to the tetrapositive state by means of 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 $\text{Cs}_2[\text{IrCl}_6]$ /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 Na_2TeO_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

HNO_3 : conc

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

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 HNO_3 , HClO_4 , and HF. Fume down to a low volume of HClO_4 , and to the cooled mixture add sufficient H_2O to make the solution 2M in 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, H_2O , and 1M 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 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 SO₂. Filter off the tellurium precipitate and collect the filtrate in a 125-ml erlenmeyer flask. Boil to expel SO₂.

Step 6. Add 5 ml of conc HClO₄ and 2 ml of conc HNO₃; evaporate to dense fumes of HClO₄. (RuO₄ volatilizes.)

Step 7. Dilute the solution to 2M in HClO₄ 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 HNO₃; evaporate to dryness again. Repeat the last evaporation process. (Iridium is converted to IrCl₆²⁻.) 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 HNO₃ 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 H₂O 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 HNO₃, 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 HNO₃. 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}Ir . Similarly, ^{193}Ir and ^{189}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 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 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 H_2O

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

HNO_3 : conc

H_2SO_4 : conc

NH_4OH : conc

$(\text{NH}_4)_2\text{SO}_4$: solid

Sodium citrate: 10% in H_2O

H_2S : 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 H_2O , add 1 ml of HNO_3 , and dilute to 1 l with H_2O .

Pipette 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask, add 3 ml of conc H_2SO_4 , boil down to SO_3 fumes to remove NO_3^- ion, and cool to room temperature. Dilute to 8 to 10 ml with H_2O , and cautiously neutralize with conc NH_4OH ; 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 NH_4OH about every 30 min. When the plating is complete, wash the cathode several times with distilled H_2O 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 NH_4OH . (A deep blue-violet color indicates that sufficient NH_4OH has been added.) Dilute to 25 ml with H_2O . Precipitate nickel by the addition of 15 ml of 1% alcoholic DMG reagent. Centrifuge and wash the precipitate with 30 ml of H_2O that contains 1 drop of conc NH_4OH . Discard the supernate and washings.

Step 2. Dissolve the nickel-DMG precipitate in 2 ml of conc HCl and dilute to 15 ml with H_2O . (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 NH_4OH . Centrifuge and wash as in *Step 1*.

Step 3. Repeat *Step 2.*

Step 4. Dissolve the nickel-DMG precipitate in 10 ml of conc HNO₃, 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 HNO₃. Boil until NiCl₂ precipitates and then dilute to 20 ml with H₂O. (Be certain that the heating is continued for sufficient time to remove HNO₃.)

Step 5. Add 3 drops of conc HCl and 4 drops each of copper and palladium carriers. Heat to boiling and pass in H₂S for 5 min. Filter the sulfide scavenger precipitate and discard.

Step 6. Boil out H₂S, add 2 drops of conc HCl, add 4 drops each of copper and palladium carriers, dilute to 20 ml with H₂O, heat, and remove another sulfide scavenger precipitate with H₂S. Boil out H₂S from the filtrate and transfer to a 40-ml centrifuge tube.

Step 7. Dilute to 20 ml with H₂O. Add 8 drops of iron carrier and precipitate Fe(OH)₃ from a hot solution by the addition of conc NH₄OH (1 ml in excess). Centrifuge and discard Fe(OH)₃ scavenger precipitate.

Step 8. Acidify the supernate with HCl or HNO₃. Add 8 drops of iron carrier and remove a second Fe(OH)₃ scavenger. Transfer the supernate to a 100-ml beaker.

Step 9. To the supernate from the Fe(OH)₃ scavenger, 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 CHCl₃ and extract nickel-DMG (Note 3).

Step 10. Wash the CHCl₃ layer twice with 50-ml portions of H₂O that each contain 1 drop of conc NH₄OH. Discard washings.

Step 11. Back-extract nickel into 20 ml of 6M HCl. Transfer the H₂O layer to a 125-ml erlenmeyer flask (Note 4), and boil nearly to dryness. Add 4 to 5 ml of conc HNO₃. Boil nearly to dryness. Add ~3 ml of conc H₂SO₄ and heat to SO₃ fumes (Note 5). Cool to room temperature.

Step 12. Add 8 ml of H₂O and cautiously neutralize with conc NH₄OH (1 ml in excess). Add 1 g of (NH₄)₂SO₄, dilute to 20 ml with H₂O, 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 NH₄OH about every 30 min.) After plating, wash with H₂O 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 HNO₃, 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)₃ in *Step 7*.

3. Freshly precipitated nickel-DMG ordinarily extracts rapidly into CHCl₃. If it does not do so, add a further 50 ml of CHCl₃ and shake the separatory funnel vigorously. The CHCl₃ and H₂O 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 CHCl₃ layer indicates that back-extraction is complete.

5. For successful plating, all organic material and nitrates must be removed.

6. If 36-h ⁵⁷Ni is being counted, mount the sample and cover with 1-mil Dural to absorb the radiations of 2×10^5 -yr ⁵⁹Ni and 300-yr ⁶³Ni.

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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)₃ scavenges. The palladium is then precipitated as the sulfide and converted again to the dimethylglyoxime complex, Pd(C₄H₇N₂O₂)₂, in which form it is weighed. The chemical yield is 60 to 70%.

2. Reagents

Palladium carrier: 10 mg palladium/ml, added as PdCl₂ in H₂O; standardized

Silver carrier: 10 mg silver/ml, added as AgNO₃ in H₂O

Iron carrier: 10 mg iron/ml, added as FeCl₃•6H₂O in very dilute HCl

HCl: 0.4M; 6M; conc

HNO₃: conc

NH₄OH: conc

H₂S: gas

Dimethylglyoxime (DMG) reagent: 1% solution in 95% ethanol

Aerosol: 0.1% in H₂O

Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 16.65 g of PdCl₂ in H₂O 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 H₂O and absolute ethanol. Dry at 110°C for 15 min, cool, and weigh as Pd(C₄H₇N₂O₂)₂.

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 H₂S to precipitate PdS. Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate by boiling with 0.8 ml of conc HNO₃ 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 HNO₃, boil nearly to dryness, add 2 ml of conc HCl, and boil nearly to dryness. Add 15 ml of H₂O, 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 NH₄OH, 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 H_2S .
Centrifuge and discard the supernate.

Step 13. Dissolve the PdS precipitate in 1 $\text{m}\ell$ of conc HNO_3 and take the solution almost to dryness by heating over a flame. Add 20 $\text{m}\ell$ of 0.4M HCl , stir, and centrifuge. Transfer the supernate to a clean centrifuge tube.

Step 14. To the supernate add 5 $\text{m}\ell$ of DMG reagent and 1 drop of aerosol. Centrifuge and discard the supernate. Wash the precipitate by centrifugation first with 30 $\text{m}\ell$ of 0.4M HCl and then with 30 $\text{m}\ell$ of absolute ethanol. With the aid of ethanol, transfer the precipitate onto a weighed filter circle. Wash with small portions of H_2O and absolute ethanol. Dry at 110°C for 5 min, cool, weigh, and mount. Count the betas from ^{109}Pd and ^{112}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_3 solution. The silver is then purified by Fe(OH)_3 scavenging and Ag_2S 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_3 , in which form it is counted. The chemical yield exceeds 80%.

2. Reagents

Silver carrier: primary standard, 10 mg silver/ml, added as AgNO_3 in very dilute HNO_3

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

HCl : conc

HNO_3 : conc

H_2SO_4 : conc

HIO_3 : 2M

NaOH : 6M

NH_4OH : conc

$(\text{NH}_4)_2\text{S}$: saturated solution

Ethanol: 95%

3. Preparation of Carrier

Dissolve 15.75 g of AgNO_3 , primary standard grade, in a minimum amount of H_2O , add a few drops of HNO_3 , 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_3 and dilute the solution to 20 ml with H_2O . 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_4OH , dilute to 20 ml with H_2O , 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 $(\text{NH}_4)_2\text{S}$ solution. Stir vigorously, centrifuge (Note 2), and discard the supernate.

Step 4. Dissolve the Ag_2S precipitate by heating with 1 ml of conc HNO_3 . Dilute to 20 ml with H_2O 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_2S by heating with 1 ml of conc HNO_3 . Dilute with 20 ml of H_2O , make the solution alkaline with 6M NaOH , and then add 3 drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Add 4 drops of conc H_2SO_4 and heat over a burner until a clear solution is obtained. Cool.

Step 7. While stirring, add 20 ml of H_2O and then 1 ml of 2M HIO_3 . Centrifuge and discard the supernate.

Step 8. Dissolve the AgIO_3 in 4 drops of conc NH_4OH and dilute to 20 ml with H_2O . Centrifuge and transfer the supernate to a clean 40-ml centrifuge tube.

Step 9. Add 3 drops of conc H_2SO_4 to the solution, stir, and filter the AgIO_3 precipitate onto a weighed filter circle. Wash the precipitate with a large amount of H_2O 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}Pd and $^{111\text{m}}\text{Pd}$ to decay to ^{111}Ag . The additional silver resulting from this waiting period is only $\sim 0.5\%$ of the total.
2. Although the precipitation of AgCl from acidic solution is specific for Ag^+ among the cations in fission products, it is possible that the precipitate may be contaminated by bromide and iodide. The Ag_2S precipitations are performed to remove any contaminating halogen activities.
3. Beta-counting for 7.4-d ^{111}Ag activity is begun ~ 16 h after the chemistry is completed; this delay permits 3.2-h ^{112}Ag to decay sufficiently so that it will not interfere.

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 H_2O , and disassemble it. Wash the silver-plated platinum disk thoroughly with absolute ethanol, allow to dry at room temperature, weigh, and mount.

(October 1989)

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 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, Ag_2O should be precipitated with NaOH. The precipitated oxide is washed thoroughly twice with H_2O , 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.

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)₃ scavenging precipitations. Last traces of contaminating activities are removed by extracting AuCl₃ from 1*M* 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 AuCl₃ in ~0.1*M* HCl; used as a primary standard

Silver carrier: 10 mg silver/ml, added as AgNO₃ in H₂O

Tellurium(VI) carrier: 10 mg tellurium/ml, added as H₂TeO₄ • 2H₂O in H₂O

Iron carrier: 10 mg iron/ml, added as FeCl₃ • 6H₂O in 1*M* HCl

HCl: 0.1*M*; 1*M*; 2*M*; conc

HNO₃: conc

HI: conc

Aqua regia: three parts by volume of conc HCl + one part conc HNO₃

NaOH: conc

Sulfosalicylic acid: 5% in H₂O

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 0.1*M* HCl. The solution is used without further standardization.

4. Procedure

Step 1. To the sample (Note 1) contained in 20 ml of 1*M* 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 H₂O and decanting. Repeat. Digest the gold precipitate with 1 ml of conc HNO₃ by boiling for 1 min in the hood. Centrifuge and discard the supernate.

Step 3. Fill the tube with H₂O and decant. Dissolve the precipitate in 2 ml of conc HCl and 3 or 4 drops of conc HNO₃. Boil off all the HNO₃.

Step 4. Dilute to 20 ml with 1*M* HCl and repeat *Steps 1, 2*, and *3* twice.

Step 5. Dilute the solution to 20 ml with 1*M* 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)₃ 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 1*M* HCl. Extract with 25 ml of ethyl acetate. Wash the ethyl acetate layer twice with 5-ml portions of 2*M* 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 $\text{Fe}(\text{OH})_3$ scavenging step.

4. This procedure has been used to determine 2.69-d ^{198}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 NH₄OH; 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 ScO₃/ml (see the procedure for SCANDIUM I)

HCl: conc

NH₄OH: conc

H₂S: 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 H₂S until As₂S₃ 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 H₂S and add conc NH₄OH dropwise until the solution is alkaline and Sc(OH)₃ 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 NH₄OH.

(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 Fe(OH)_3 . The cadmium, in 4*M* HCl, is then placed on an anion-exchange resin (Dowex AG 1-X8) and eluted with 1.5*M* H_2SO_4 . Finally, the cadmium is converted to the elemental form by electroplating. The chemical yield is $\sim 80\%$.

2. Reagents

Cadmium carrier: 10 mg cadmium/*ml*, added as $\text{Cd}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$ in very dilute HCl; standardized

Silver carrier: 10 mg silver/*ml*, added as AgNO_3 in very dilute HNO_3

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

Palladium carrier: 10 mg palladium/*ml*, added as PdCl_2 in H_2O

Lanthanum carrier: 10 mg lanthanum/*ml*, added as $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O

HCl: conc; 6*M*; 3*M*; 0.1*M*

H_2SO_4 : 1.5*M*; conc

NH_4OH : conc

NH_4Cl : 3*M*

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

NaCN : 2*M*

NaOH : 10*M*

H_2S : gas

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

Methyl red indicator solution

Ethanol: 95%; absolute

3. Preparation and Standardization of Carrier

Dissolve 27.4 g of $\text{Cd}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$ in H_2O , make the solution slightly acidic with HCl, and dilute to 1 *l* with H_2O . 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 H_2O , add 2 *ml* of 3*M* NH_4Cl and 2 *ml* of 1.5*M* $(\text{NH}_4)_2\text{HPO}_4$, 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 $\text{CdNH}_4\text{PO}_4 \bullet \text{H}_2\text{O}$.

4. Procedure

Step 1. Add the sample to 2.0 *ml* of cadmium carrier in a 40-*ml* glass centrifuge tube. Add sufficient 6*M* HCl to make the solution 0.1*M* with respect to this acid. Bubble in H_2S for ~ 3 min, centrifuge, and discard the supernate.

Step 2. To the precipitate add 2 *ml* of conc HCl and boil to expel H_2S . Dilute to 20 *ml* with H_2O , add 2 drops of iron carrier, and make alkaline by the dropwise addition of conc NH_4OH . 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 H_2SO_4 dropwise until the solution is acid to methyl red indicator. Add 10 drops of 6*M* 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 H_2S , 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 3*M* HCl and 3 drops of palladium carrier. While the solution is being heated on a steam bath, saturate it with H_2S . 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.

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 $\sim 40\%$ 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

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)

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 radios scandium is the extraction of the element from a solution 10*M* in HNO₃ by 0.5*M* 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 LaF₃ scavenging while the scandium is complexed, and La(OH)₃•Fe(OH)₃ 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 ScCl₃ in very dilute HCl; standardized
Iron carrier: 10 mg iron/ml, added as FeCl₃•6H₂O in very dilute HCl
Lanthanum carrier: 10 mg lanthanum/ml, added as La(NO₃)₃•6H₂O in very dilute HNO₃
Cerium(IV) carrier: 10 mg cerium/ml, added as Ce(NO₃)₄
HCl: 6*M*
HNO₃: conc; 10*M*
HClO₄: conc
H₂SO₄: conc
NH₄OH: conc
NH₂OH•HCl: solid
H₃BO₃: saturated aqueous solution
NH₄HF₂: mixture of two volumes of 6*M* NH₄OH and one volume of 27*M* HF
NH₄NO₃: 2% aqueous solution
NH₄Cl: 0.1*M*
Methyl red indicator solution: 0.5% in 90% ethanol
Ethanol: absolute
Rubber cement: 6% in benzene

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

3. Preparation and Standardization of Carrier

Dissolve 20.0 g of Sc₂O₃ in a minimum of conc HCl, add 5 ml of HCl, and make the solution up to a volume of 1 l with H₂O.

Pipette 5.0 ml of the above carrier solution into a 100-ml beaker and dilute to 20 ml with H₂O. Add 5 ml of conc NH₄OH to precipitate Sc(OH)₃. Filter the solution through filter paper. Rinse the beaker with 5 ml of 0.1*M* NH₄Cl and filter the washings through the paper containing the Sc(OH)₃. Transfer the precipitate to a weighed porcelain crucible and ignite at 900°C for 1 h. Cool and weigh as Sc₂O₃.

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 10*M* in HNO₃, add 5 drops of cerium(IV) carrier [as Ce(NO₃)₄], and make the volume ~40 ml by the addition of 10*M* HNO₃. Add ~100 to 200 mg of NH₂OH•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 H₂O layer. Wash the heptane layer with 10 ml of 10*M* HNO₃ 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 NH₄HF₂ and stir vigorously for 5 min. Add 5 ml of H₂O, stir for 2 min, add 5 ml of conc HClO₄, and heat on a steam bath for 10 min. (ScF₃ precipitates at this point.) Centrifuge and discard both the organic and aqueous supernates. To the ScF₃ precipitate add 1 ml of conc H₂SO₄ and 3 to 4 drops of cerium(IV) carrier; heat to SO₃ fumes. Cool.

Step 3. Dilute to 10 ml with H₂O and heat to dissolve any solid material. Add 100 to 200 mg of NH₂OH•HCl to reduce cerium(IV), 3 ml of NH₄HF₂, and 2 to 3 drops of methyl red indicator solution. Add conc NH₄OH until the solution is barely acidic. (CeF₃ 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 NH₄OH. Dilute to 20 ml with H₂O and heat on a steam bath to coagulate the La(OH)₃-Fe(OH)₃ precipitate. Centrifuge, transfer the supernate to a clean 40-ml plastic centrifuge tube, and discard the precipitate.

Step 5. Add 6 ml of conc HClO₄ 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 ScF₃.) Add 4 drops of cerium(IV) carrier, dissolve the precipitate in 1 ml of conc H₂SO₄, and heat to SO₃ fumes. Cool.

Step 6. Repeat *Steps 3* through *5* twice; the second time, stop with the formation of ScF₃.

Step 7. Dissolve the ScF₃ precipitate in 2 ml of saturated H₃BO₃ solution and 3 ml of conc HNO₃. Dilute to 20 ml and transfer to a clean glass centrifuge tube. Add 10 ml of conc NH₄OH to precipitate Sc(OH)₃, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of H₂O and discard the washings. Add 2 ml of conc H₂SO₄ and evaporate to fumes of SO₃. Cool, dilute to 20 ml with H₂O, and add an excess of NH₄OH. Centrifuge and discard supernate.

Step 8. Dissolve the Sc(OH)₃ 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 NH₄OH to precipitate Sc(OH)₃. Filter onto filter paper and

wash the precipitate with H₂O. Ignite at 900°C in a porcelain crucible for 20 min. Cool. Powder the Sc₂O₃ with the fire-polished tip of a glass stirring rod. Transfer the Sc₂O₃ 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 Sc₂O₃ at 110°C for 10 min, cool, weigh, and mount.

(October 1989)

SCANDIUM II
B. P. Bayhurst

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 10*M* in HCl, (2) $Zr_3(PO_4)_4$ scavenges, and (3) 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 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 Sc_2O_3 /mL, added as $ScCl_3$ in very dilute HCl; standardized (see SCANDIUM I procedure)

Zirconium holdback carrier: 10 mg zirconium/mL, added as $ZrO(NO_3)_2 \bullet 2H_2O$ in 1*M* HNO_3

Lanthanum carrier: 10 mg lanthanum/mL, added as $La(NO_3)_3 \bullet 6H_2O$ in very dilute HNO_3

HCl: conc; 10*M*

HNO_3 : conc

$HClO_4$: conc

NH_4OH : conc

$NaOH$: 10*M*

$NH_4H_2PO_4$: 1.5*M*

NH_4HF_2 -HF reagent: 4*M* in NH_4HF_2 and 1*M* in HF

$NH_2OH \bullet HCl$: solid

Methyl red indicator solution

0.05*M* alpha-HIB(alpha-hydroxyisobutyric acid): adjusted to pH 5.2 with NH_4OH

Anion-exchange resin: Dowex AG 1-X8, 50 to 200 mesh (washed with 10*M* HCl)

Cation-exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh (NH_4^+ form)

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 $HClO_4$; fume nearly to dryness. Dilute to 20 mL with H_2O and precipitate $Sc(OH)_3$ with 10*M* $NaOH$. Centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, dilute to 20 mL with H_2O , and precipitate $Sc(OH)_3$ with conc NH_4OH .

Step 2. Dissolve the precipitate in a minimum of conc HCl, dilute to 20 mL with H_2O , and repeat the precipitations of $Sc(OH)_3$ with $NaOH$ and NH_4OH . Centrifuge, discard the supernate, and wash the precipitate with 20 mL of H_2O .

Step 3. Dissolve the precipitate in 5 mL of conc HCl and place the solution on a Dowex A-X8 anion-exchange resin column (50 to 200 mesh). Collect the effluent in a 125-mL erlenmeyer flask. Pass 15 mL of 10*M* 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 H_2O , and make the solution 2 to 3*M* in HCl. Add 5 drops of 1.5*M* $NH_4H_2PO_4$ solution, heat on a steam bath for a few minutes, and let stand until the $Zr_3(PO_4)_4$ precipitate coagulates. Centrifuge, transfer the supernate to a clean tube, and discard the precipitate. Add another 2 drops of zirconium carrier and again precipitate $Zr_3(PO_4)_4$. Carry out three to four additional $Zr_3(PO_4)_4$ precipitations. Transfer the supernate (after the final precipitation) to a 40-mL plastic centrifuge tube.

Step 5. Add 3 mL of NH_4HF_2 -HF reagent and neutralize the solution to a methyl red end point with conc NH_4OH . (The scandium is now

in the form of fluorocomplexes.) Add 100 mg of $\text{NH}_2\text{OH} \bullet \text{HCl}$, 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 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 ScF_3 , centrifuge, and discard the supernate. Add 1 ml of 10M NaOH, stir, and heat to convert ScF_3 to Sc(OH)_3 . Dilute to 15 ml with H_2O , centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl and precipitate Sc(OH)_3 by adding conc NH_4OH . Centrifuge, discard the supernate, and wash the precipitate with 30 ml of H_2O to remove NH_4^+ ion. Centrifuge and discard the supernate.

Step 7. Dissolve the precipitate in 4 to 6 drops of conc HNO_3 and dilute to 30 ml with H_2O . Add 2 to 3 ml of Bio-Rad AG 50W-X4, minus 400 mesh cation-exchange resin, stir for ~1 min, centrifuge, and discard the supernate. Use a small amount of H_2O 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 Sc(OH)_3 . Combine the contents of all tubes that contain Sc(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 H_2O , and add conc NH_4OH to precipitate Sc(OH)_3 . Centrifuge and discard the supernate. Dissolve the precipitate in a minimum of conc HCl, add filter paper pulp slurry, and again precipitate Sc(OH)_3 with conc NH_4OH . Filter through filter paper. Transfer the paper to a porcelain crucible and ignite at 1000°C for 15 min. Weigh and mount the Sc_2O_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 $La(NO_3)_3 \bullet 6H_2O$ 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

TMPolypropylene Columns; source: Bio-Rad Laboratories, Richmond, California; column dimensions: 4-in. length, ~9-ml reservoir volume, ~2-ml resin bed volume, and ~1½ 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 0.75*M* HCl solution with 0.5*M* 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
 $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1*M* HNO_3

HCl : 0.75*M*; 1.5*M*; 6*M*; conc

HNO_3 : 6*M*

HF : conc; 5*M*

H_3BO_3 : saturated aqueous solution

NH_4OH : conc

Ethanol: absolute

6% rubber cement in benzene

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

HDEHP: 0.5*M* 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 $(\text{NH}_4)_2\text{C}_2\text{O}_4$ while stirring. Heat for 10 min on a steam bath and then cool in an ice bath for 4 min. Centrifuge the $\text{Y}_2(\text{C}_2\text{O}_4)_3$ 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 4*M* in HNO_3 . Add 2 ml of zirconium holdback carrier and make the solution 4*M* in HF . Centrifuge the YF_3 , decant the supernate, and wash the precipitate with 10 ml of 5*M* 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 4*M* in HF . Centrifuge the YF_3 , decant the supernate, and wash the precipitate with 10 ml of 5*M* 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 $\text{Y}(\text{OH})_3$ 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 $\text{Y}(\text{OH})_3$ in 2.0 ml of 1.5*M* HCl . Transfer the solution with 8 ml of 0.75*M* 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 0.75*M* HCl and discard the washings. Back-extract the yttrium into 10 ml of 6*M* 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 $\text{Y}(\text{OH})_3$, 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 $\text{Y}(\text{OH})_3$ in 1 $\text{m}\ell$ of 6*M* HCl, dilute the solution to 20 $\text{m}\ell$, centrifuge, and transfer the supernate to a clean centrifuge tube. Add paper pulp and then add an excess of conc NH_4OH to precipitate $\text{Y}(\text{OH})_3$. Filter onto filter paper and wash the precipitate with H_2O . Ignite at 900°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°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
HNO₃: conc
HCl: conc
HF: conc
 $\text{H}_2\text{C}_2\text{O}_4$: 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 $\text{NH}_4\text{OH}/\ell$)
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 l 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 HNO₃ 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 $\text{Y}(\text{OH})_3$.] Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate in a minimum of HNO₃ 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 HNO₃, 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 $\text{Y}(\text{OH})_3$ has not dissolved completely, add a few drops of HNO₃ and heat.] Precipitate $\text{Y}(\text{OH})_3$ 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 HNO₃ 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 ~ 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 ~ 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 Y_2O_3 at 1000°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(NO₃)₃: saturated (~2.5M); dissolve 5 lb of Al(NO₃)₃•9H₂O in 1050 ml of H₂O to produce ~2400 ml of solution. Heating speeds up the solution process.

Al(NO₃)₃: 1.9M; three parts by volume of saturated Al(NO₃)₃ and one part of H₂O

NH₄NO₃-HNO₃: 10M NH₄NO₃-0.2M HNO₃; dissolve 7 lb of NH₄NO₃ in H₂O, add 50 ml of conc HNO₃, and dilute to 4 l with H₂O.

LiOH: 4M

Al(NO₃)₃•9H₂O: solid

Tri-*n*-butyl phosphate (TBP)

Iron carrier: 10 mg iron/ml, added as Fe(NO₃)₃•9H₂O in very dilute HNO₃

Yttrium carrier: 12.67 mg Y₂O₃/2 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(NO₃)₃•9H₂O and 4M LiOH to make the pH ~0.9 to 1 and the Al(NO₃)₃ 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(NO₃)₃, stir for 2 to 3 min, and discard the aqueous phase. Repeat the wash with Al(NO₃)₃ solution. To the TBP phase add 100 mg 10M NH₄NO₃-0.2M HNO₃, stir for 2 to 3 min, and discard the aqueous phase. Repeat the wash.

Step 3. Add 30 ml of H₂O, stir for ~2 min, and drain the H₂O 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 NH₄OH, heat on a steam bath to coagulate the Y(OH)₃ precipitate, centrifuge, and discard the supernate. Dissolve each precipitate in a few drops of HNO₃ and combine the solutions in a clean 40-ml plastic centrifuge tube. Make the solution ~4M in HNO₃ 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 NH₄OH, 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)₃ with NH₄OH and discard the supernate. [The lanthanides and actinides are carried on the Fe(OH)₃.] Dissolve the Fe(OH)₃ 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 (^{91}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 $\text{Y}_2(\text{C}_2\text{O}_4)_3$, 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 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 $\text{Ce}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O ; standardized
Lanthanum carrier: 10 mg lanthanum/ml, added as $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O
Zirconium carrier: 10 mg zirconium/ml, added as $\text{ZrO}(\text{NO}_3)_2 \bullet 2\text{H}_2\text{O}$ in 1M HNO_3
HCl: 6M; conc
 HNO_3 : conc
HF: conc; 5M
 H_3BO_3 : saturated aqueous solution
 HIO_3 : 0.35M
 NH_4OH : conc
 NaBrO_3 : saturated aqueous solution
 $(\text{NH}_4)_2\text{C}_2\text{O}_4$: saturated aqueous solution
 H_2O_2 : 30%

3. Preparation and Standardization of Carrier

Dissolve 31.0 g of $\text{Ce}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O 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 H_2O . 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 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 HNO_3 ; pipette in the sample for analysis. Add 1 ml of saturated 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% H_2O_2 dropwise while vigorously stirring (Note 2) until the solution has a light reddish-brown color. Heat on the steam bath until the Br_2 color disappears; add 1 to 2 drops of H_2O_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 CeF_3 and 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 H_3BO_3 solution and suspend the precipitate by stirring. Then add 4 ml of conc 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 HNO_3 and 1 ml of saturated $NaBrO_3$ solution. Heat on a steam bath for ~ 10 min.

Step 5. Add 20 ml of 0.35M HIO_3 and stir vigorously. Cool for 5 to 10 min in an ice bath. Centrifuge and discard the supernate; retain the $Ce(IO_3)_4$ precipitate (Note 3).

Step 6. Suspend the precipitate in a solution made up by the addition of 8 ml of H_2O , 3 ml of conc HNO_3 , and 3 ml of 0.35M 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 HNO_3 and 1 to 2 drops of conc HCl , and slurry the $Ce(IO_3)_4$ by stirring vigorously. Add 0.2 ml of 30% H_2O_2 and stir until dissolution of $Ce(IO_3)_4$ is complete. Add 1 ml of saturated $NaBrO_3$ and 4 ml of conc 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 HNO_3 , 0.2 ml of conc HCl , and 0.2 to 0.3 ml of 30% H_2O_2 . Add 20 ml of 0.35M HIO_3 to the clear solution to precipitate $Zr(IO_3)_4$ (Note 4). Centrifuge and transfer the supernate to a 50-ml plastic tube; discard the $Zr(IO_3)_4$ precipitate.

Step 11. Add 5 ml of conc HF to precipitate CeF_3 . Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5M HF. Centrifuge and discard the supernate.

Step 12. Dissolve the CeF_3 by making a slurry in 1 ml of saturated H_3BO_3 and adding 2 ml of conc 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 H_2O , make strongly alkaline with conc NH_4OH , and precipitate $Ce(OH)_3$. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H_2O . Centrifuge and discard the supernate.

Step 14. Dissolve the $Ce(OH)_3$ in 1 to 2 ml of 6M HCl. Heat on the steam bath to ensure complete dissolution.

Step 15. Add 25 ml of saturated $(NH_4)_2C_2O_4$ to precipitate $Ce_2(C_2O_4)_3$. 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 CeO_2 (Note 5), mount, and count (Note 6).

Notes

1. In a strongly acidic (HNO_3) solution, BrO_3^- ion oxidizes cerium(III) to cerium(IV).

2. Cerium(IV) is reduced by H_2O_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 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 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 Al/cm^2 to cut out the 32.5-d ^{141}Ce and the 290-d ^{144}Ce betas. This gives only the activity from the 17.5-min ^{144}Pr . To eliminate 33-h ^{143}Ce , allow 20 d from the end of bombardment before beginning the analysis. To determine ^{141}Ce , it is best to count with no added absorber and use a least squares separation of the ^{141}Ce and ^{144}Ce - ^{144}Pr activities.

(October 1989)

CERIUM-144

J. W. Barnes

1. Introduction

The procedure described here has been successfully employed for the analysis of ^{144}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 HNO_3 solution with dibutyl phosphate (DBP) in CCl_4 to remove contaminants such as zirconium, neptunium, thorium, plutonium, and uranium; (c) a 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 HNO_3 ; standardized HNO_3 : conc; 9M

HF: conc

H_3BO_3 : saturated aqueous solution

NH_4OH : conc

NaBrO_3 : 2M

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

H_2O_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 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 H_2O . 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 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 NaBrO_3 and heat on a steam bath for 10 min. Dilute to 30 mL and add sufficient conc NH_4OH to precipitate $\text{CeO}_2 \bullet \text{XH}_2\text{O}$. Centrifuge and discard the supernate. Dissolve the precipitate in 2 mL of conc HNO_3 , and add 3 to 5 drops of 30% H_2O_2 and 7 to 8 mL of H_2O .

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 H_2O , 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 H_2O and discard the washings.

Step 5. Stir the precipitate with 1 mL each of saturated H_3BO_3 solution and conc HNO_3 ; heat if necessary to obtain dissolution. Dilute to 20 to 30 mL with H_2O and add an excess of conc NH_4OH . Centrifuge and discard the supernate.

Step 6. Pretreat 50 mL of hexone with a mixture of 50 mL of 9M HNO_3 and 2 mL of 2M NaBrO_3 ; shake for ~1 min and discard the aqueous layer.

Dissolve the precipitate from *Step 5* in 10 ml of 9*M* HNO₃ and add 2 ml of 2*M* NaBrO₃. 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 9*M* HNO₃ that contains 2 to 3 drops of 2*M* NaBrO₃ and discard the washings. Back-extract the cerium by shaking the hexone solution with 5 ml of H₂O that contains a few drops of 30% H₂O₂. Discard the hexone layer.

Step 7. Add conc NH₄OH to the aqueous layer until an orange precipitate barely persists. Add conc HNO₃ dropwise until the precipitate dissolves, and then add 10 to 15 ml of saturated (NH₄)₂C₂O₄. 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 CeO₂, mount, and beta-count through a 217-mg/cm² aluminum absorber (Note).

Note

This procedure probably can be used for ¹⁴³Ce, but it has not been thoroughly studied for that isotope.

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THE LANTHANIDES

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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

HClO₄: conc
HCl: conc; 6*M*
HNO₃: conc
H₃BO₃: saturated
H₂C₂O₄: saturated; 0.5%
HF: conc
H₃PO₄: conc
H₂SO₄: conc
H₂O₂: 30%
NH₄OH: conc
NH₂OH•HCl: 5*M* aqueous solution
Ethanol: 95%
Zirconium carrier: 10 mg zirconium/*mL*, added as ZrO(NO₃)₂•2H₂O in 1*M* HNO₃
Tellurium carrier: 10 mg tellurium/*mL*, added as Na₂TeO₃ in H₂O
Barium carrier: 10 mg barium/*mL*, added as Ba(NO₃)₂ in H₂O

Alpha-HIB (alpha-hydroxyisobutyric acid) reagent: ~0.05*M*, adjusted to solutions of desired pH with conc NH₄OH; stored in 6.5-gal. Nalgene bottles. Solutions of acid concentrations 0.06 and 0.08*M* made by dilution with H₂O.

Dowex AG 50W-X4 or AG 50W-X8 cation-exchange resin: minus 400 mesh, NH₄⁺ 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

¹⁴⁵Pm tracer: produced by ¹⁴⁴Sm(n,γ) ¹⁴⁵Sm → ¹⁴⁵Pm; standardized

0.01*M* EDTA: 3.743 g of disodium ethylene-diamine tetraacetate/*l*

0.01*M* La³⁺ in 1*M* HCl: prepared from La₂O₃ NH₄Cl: 25% wt/vol in H₂O

pH 10 buffer: 61.5 g of NH₄Cl dissolved in 400 *mL* of conc NH₄OH

Arenazo indicator: 3-(2-azonophenylazo)-4,5-dihydroxy-2,7-naphthylene disulfonic acid trisodium salt: 0.05% in H₂O

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 NH₄OH diluted to 200 *mL* with H₂O

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 H₂O, 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 HNO₃; 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 HNO₃ 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 ¹⁴⁵Pm

The solution should contain 800 to 1200 counts/min of ¹⁴⁵Pm/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 NH₄OH. 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 H₂C₂O₄. 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 μ m. The resin is washed successively with 6M HCl, 1M NH₄CNS, 6M HCl, 1M NH₄OH, and H₂O. 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.

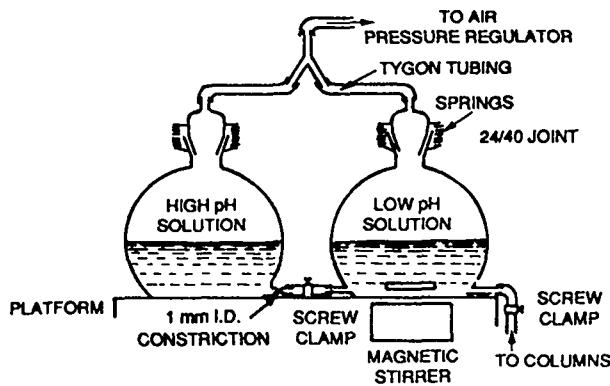


Fig. 1. Gradient elution equipment.

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 ~30 ml in a 125-ml erlenmeyer flask and add an excess of 0.01 M EDTA from a 10-ml burette (0.6 to 0.7 ml/mg of lanthanide oxide and ~0.9 ml/mg of Y_2O_3). Add ~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 ~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 ~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_4 , and 1 ml of conc HNO_3 ; fume to near dryness. Add 3 ml of conc HNO_3 and enough H_2O to transfer the solution to a 40-ml plastic centrifuge tube. Add H_2O 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_2O 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_3BO_3 ; add 2 ml of conc HNO_3 , 10 ml of H_2O , 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_2O that contains a few drops of HF. Centrifuge and discard the supernate.

Step 3. Slurry the precipitate with 2 ml of saturated H_3BO_3 , add 2 ml of conc HNO_3 , and heat on a steam bath, if necessary, to dissolve the precipitate. Add 15 ml of H_2O .

Step 4. Add 8 ml of conc NH_4OH , 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_2O to which a few drops of conc NH_4OH 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_3 , 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_2O . Add 8 ml of conc NH_4OH and 3 drops of 5M $\text{NH}_2\text{OH} \bullet \text{HCl}$. Heat on a steam bath for ~1 min, digest, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of H_2O that contains a few drops of NH_4OH .

Step 7. Dissolve the precipitate in 6 drops of conc HCl and dilute the solution to ~30 ml with H_2O . Add ~30 drops (by transfer pipette) of minus 400 mesh or 200 to 400 mesh cation-exchange resin slurry in H_2O . 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_2O 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_2O . Rinse the centrifuge tube with 1 to 2 ml of H_2O , add the rinsings to the column, allow to settle, and remove the H_2O . (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 $H_2C_2O_4$ 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 $H_2C_2O_4$ acid to the centrifuge tubes and digest the oxalates for 15 min on a steam bath. Centrifuge, suspend the oxalates in ~5 ml of H_2O , 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 NH_4OH 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 quinolinate 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 HNO_3 that contains ~100 mg of $KClO_3$. For heavy lanthanides, ignite and dissolve the 8-quinolinate in ~2 ml of conc HCl and 0.5 ml of conc 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-quinolinate in 2 ml of conc HCl and 1 drop of conc HNO_3 . Heat the solution on a steam bath and cool. Then add 6 ml of conc 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 H₂O 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 CeO₂ does not dissolve with the HCl treatment described above. After the sample sandwich is placed in the flask, add ~2 ml of conc H₂SO₄ and heat the mixture to SO₃ fumes over a flame. Then add a mixture of two parts of conc H₂SO₄ and one part of 30% H₂O₂ 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 H₂O 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 NH₄OH in *Step 6*. In these instances, the precipitate is first washed with 10 ml of 6M NaOH and then with H₂O.

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 3×10^{-5} to 2×10^{-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 ~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 ~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 ~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 HNO₃ 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

HNO₃ 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 ~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 ~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⁻². This variation does not pose a serious problem because several rolls of tape can be obtained from one batch.

References

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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 HNO_3 solution into *n*-heptane that contains di-2-ethylhexyl orthophosphoric acid (HDEHP); the resulting organic phase is scrubbed with dilute 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 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

HNO_3 : 0.05*M*; 4*M*

0.5*M* HDEHP: a solution of di-2-ethylhexyl orthophosphoric acid (mol wt 322.4) in *n*-heptane

0.1*M* 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, ~ 0.3 mg each of the other lanthanide carriers may be added. If promethium is to be determined, add ^{145}Pm tracer. (The maximum quantity of carrier that can be used is 60 mg.)

Step 2. Add 3 ml of conc HClO_4 , boil the solution to thick fumes of 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 H_2O and add washings to the centrifuge tube.

Step 3. If the sample does not contain 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 HClO_4 , dilute the solution to 20 ml and add 6 to 8 ml of conc NH_4OH . Heat for 2 min on a steam bath, centrifuge, and discard the supernate. Wash the precipitate in 1 to 2 ml of conc HNO_3 and wash down the sides of the tube with a small volume of H_2O . 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 0.05*M* HNO_3 . Transfer the solution to a 60-ml separatory funnel, add 10 ml of 0.5*M* 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 0.05*M* 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 4*M* 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 4*M* HNO₃. Discard the organic phase.

Step 7. Scrub the combined aqueous extracts with two 10-ml portions of 0.1*M* 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 HNO₃ solution (lower phase) into a 40-ml centrifuge tube and discard the heptane.

Step 9. Add 6 to 8 ml of conc NH₄OH, centrifuge, and discard the supernate. Wash the precipitate with H₂O 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 0.05*M* HNO₃ in *Step 5*, scrub with four 10-ml portions of 0.75*M* HNO₃. 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)₃ from *Step 9* in ~4 drops of conc HCl, add 20 ml of H₂O, 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 H₂C₂O₄ and digest the oxalate precipitates for 15 min on a steam bath. Centrifuge and discard the supernates. Suspend each precipitate in 5 ml of H₂O, break up the lumps, and filter onto a filter circle. Wash each oxalate with three 5-ml portions of H₂O, 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 H₂O 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 La³⁺ 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 0.0125M EDTA and 0.025M La³⁺ 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 μm —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- ℓ 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

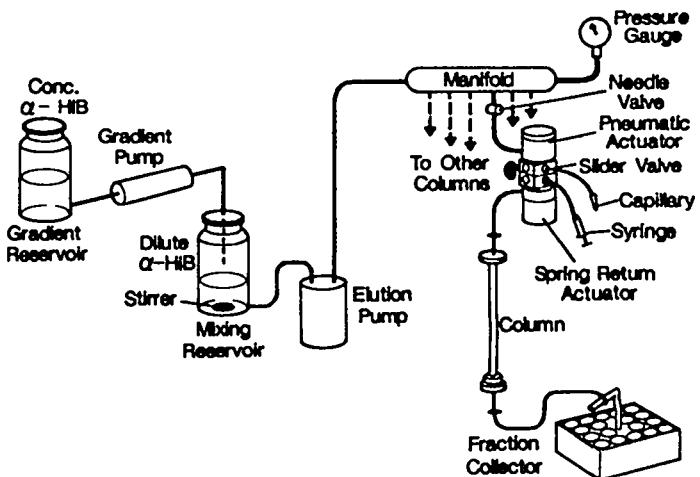


Fig. 1. Chromatographic system.

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 (~ 200 ft for six columns)

TFE Tubing: $\frac{1}{8}$ in., many commercial sources; used for all delivery lines before pump (~ 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. Swaglok 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

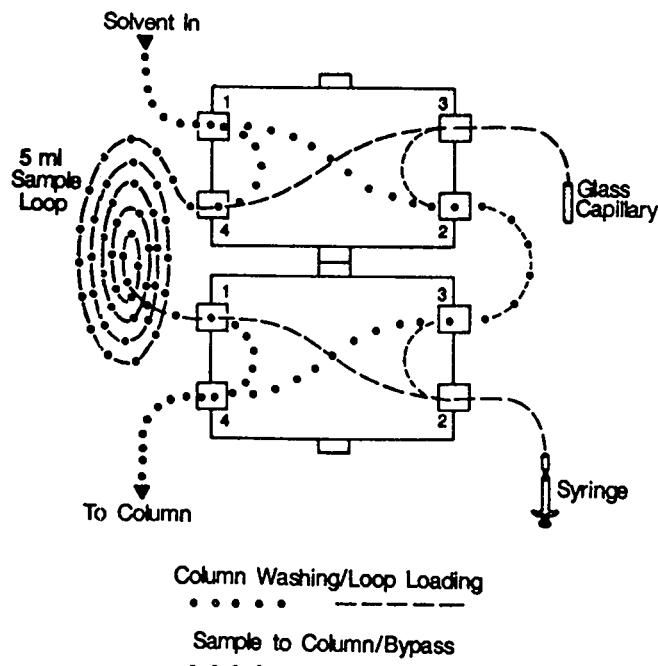


Fig. 2. Injection system.

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

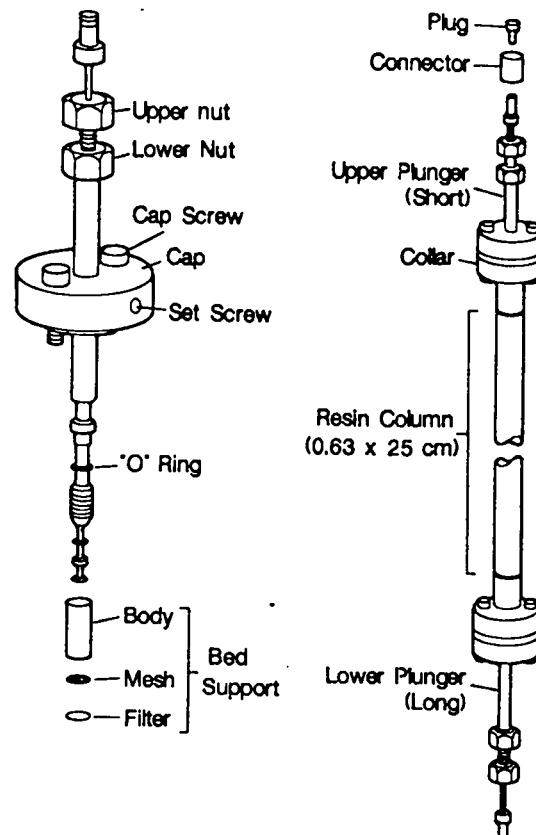


Fig. 3. Type LC columns.

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

$\text{H}_2\text{C}_2\text{O}_4$: saturated aqueous solution

Cation-exchange resin: Dowex AG 50W-X12 (Dowex AG 50W-X8 is also acceptable); particle size, 24- to 43- μm (Dowex AG 50W-X12 minus 400 mesh is acceptable for single lanthanide separations)

Alpha-hydroxyisobutyric acid (alpha-HIB): 5M
Alpha-HIB solutions:

| Molar conc | 5M Alpha-HIB | Conc NH ₄ OH |
|------------|--------------|-------------------------|
| 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 NH₄OH, and four parts H₂O; 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 H₂O 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 H₂O 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 H₂O. 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 H₂O by either pulling the liquid through the capillary with the syringe or filling the syringe with 5 ml of H₂O 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 H₂O. (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 $\sim 1000 \text{ ml}$ of $0.42M$ alpha-HIB solution for six columns.

Step 4. Add a few drops of precipitating agent—8-quinolinol reagent or saturated $\text{H}_2\text{C}_2\text{O}_4$ solution—to the collection tubes of every third row. Lutetium, thulium, and scandium are precipitated as 8-quinolinates, 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_2O three times each for 5 min. Discard effluents.

Step 8. Pump H_2O 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 $\text{H}_2\text{C}_2\text{O}_4$ 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°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 H_2O . 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.

| <u>Concentration of Alpha-HIB (M)</u> | <u>Lanthanide</u> |
|---|-------------------|
| 0.04 | scandium |
| 0.055 | ytterbium |
| 0.055-0.065 | thulium |
| ~ 0.065 | erbium |
| ~ 0.075 | holmium |
| 0.075-0.09 | yttrium |
| ~ 0.09 | dysprosium |
| 0.09-1.05 | terbium |
| 0.12-0.14 | gadolinium |
| 0.14-0.165 | europtium |
| 0.17-0.18 | samarium |
| 0.17-0.20 | promethium |
| 0.21-0.235 | neodymium |
| ~ 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 H_2O 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 H_2O 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 H_2O .

Step 5. Carefully insert an upper plunger into each column, force H_2O 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 H₂O-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 H₂O 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 H₂O 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 H₂O to see that all columns are flowing at about the same rate.

Step 12. Pump H₂O 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 reseat 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}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 3*M* 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 0.5*M* 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; 6*M*; 3*M*; 2*M*

HNO_3 : conc

HClO_4 : conc

HF: conc

$\text{H}_2\text{C}_2\text{O}_4$: 0.5*M*

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

n-heptane

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

AG 50W-X4 cation resin column, 100 to 200 mesh, H^+ form; stored as a slurry in H_2O
AG 2-X8 anion resin column, 100 to 200 mesh, 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 HNO_3 . Add 5 ml of conc HClO_4 , fume to near dryness, and then add 3 ml of 3*M* HCl.

Step 2. Transfer the solution to the top of a 5-cm by 8-mm AG 50 W-X4 (100 to 200 mesh, H^+ form) cation resin column. Wash off uranium and other contaminating activities first with 16 ml of 3*M* HCl and then with 4 ml of conc HCl. Elute the thorium with 10 ml of 0.5*M* $\text{H}_2\text{C}_2\text{O}_4$ and collect the eluate in a 50-ml erlenmeyer flask.

Step 3. Add 5 ml of conc HClO_4 and 2 ml of conc 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 $\text{NH}_2\text{OH}\bullet\text{HCl}$. (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 0.5*M* 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, 6*M*, and 2*M* 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.

(October 1989)

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 ($>12M$) 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 $\text{Al}(\text{NO}_3)_3$ - 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 HNO_3

Lanthanum carrier: 10 mg lanthanum/ mL , added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

Zirconium carrier: 10 mg zirconium/ mL , added as purified $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in H_2O

HCl: conc; gas

HNO_3 : conc; 6M

H_2SO_4 : conc

HIO_3 : 1M (filtered)

$\text{H}_2\text{C}_2\text{O}_4$: saturated solution (filtered); 1% solution

NH_4OH : conc

H_2S : gas

SO_2 : gas

2.4M $\text{Al}(\text{NO}_3)_3$ in 1.2M HNO_3 (filtered)

KClO_3 : solid

Methanol: absolute

Mesityl oxide

Anion-exchange resin column: AG 1-X10, 100 to 200 mesh; stored as a slurry in H_2O .

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 HNO_3 in a platinum dish, and there are periodic additions of small amounts of 0.1M HF. If $\text{Th}(\text{NO}_3)_4$ is used as carrier, it is dissolved in $\sim 0.001M$ HNO_3 and filtered. To a 10.0- mL aliquot (four standardizations are usually carried out) of the carrier, 10 drops of conc HCl are added and the solution is boiled over a Fisher burner. Then 4 mL of saturated $\text{H}_2\text{C}_2\text{O}_4$ are added and the solution is boiled for 2 min. The $\text{Th}(\text{C}_2\text{O}_4)_2$ 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°C for 1 h. The carrier is weighed as ThO_2 .

4. Procedure

Step 1. Into a 40- mL short-taper glass centrifuge tube, pipette 2.0 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 NH_4OH , centrifuge, and discard the supernate.

Step 2. To the precipitate add 8 mL of conc HNO_3 , 15 mL of H_2O , and 7 mL of 1M HIO_3 . Centrifuge the $\text{Th}(\text{IO}_3)_4$ precipitate and discard the supernate. Wash the precipitate with 15 mL of a solution that is 4M in HNO_3 and 0.25M in HIO_3 . Centrifuge and discard the supernate.

Step 3. To the precipitate add 1 mL of conc 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 H₂O and bubble in SO₂ gas until the solution becomes essentially colorless. Dilute to 10 ml with H₂O and boil until the solution is water-white. Add 4 ml of saturated H₂C₂O₄ 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 HNO₃ and ~100 mg of solid KClO₃. Heat cautiously to boiling to destroy oxalate. Dilute to 15 ml with H₂O and use an excess of conc NH₄OH to precipitate Th(OH)₄. 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 HNO₃ (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 H₂O and make the solution alkaline with conc NH₄OH. Centrifuge the Th(OH)₄ precipitate and discard the supernate.

Step 7. Dissolve the precipitate with 6 drops of 6M HNO₃. Use 10 ml of 2.4M Al(NO₃)₃-1.2M HNO₃ 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 H₂O, and collect both H₂O layers in a 40-ml short-taper centrifuge tube. Dilute to 15 ml and add 8 ml of conc HNO₃ and 7 ml of 1M HIO₃ (Note 2). Centrifuge the Th(IO₃)₄ precipitate and wash as in *Step 2*.

Step 8. Repeat *Steps 3* through *6*.

Step 9. To the Th(OH)₄ precipitate, add 5 drops of bismuth carrier and 10 drops of conc H₂SO₄. Dilute to 10 ml with H₂O and saturate the solution with H₂S. Filter through filter paper and collect the filtrate in a 40-ml short-taper centrifuge tube. Wash the precipitate with a small amount of H₂O and combine the wash with the filtrate; discard the precipitate. Make the filtrate alkaline with conc NH₄OH, 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% H₂C₂O₄ 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 ThO₂ 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 ThO₂ adheres to the crucible.) Grind the ThO₂ 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}Th is used as carrier, there is a problem with growth of beta activities from the carrier. Examination of the decay chain of ^{232}Th shows that the amount of beta activity depends upon the quantity of ^{228}Th present. In the chain, the longest-lived parent of ^{228}Th (half-life 1.9 yr) is ^{228}Ra (half-life 6.7 yr). Thus, the amount of ^{228}Th present in ^{232}Th depends upon the time at which ^{228}Ra is separated. The beta-emitters succeeding ^{228}Th grow in essentially with the half-life of ^{224}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}U , ^{237}Np , and ^{238}U , respectively. If a weighed quantity of ^{235}U or ^{238}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}U or ^{238}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}Th the situation is different. The decay product of this isotope is ^{233}Pa , which is also the immediate decay product of ^{237}Np . By separating ^{233}Pa from a known weight of ^{237}Np and counting the former, one has a direct relationship for ^{233}Pa of counts *vs* disintegrations. For a sample of ^{233}Th one takes two known aliquots that differ by a factor of ~ 1000 in activity. (The ratio of ^{233}Pa to ^{233}Th half-lives is 1693:5.) The weaker aliquot is counted for ^{233}Th immediately upon separation of protactinium. The stronger one is permitted to decay until it is all ^{233}Pa and is then counted. From the previous (^{237}Np) calibration, one then can find the disintegrations of ^{233}Pa for this sample. The sample is corrected for decay back to the time the weaker sample was counted for ^{233}Th , thus the number of atoms is obtained for the latter when aliquot correction is made.

Notes

1. The HNO₃ 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}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}Th is employed to determine chemical yield. The chemical yield is 50 to 70%.

(A) Determination in Coral Samples

2. Reagents

^{228}Th tracer: known amount; 5 to 100 counts/min
 HNO_3 : conc
 HClO_4 : 70%; 3M
 HCl : 3M
 $\text{H}_2\text{C}_2\text{O}_4$: 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)

3. Procedure

Step 1. Transfer ~20 g of coral, weighed to the nearest 0.1 g, to a 600-ml beaker. Add ^{228}Th tracer in known amount (5 to 100 counts/min) and wash down the sides of the beaker with H_2O .

Step 2. With a watch glass in place on top of the beaker, gradually add 75 ml of conc 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% HClO_4 . (During this and subsequent steps that involve fuming with 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 H_2O .

Step 3. Add conc NH_4OH until the solution is barely acid and then use 3M NH_4OH and 3M 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 H_2O . Discard the washings. Wash again with 50 ml of H_2O and discard the washings.

Step 6. Extract the thorium from the benzene by stirring for 3 min with 100 ml of 3M 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 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% HClO_4 , and boil until white fumes appear. Cool to room temperature and dilute to ~3.5 ml with H_2O .

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 H_2O 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 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 additonal 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 H₂O. 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 HClO₄ and is then ready for use.

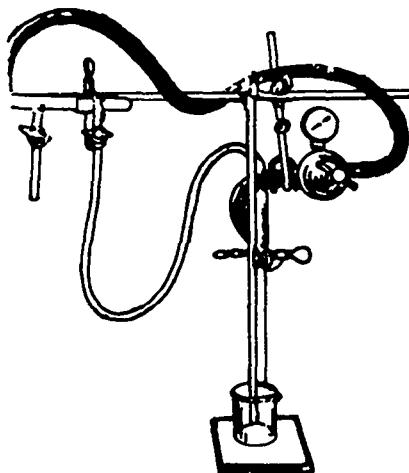


Fig. 1. Resin column.

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
 ^{234}Th TRACER
G. A. Cowan

1. Introduction

In the separation of ^{234}Th from uranium, the latter, originally present in the form of $\text{UO}_2(\text{NO}_3)_2$, is converted to a soluble carbonate complex. At pH 8.0 to 8.5, the cupferrate of ^{234}Th is made and separated from the uranium by extraction into CHCl_3 . The thorium is back-extracted into dilute HNO_3 that contains Br_2 , which decomposes the cupferrate and allows extraction of all the organic material and excess Br_2 into the organic phase.

2. Reagents

$\text{UO}_2(\text{NO}_3)_2$: 1 g uranium/10 ml, added as U_3O_8
or $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in dilute HNO_3
 HNO_3 : 3M
 $(\text{NH}_4)_2\text{CO}_3$: saturated aqueous solution
 Br_2 water: saturated solution
Cupferron: 6% aqueous solution (freshly prepared
and kept in the refrigerator)
 CHCl_3
Hydripon paper (short range)

3. Procedure

Step 1. Pipette 10 ml of $\text{UO}_2(\text{NO}_3)_2$ solution into a 250-ml beaker; treat with saturated $(\text{NH}_4)_2\text{CO}_3$ solution and H_2O until the yellow precipitate that first forms has dissolved. Add sufficient $(\text{NH}_4)_2\text{CO}_3$ 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_3 . Shake well and transfer the CHCl_3 layer that contains the ^{234}Th to a clean separatory funnel. Repeat the CHCl_3 extraction and combine the extracts.

Step 3. Wash the CHCl_3 extracts with 20 ml of H_2O to which has been added 1 ml of cupferron

reagent and sufficient $(\text{NH}_4)_2\text{CO}_3$ solution to make the pH 8.0 to 8.5. Transfer the CHCl_3 phase to a clean separatory funnel.

Step 4. To the CHCl_3 phase add 10 ml of 3M HNO_3 and a few milliliters of saturated Br_2 water and shake. Discard the CHCl_3 phase and wash the aqueous phase twice with CHCl_3 ; discard the washings. Transfer to a 250-ml beaker and boil for a minute to remove the last traces of CHCl_3 . Transfer the solution to a volumetric flask of the appropriate size and make up to volume with H_2O .

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 ^{234}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 H₂C₂O₄. Because Th(C₂O₄)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 NO₃⁻, F⁻, SO₄²⁻, or PO₄³⁻, 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 HClO₄. 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 HNO₃ and HClO₄, 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 ~1 g with one Dowex 50-X4 column. Up to ~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 ²³¹Th was prepared from 2 kg of orally during several ether extractions. Finally, a cation column was employed to concentrate the activity in 1 to 2 drops of H₂C₂O₄ (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 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\ell$ of aqueous solution

HF: conc

HClO_4 : conc; 3M

HCl: conc; gas; 6M; 3M

HNO_3 : conc

NH_4OH : conc

$\text{H}_2\text{C}_2\text{O}_4$: 0.5M

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 ~ 1 ml of 2M 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 NH_4OH 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 ~ 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.

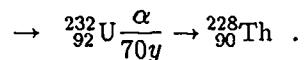
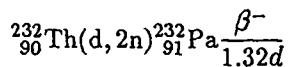
4. Preparation and Standardization of Tracers and the Calculations Involved in Their Use

In analyses for the beta-emitters ^{231}Th and ^{234}Th , the best tracer is ^{230}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}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}Th and ^{234}Th are determined by mixing a known amount of ^{230}Th tracer with a known quantity of the appropriate uranium parent—either ^{235}U or ^{238}U . After a HClO_4 fuming to ensure exchange and to eliminate nitrate that may be present, the solution is diluted to 2 to 3M in 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 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}Th or ^{234}Th for use as tracers are given in Sec. 7.

The best tracer to use in analysis for ^{230}Th is ^{228}Th , which should be as free from ^{229}Th as possible. Because ^{230}Th and ^{228}Th are both alpha emitters, the final plate is pulse-analyzed to find the ratio of the two. The alpha energy of ^{229}Th (compared to that of ^{228}Th) is so much closer to

the alpha energy of ^{230}Th that tail corrections are much larger and more subject to error when ^{229}Th is present in the ^{228}Th tracer. This tracer is made by the (d, 2n) reaction on ^{232}Th .



It is possible to standardize a solution of ^{228}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}Th and a known ^{230}Th solution, fume with 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}Th to ^{230}Th (which, when multiplied by the alpha count of ^{230}Th , gives the correct alpha-count rate for ^{228}Th).

If ^{228}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}Th . The energy from 4.6% of the alphas of the ^{224}Ra daughter of ^{228}Th coincides with the alpha peak of ^{228}Th . The time of last separation of the daughter is noted when the 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}Ra and the subscript 1 refers to ^{228}Th . Because N_1^0 is constant

for the times involved, it is convenient to prepare a plot of N_2/N_1° 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° is read from the graph, multiplied by 0.046, and subtracted from the counts under the ^{228}Th peak.

To get the counting rate of ^{230}Th in a sample with ^{228}Th tracer, the ratio of the $^{230}\text{Th}/^{228}\text{Th}$ peaks is multiplied by the alpha-counting rate of ^{228}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 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 H_2O and transfer to a short-taper 40-ml glass centrifuge tube. There may be a fine-grained residue of SiO_2 in the flask, but thorium loss at this point is not very great.

Step 2. Add an excess of conc NH_4OH , mix well, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate from *Step 2* in 1 ml of 3M HCl, and dilute with H_2O to half the volume of the tube. Add conc NH_4OH 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 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 HClO_4 and 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 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 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 HNO_3 and 0.5 ml of conc 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 $H_2C_2O_4$ and push down the column with very light air pressure. Be sure that the leading edge of the $H_2C_2O_4$ band does not reach the bottom of the resin and get discarded with the other effluent. Add 0.7 ml of 0.5M $H_2C_2O_4$ 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 $H_2C_2O_4$ 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_3 and make up to 500 ml with H_2O . 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 ^{234}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_4OH slowly while stirring until $Fe(OH)_3$ precipitates and then centrifuge for 5 min (Note 2).

Step 4. Decant and dissolve the precipitate in 5 ml of conc HNO_3 , dilute with H_2O , and again precipitate $Fe(OH)_3$ with conc NH_4OH .

Step 5. Centrifuge, decant, and dissolve the precipitate in 5 ml of conc HNO_3 ; use H_2O to wash the solution into a platinum dish. Add 10 ml of conc $HClO_4$ and 5 ml of conc HF.

Step 6. Take to fumes of $HClO_4$ three times; wash the sides of the dish with water after each fuming (Note 3).

Step 7. Dilute the $HClO_4$ solution to ~25 ml with H_2O .

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 $HClO_4$ 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 $H_2C_2O_4$ and catch the eluate in a centrifuge tube. Add 5 ml of conc HNO_3 and 5 ml of conc $HClO_4$; take to fumes of $HClO_4$ three times. Wash the breaker down with H_2O after each fuming.

Step 11. Add the solution, which is diluted with H_2O 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 $H_2C_2O_4$, and collect the first 12 drops of eluate on a platinum plate. Evaporate to dryness under a heat lamp, and flame.

Step 14. Count ^{234}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 (~93.5% ^{235}U) and ^{234}Th is obtained from normal uranium after the ^{231}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}Th or ^{234}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 HNO_3 and HClO_4 . If an amount of uranium up to ~ 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}Th or ^{234}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 HCl , and some oxidizing agent such as BrO_3^- ion, Br_2 water, or Cl_2 gas is used to oxidize the uranium to uranium(VI). The solution is then saturated with HCl gas at room temperature and uranium is adsorbed on an AG 1-X8 column.

For 10 g of uranium, a column ~ 25 -mm diam that holds 150 to 200 ml of resin bed is satisfactory. The resin is prewashed with conc HCl that contains ~ 0.5 ml of 2M 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 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 HCl as above. The solution is evaporated to a small volume, fumed with 1 ml each of conc HNO_3 and HClO_4 , and treated with the AG 50-X4 column step as described in Sec. 4.

A ^{231}Th source reading >1 r was prepared from 2 kg of oralloy. The uranium metal was dissolved in an excess of conc HNO_3 , and this solution was evaporated until the temperature became constant at $\sim 118^\circ\text{C}$. [This is the boiling point of $\text{UO}_2(\text{NO}_3)_2 \bullet 6\text{H}_2\text{O}$.] This solution, which

freezes at $\sim 60^\circ\text{C}$, is cooled to 70 to 80°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 ~ 4 l. An aqueous layer of ~ 600 ml is withdrawn. The ether solution is scrubbed with three 3-ml portions of H_2O 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 H_2O . 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 HNO_3 and 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}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 ~ 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}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}Pa in the presence of fission-product material, 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 HCl and the protactinium is extracted into diisopropyl carbinol; the zirconium remains in the aqueous phase. The protactinium is back-extracted with 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 3.2×10^{14} fissions 3 d after the end of bombardment. Final activity was 8 ± 5 counts/min and the yield was 76%.

2. Reagents

^{231}Pa tracer

Zirconium carrier: 10 mg zirconium/ml, added as $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1*M* HNO_3

Lanthanum carrier: 10 mg lanthanum/ml, added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

Barium carrier: 30 mg barium/ml, added as BaCl_2 in H_2O

HCl : 6*M*; conc

HNO_3 : conc

HF : conc

HIO_3 : 1*M*

H_3BO_3 : saturated aqueous solution

Diisopropyl carbinol

3. Procedure

Step 1. To the fission-product mixture in ~2*M* HCl in a 50-ml plastic centrifuge tube, add 3 ml of conc HNO_3 , 2 ml of zirconium carrier, 2 ml of conc HF , and ^{231}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 H_2O 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 H_2O ; discard both the supernate and the washings. Dissolve the $\text{Ba}[\text{ZrF}_6]$ precipitate by treating with 3 ml of saturated H_3BO_3 , 1 ml of conc HNO_3 , and 2 ml of H_2O .

Step 4. Heat the mixture on a steam bath until the precipitate dissolves completely. Add 15 ml of 1*M* HIO_3 and allow to stand for 5 to 10 min. Centrifuge (Note 2), wash with H_2O , and discard the supernate.

Step 5. Add 5 ml of conc HCl to the iodate precipitate and heat on the steam bath for ~2 min. Add 2 ml of H_2O 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 6*M* 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 6*M* 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 HNO_3 and 0.5 ml of conc 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 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 HCl . Heat and add 2 ml of H_2O . Transfer the solution to a 60-ml separatory funnel. Complete the transfer with 10 ml of 6*M* HCl . Shake the solution with 10 ml of diisopropyl carbinol. Wash the carbinol phase with two 10-ml portions of 6*M*

HCl and discard the aqueous phases. Transfer the carbinol phase to a plastic centrifuge tube. Add 0.8 ml of H₂O 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 ²³¹Pa. Count betas of ²³³Pa under a 10 mg/cm² aluminum absorber.

Notes

1. Only a small amount of ²³¹Pa 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(IO₃)₆.

(October 1989)

URANIUM-232 AND URANIUM-233

D. W. Efurd and F. R. Roensch

1. Introduction

The following procedure was devised to provide samples suitable for measuring the ^{232}U and ^{233}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

HNO_3 : conc

HClO_4 : conc

HBr : 47% ultrapure; nonstabilized

$\text{CH}_3\text{OH}-\text{HNO}_3$: 90% by volume of methanol and 10% 5*M* HNO_3

Type 1 reagent-grade H_2O

Anion-exchange resin: Bio-Rad macroporous resin AG MP-1, 50 to 100 mesh; washed 20 times with Type 1 reagent-grade H_2O 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°C and evaporate to dryness. Add 3 drops of conc HNO_3 and 3 drops of conc HClO_4 and heat at 130°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 $\text{CH}_3\text{OH}-\text{HNO}_3$ mixture.

Step 2. Pass the solution through an anion-exchange column (Note) that has been preconditioned with three 1-ml aliquots of the $\text{CH}_3\text{OH}-\text{HNO}_3$ mixture. Collect the eluate in a 40-ml glass centrifuge tube. Elute the remaining

uranium from the column with three 1-ml H_2O washes and collect the washes in the same centrifuge tube. Evaporate the solution to dryness. Add 0.5 ml of conc 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 H_2O . Place the sample on a heating block and evaporate to dryness. Add 3 drops of conc HNO_3 and 3 drops of conc 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}U that employs ^{232}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 CHCl_3 . Separation of lanthanides, partial removal of neptunium, and further decontamination from plutonium is obtained by adsorption of uranium from conc HCl solution onto a Dowex A2 anion-exchange resin column. Washing of the column with 10M and then with 5M HCl removes adsorbed plutonium and neptunium, respectively. Uranium is eluted from the column by means of 0.1M HNO_3 and then is electroplated on platinum. The chemical yield, determined by alpha-counting the ^{232}U tracer, is 50 to 90%. The ^{235}U is fission-counted.

2. Reagents

^{232}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 H_2O

Iron carrier: 10 mg iron/ml, added as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in very dilute HNO_3

HCl: 5M; 10M; conc

HNO_3 : 0.1M; 6M

NH_4OH : conc

$\text{NH}_2\text{OH} \cdot \text{HCl}$: 5M

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ in H_2O : 4%

Aqueous cupferron reagent: 6%

Methyl red indicator solution: 0.1% in 90% ethanol

Methanol: anhydrous

CHCl_3

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

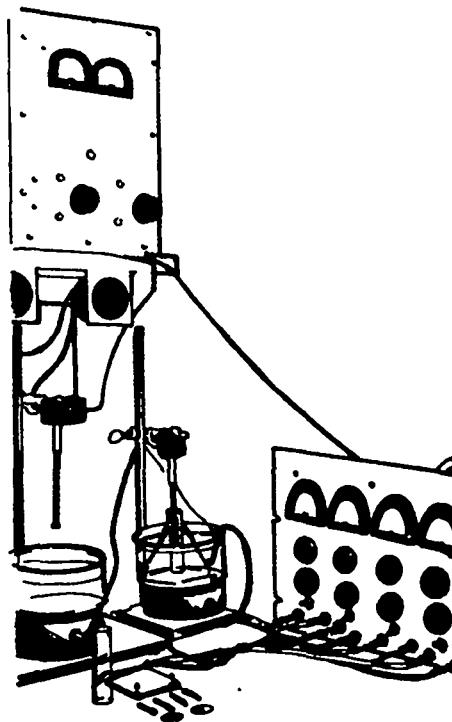


Fig. 1. Plating assembly.

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°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.

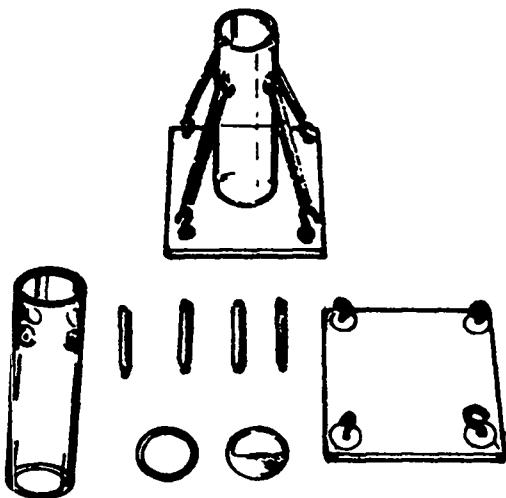


Fig. 2. Parts of plating cell.

4. Procedure

Step 1. To an aliquot of sample <20 ml (Note 1) in a 40-ml centrifuge tube, add 1 ml of ^{232}U tracer and 3 drops of lanthanum carrier; bubble in 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 H_2O . 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 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 CHCl_3 layer. Extract the aqueous phase three additional times with CHCl_3 . To the aqueous layer add 3 drops of lanthanum carrier and bubble in 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 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 NH_4OH . Make the solution barely red to the indicator by the dropwise addition of 6M 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 HNO_3 . Check acidity at two additional 10-min intervals; at the end of 40 min add 3 drops of conc NH_4OH . 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}U foils.

Notes

1. The aliquot of sample taken must have a ^{235}U content similar to those of the ^{235}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

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}U used as tracer. The uranium is first adsorbed on an anion-exchange resin column from a solution at least 10M in HCl. The bulk of the fission products is removed from the uranium by elution with 8M HNO₃, and then some decontamination from neptunium and plutonium is accomplished by column washes with 3M 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 HI-HCl mixture. Then the resin is treated with H₂O₂ to oxidize the uranium to the +6 state, and neptunium is removed with 3M 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}U tracer: amount to be added is determined by the alpha-counting technique employed

HCl: 2M; 3M; conc

HNO₃: 8M

HI-HCl mixture: 1:9 by volume of 47% HI and conc HCl

H₂O₂-HCl reagent: one part by volume of 30% H₂O₂ to 40 parts of 9M HCl

NH₄OH: conc

NH₄Cl: solid

Ethanol: absolute

Methyl red indicator solution: 0.5% in ethanol

Bio-Rad AG 1-X8 anion-exchange resin, 100 to 200 mesh; water slurry

3. Procedure

Step 1. Place an aliquot of sample solution (<50 mL) in a 125-mL erlenmeyer flask; add 1 mL of ^{232}U tracer and 20 mL of conc HCl; and evaporate the solution to dryness. Repeat twice the addition of HCl and evaporation. Take up the residue in 10 to 20 mL of conc HCl; heat if necessary to effect solution.

Step 2. Add the solution to an AG 1-X8 anion-exchange resin column (prewashed with conc 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 HCl and pass the wash through the resin column. Discard the effluents.

Step 3. Wash the column twice with 8M HNO₃ (Note 2) and twice with 3M HCl. Discard the effluents. Elute the uranium with two 6-mL portions of H₂O 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 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 HCl and pass the wash through the resin column. Discard the effluents.

Step 5. Wash the column (a) twice with 8M HNO₃, (b) twice with conc HCl, (c) twice with HI-HCl mixture, (d) once with conc HCl, (e) twice with H₂O₂-HCl reagent, (f) and then twice with 3M HCl. Discard all effluents. Elute the uranium with two 6-mL portions of H₂O into a clean 125-mL erlenmeyer flask.

Step 6. Evaporate to dryness the solution that contains the uranium. Destroy the HI by heating to dryness twice after adding 1-mL portions of conc

HNO_3 . Convert to the chloride by two successive evaporation 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_2O to transfer the solution to an electroplating cell. Rinse the erlenmeyer flask with 5 mL of H_2O and add the rinse to the plating cell.

Step 8. To the cell add ~ 0.5 g of NH_4Cl and 3 drops of methyl red indicator solution. Make the solution alkaline with conc NH_4OH and then barely acidic with 2 M 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_4OH 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.

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 ³ | 1 by 5 | 4 |
| 0.0375 to 0.075 | 10 ³ -3 \times 10 ⁴ | 1 by 7 | 6 |
| 0.075 to 1.50 | 3 \times 10 ⁴ -3 \times 10 ⁶ | 1 by 15 | 10 |
| 1.50 to 4.50 | 3 \times 10 ⁶ -10 ⁷ | 1 by 20 | 15 |
| >4.5 | >10 ⁷ | 1 by 30 | 25 |

2. For samples that have plutonium levels $>10^5$ cpm, the procedure is modified, beginning with *Step 3*. Wash the column twice with 8 M HNO_3 , twice with conc HCl , twice with HI-HCl mixture, once again with conc HCl , and twice with 3 M HCl . Discard the effluents. Elute the uranium with two 6- mL portions of H_2O into a clean 125- mL erlenmeyer flask. Evaporate to dryness and destroy the HI by heating to dryness twice after adding

1- mL portions of conc HNO_3 . Convert to the chloride by two successive evaporation 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 8 M HNO_3 , twice with conc HCl , twice with 3 M HCl ; elute the uranium with two 6- mL portions of H_2O into an electroplating cell. Plate as in *Step 8*.

(October 1989)

URANIUM-237

W. G. Warren

1. Introduction

In this carrier-free procedure for the determination of ^{237}U , the element is first adsorbed on an anion-exchange resin column from a solution at least 10*M* in HCl. The bulk of the fission products is removed from the uranium by elution with 8*M* HNO₃; the plutonium is removed by elution with a mixture of conc HI and HCl. The resin is then treated with H₂O₂ to ensure oxidation of uranium to the +6 state, and the neptunium is removed from the column by means of 3*M* HCl. The uranium is eluted with H₂O and placed on another anion resin column from conc HCl solution. Further decontamination of the element is accomplished by column washings with 8*M* HNO₃, 10*M* HCl, and 3*M* HCl. Following elution of uranium with H₂O, the element is placed on a cation-exchange resin column, which is then washed with 0.1*M* HCl—a treatment that presumably removes traces of tellurium and iodine. The uranium is eluted with 3*M* HCl and is electroplated onto platinum.

The procedure is carried out in the presence of ^{233}U tracer, and yield is determined by alpha-counting this isotope. Uranium-237 is determined by beta-counting.

2. Reagents

^{233}U tracer: amount to be added is determined by the alpha-counting technique employed
HCl: 0.1*M*; 2*M*; 3*M*; 10*M*; conc
HNO₃: 8*M*
HI-HCl mixture: 1:9 by volume of 47% HI and conc HCl
 NH_4OH : conc
 NH_4Cl : solid
Ethanol: absolute
Methyl red indicator solution: 0.5% solution of the indicator in ethanol

H₂O₂ reagent: 0.5 ml of 30% H₂O₂ to 40 ml of 9*M* 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}U tracer and 20 ml of conc HCl; evaporate the solution to dryness. Repeat twice the addition of HCl and evaporation. Take up the residue in 10 to 20 ml of conc 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 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 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 8*M* HNO₃, (b) twice with 4 ml of conc HCl, (c) once with 6.5 ml and then 2 ml of HI-HCl mixture, (d) again with 4 ml of conc HCl, (e) twice with 4-ml portions of H₂O₂ reagent (I₂ is removed and the resin column is decolorized), and (f) twice with 4-ml portions of 3*M* HCl. Discard all effluents. Elute the uranium with two 4-ml portions of H₂O 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 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 HCl and pass the wash through the resin column. Discard the effluents.

Step 5. Wash the column twice with 4 ml of 8M HNO₃, 4 ml of 10M HCl, and 4 ml of 3M HCl. Discard all effluents. Elute the uranium with two 4-ml portions of H₂O, 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 NH₄Cl and 3 drops of methyl red indicator solution. Make the solution alkaline with conc NH₄OH 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 NH₄OH 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 μg uranium/50 λ of solution; made up by dissolving normal uranium in HNO_3 ; the final acid concentration is $\sim 3M$.

HCl : conc

HNO_3 : 3M; conc

$\text{Al}(\text{NO}_3)_3$ reagent: 700 g $\text{Al}(\text{NO}_3)_3 \bullet 9\text{H}_2\text{O}/\ell \text{H}_2\text{O}$.

Before use, this reagent is treated in the following manner: 35 mL of conc 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 H_2O . 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 HNO_3 and 1 mL of H_2O ; again evaporate to dryness. Repeat the additions and the evaporation twice.

Step 2. To the residue, add 1 mL of H_2O and 5 mL of conc 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 H_2O , and add the washings to the sample holder. Add ether up to the arm of the sample holder, add 8 mL of H_2O 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 N_2 to take off the ether completely.

Step 4. With three H_2O 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 HNO_3 to the dish, swirl, and transfer the rinsings to the volumetric flask. Repeat the HNO_3 rinse.

Step 5. Rinse the sides of the platinum dish with 5 mL of H_2O , add 0.5 mL of conc HNO_3 , evaporate the solution to 1 to 2 drops, and transfer to the 2- mL volumetric flask. Add 3 drops of 3M HNO_3 to the dish, swirl, and transfer to the volumetric flask. Repeat the addition of 3M HNO_3 and repeat the entire step twice.

Step 6. Make the solution up to volume with 3M 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 HNO_3 . Use a micropipette, coated on the outside with paraffin up to the first bulb, to withdraw a 50- λ 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 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 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.

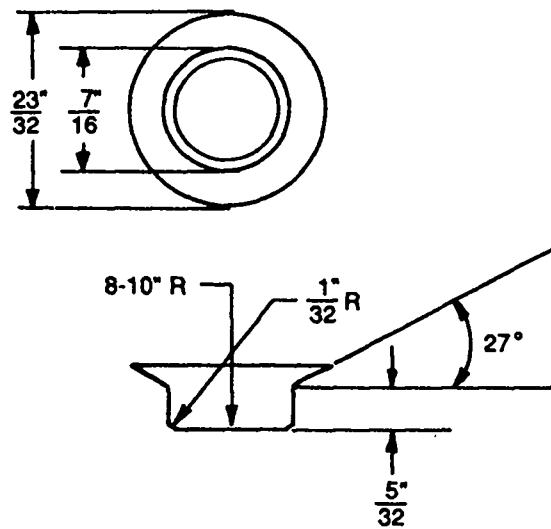


Fig. 1. Specifications for Pt dishes.

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 λ (0.2 μ g) of the uranium standard in the manner described in *Step 6*, including the 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 ± 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.

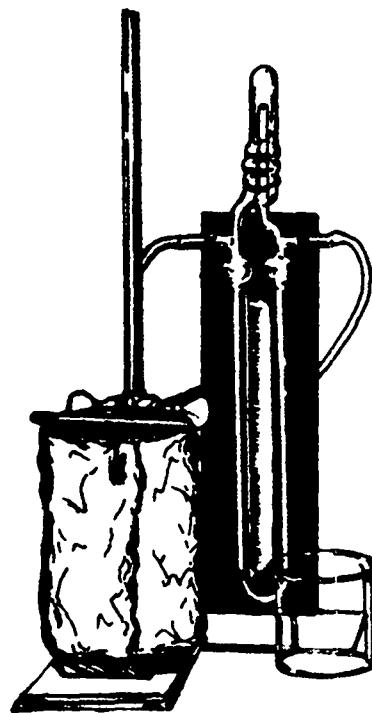


Fig. 2. Fusion apparatus.

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 H₂O. Then add 200 ml of conc HNO₃ to the flux and reflux this solution overnight. Pour off the acid and rinse the flask and dishes several times with distilled H₂O. 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 H₂O. Store in Petri dishes. Clean the platinum dishes that contained the standard uranium in a separate flask.

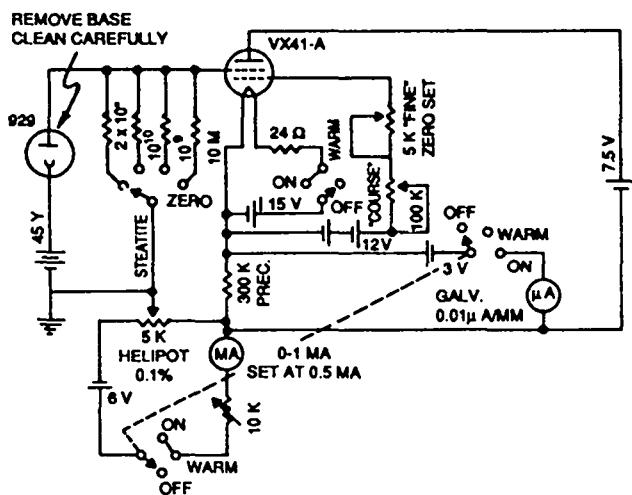


Fig. 3. D. C. Fluorophotometer schematic.

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.)

AMMETER FOR ULTRAVIOLET LIGHT SOURCE

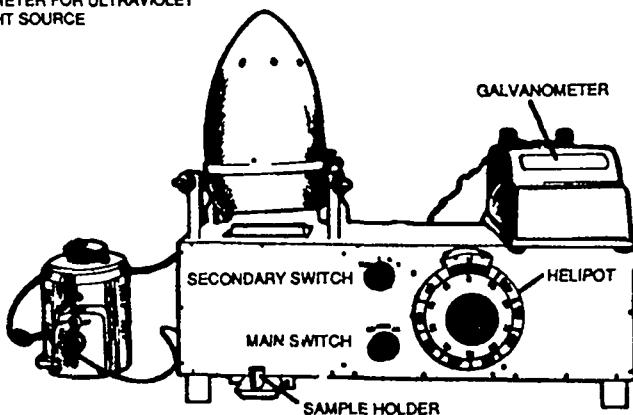


Fig. 4. D. C. Fluorophotometer.

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 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- λ aliquot sample:

A = average of the helipot readings when the 50- λ
aliquots contain no added standard uranium.

B = average of the helipot readings when the 50- λ
aliquots contain added standard uranium.

D = uranium content in 1 μ g of the standard in
the 50- λ aliquots.

$(\frac{A}{B-A}) D$ = μ g of uranium in 50- λ 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 μ 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 NO_3^- ion.

2. Reagents

H_2SO_4 : 5% by volume (5 ml of conc H_2SO_4 to 95 ml of H_2O)

H_2SO_4 : conc

HClO_4 : conc

HCl : conc

HNO_3 : conc; 2.5M

H_2O_2 : 30% solution

Uranium metal: pure

Ferric ammonium sulfate: ~0.1M

Ceric sulfate: standardized. Make up an aqueous solution ~0.01M and standardize against pure uranium in the following manner. Weigh out to the nearest 0.1 ~1 g of pure uranium and dissolve the metal in conc HCl ; add a few drops of conc HNO_3 if necessary. Make the solution up to exactly 100 ml by the addition of 2.5M 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 H_2O)

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 HCl and 30% H_2O_2 ; proceed to *Step 2*. If the sample is an oxide, dissolve it in a minimum of conc HClO_4 , add 100 ml of 5% H_2SO_4 , and proceed to *Step 3*. If the sample is in liquid form, start with *Step 2*.

Step 2. Add 5 ml of conc H_2SO_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 HClO_4 are added before the second and third evaporation. After the final evaporation, add 100 ml of 5% H_2SO_4 .

Step 3. Activate a Jones reductor by passing through it 100 ml of 5% H_2SO_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% H_2SO_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 ~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 =

$$\frac{m\ell \text{ Ce}(\text{SO}_4)_2 \times N \times F \times 100}{\text{g of sample}},$$

or grams total uranium in liquid sample =

$$m\ell \text{ Ce}(\text{SO}_4)_2 \times N \times F \times \frac{\text{total vol of sample}}{\text{aliquot vol of sample}}.$$

N = normality of $\text{Ce}(\text{SO}_4)_2$. 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% ^{235}U | 0.11760 |
| 98% ^{233}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}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 U_3O_8 highly enriched in ^{236}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}Na formed from the aluminum by the (n,α) reaction, and other induced activities such as ^{51}Cr . The major steps include (a) adsorption of the uranium from solution in a large volume of 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 ~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 HNO_3

Tellurium(IV) carrier: 10 mg tellurium/ml, added as Na_2TeO_3 in 6M 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 HCl

HNO_3 : conc

HCl: conc; 9M; 8M

HCl- HNO_3 : 9:1 by volume of the conc acids (prepared just before use)

HCl- Br_2 : 9M HCl, saturated with Br_2

HCl-HI: 9:1 by volume of conc HCl and 47% HI (prepared just before use)

5M HCl-0.3M HF

0.1M HCl-0.06M HF

NH_4OH : conc; 6M

$\text{Al}(\text{NO}_3)_3$: saturated aqueous solution (~2.5M)

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 ~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 HCl and 10 ml of conc HNO_3 . Dissolution takes ~40 min and the volume of liquid is reduced to ~140 ml. Add two 10-ml portions of the HCl- Br_2 mixture (Note 1). Cool and dilute the solution to 300 ml with 9M 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 (Al_2O_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 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 ~10 drops/20 s.) Wash the column first with 5 ml of 8M 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 H_2O and then with one 10-ml portion of H_2O (Note 3).

Step 3. Make the solution alkaline with 4 ml of conc NH_4OH (or 10 ml of 6M NH_4OH). Centrifuge and discard the supernate (Note 4). Dissolve the precipitate in 1 ml of conc 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 H_2O 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 NH_4OH . Centrifuge and discard the supernate. Dissolve the precipitate in 10 ml of conc HCl .

Step 6. Prepare another resin column as in *Step 2*. Because HF will be employed in one of the column steps, plug the tip of the column with polypropylene felt. Preequilibrate the resin with conc 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 HCl , (c) two 5-ml portions of HCl - HI , (d) two 5-ml portions of HCl - HNO_3 (the column will bubble), (e) five 5-ml portions of 5M 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 HCl -0.06M HF to elute the uranium into a 40-ml centrifuge tube (Note 6).

Notes

1. The addition of 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 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}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}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 HCl - HI washes. In six 5M 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 HCl - HNO_3 washes are omitted, a neptunium decontamination of $\sim 10^4$ is obtained with the 5M HCl -0.3M HF washes. In the first two washes with 5M 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 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. Knobeloch

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 NH_4NO_3 and $\sim 2M$ in 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

HNO_3 : fuming

HClO_4 : conc

NH_4NO_3 : solid

Diethyl ether

3. Procedure

Step 1. Transfer the sample in HCl and HClO_4 to an erlenmeyer flask of suitable size. Add a volume of fuming 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 HClO_4 .

Step 2. Add ~ 50 ml of fuming HNO_3 and evaporate to dryness again. Heat the sides of the flask to expel any residual HClO_4 .

Step 3. Dissolve the residue in ~ 40 ml of fuming 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 H_2O to make the solution $\sim 2M$ in HNO_3 , and add solid NH_4NO_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 H_2O , 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 NaOH , followed by acidification with 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}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 H_2SO_4 is recommended both to ensure exchange between the ^{237}Np tracer and ^{239}Np , and to complex uranium(VI). If the sample is a dissolved uranium foil, HNO_3 must be added before the fuming step to convert uranium to the +6 state. Neptunium(IV) and (V) are carried down by 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 H_2O

Strontium carrier: 10 mg strontium/ml, added as $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in H_2O

Zirconium carrier: 10 mg zirconium/ml, added as ZrOCl_2 in H_2O

^{237}Np standard solution: 5000 to 10 000 counts/min/ml in 2 to 4M HCl or HNO_3

HCl: 0.1M; 1M; 2M; conc

H_2SO_4 : conc

HNO_3 : conc

H_3BO_3 : saturated solution

HF: 1:1 H_2O 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- HNO_3 : equal parts by volume of 2M solutions

$\text{NH}_2\text{OH} \cdot \text{HCl}$: 5M (or saturated)

KMnO_4 : 10% solution

NH_4OH : 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 H_2O

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}Np because of the relatively low specific activity of the isotope, which is ~ 800 counts/min/ μg ; stippling produces a rather massive deposit. A preferable technique is described here. Prepare a solution of pure ^{239}Np from pile-irradiated ^{238}U that contains $\sim 10^4$ counts/min/100 μl . Weigh an aliquot of this solution onto a platinum plate and add another weighed aliquot to 1 ml of tracer. The ^{239}Np can now be used as a beta-emitting tracer to determine the absolute amount of ^{237}Np .

Evaporate the $^{239}\text{Np} + ^{237}\text{Np}$ sample to dryness with 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}Np aliquot. Use the known specific beta activity of the ^{239}Np , to calculate the activity of $^{237}\text{Np}/\text{ml}$ of solution.

4. Procedure

Step 1. Pipette 1 ml of ^{237}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 H_2O , add 10 drops of conc H_2SO_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 H₂O, 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 NH₂OH•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 (LaF₃). Centrifuge. Remove and discard the supernate. Wash the precipitate with 1 to 5 ml of HF-HNO₃.

Step 4. Dissolve the precipitate by slurring with 3 drops of saturated H₃BO₃ and adding 3 drops of conc HCl. (Ignore any small residue.) Add 3 ml of 2M HCl and precipitate La(OH)₃ by adding ~1 ml of conc NH₄OH. Centrifuge and discard the supernate. Wash the precipitate by boiling it briefly with several milliliters of H₂O.

Step 5. Dissolve the precipitate in ~5 ml of 2M HCl. Reprecipitate LaF₃ by adding 10 drops of NH₂OH•HCl and 10 drops of HF; centrifuge and discard the supernate. Wash the precipitate with 1 ml of HF-HNO₃. If the precipitate volume is >0.2 ml, repeat the hydroxide and fluoride precipitations until the volume of LaF₃ precipitate is <0.2 ml.

Step 6. Dissolve the fluoride precipitate in 1 drop each of saturated H₃BO₃ and conc HNO₃. Add 10 drops of KMnO₄ 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-HNO₃, 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-HNO₃, add the washings to the previous supernate, and discard the precipitate.

Step 8. Add 5 drops of NH₂OH•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-HNO₃, centrifuge, and discard the supernate.

Step 9. Repeat *Steps 6* and *7*.

Step 10. Add 5 drops of NH₂OH•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-HNO₃, centrifuge, and discard the supernate.

Step 11. Dissolve the precipitate with 1 drop of saturated H₃BO₃ 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 NH₄OH, and then make barely acidic with 1M HCl. Electroplate for 20 min at 0.5 A. Make alkaline with dilute NH₄OH for the last minute of plating. (A minor explosion occurred when conc NH₄OH was used.) Decant the plating solution; rinse the cell with H₂O 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 H_2SO_4 because $CaSO_4$ will precipitate and carry neptunium to some extent. Repeated fuming with 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. Efurd 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, HNO₃, and HClO₄ 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

²³⁶Np tracer: 10¹⁰ atoms

HClO₄: conc

HF: conc

HNO₃: 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

NH₂OH•HCl: solid

FeCl₂•4H₂O

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 ²³⁶Np tracer. To equilibrate the sample and tracer, add 10 ml of HClO₄ and fume over a burner at 180°C or higher. The HClO₄ 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 NH₂OH•HCl and 0.25M in FeCl₂. 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 HNO₃ for 2 min. Discard the organic layer. Wash the 8M HNO₃ 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 HClO₄ 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 HNO₃ and 3 drops of conc HClO₄. 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 HNO₃ 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 H₃PO₂ 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 LaF_3 and the great difference between adsorption of plutonium(III) and that of plutonium(IV) in 12*M* 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 LaF_3 precipitation, carried out in the presence of NH_2OH , 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 LaF_3 precipitate in 12*M* 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 μg of ^{235}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}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}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 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 H_2O

^{236}Pu : standardized solution in 3*M* HCl; or standardized spike solution (any mixture of plutonium isotopes in 3*M* HCl)

HCl: conc; 3*M*

HF: conc

HF-HNO₃: equal volumes of 2*M* solutions

HNO₃: conc

H₃BO₃: saturated aqueous solution

NH₂OH•HCl: 35% by weight in H_2O ; solid

Solution I: 0.1 *mℓ* conc HNO₃/15 *mℓ* conc HCl

Anion-exchange resin: AG 1-X10, 200 to 400 mesh; slurry in H_2O

HI stock solution: Distill HI (Mallinckrodt analytical reagent-grade, 5.5*M* in HI, 1.5% H₃PO₂ preservative) under nitrogen. The HI cannot be used without distillation because H₃PO₂ 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% N₂H₄ in H_2O) 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 $N_2HOH \bullet HCl$ /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 ~ 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 $N_2HOH \bullet HCl$ 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 ~ 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 ~ 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_2O , 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_3 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_3/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

HNO₃: conc

NH₄OH: conc

Ethanol: absolute

NH₄Cl: 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 HNO₃ 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 H₂O, and transfer the washings to the plating cell (~1.5-ml volume). Add two small spatulas of NH₄Cl and 2 drops of methyl red indicator solution. Make the solution alkaline with conc NH₄OH 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 NH₄OH. 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 H₂O 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}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 H_2O

Cesium carrier: 10 mg cesium/ml, added as CsCl in H_2O

Zirconium carrier: 10 mg zirconium/ml, added as $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 1M HNO_3

HCl : 5M; conc

H_2SO_4 : conc

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 H_2SO_4 and heat to fumes of 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 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 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}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 H_2O . Centrifuge and discard the supernate.

(b) Dissolve the precipitate in 1 to 2 drops of conc HCl and add 1 ml of 5M NH_4CNS 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 NH_4CNS solution.

(c) Elute with 10 ml of the cold 5M NH_4CNS 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 UNDERGROUND 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 4*M* HNO₃ 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 NH₄I-HCl solution. This step accomplishes extensive decontamination because most of the species that extract into HDEHP from 4*M* HNO₃ are not back-extracted by the NH₄I-HCl solution. Further purification of the plutonium can be accomplished by the usual LaF₃ 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: 0.5*M* 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: 9*M*

HNO₃: 4*M*; conc

NH₄I: saturated aqueous solution

NH₄I-HCl solution: one volume of the saturated NH₄I solution to 8 of 9*M* HCl

NH₂OH•HCl: solid

3. Procedure

Step 1. Pre-equilibrate the 0.5*M* HDEHP with an equal volume of 4*M* HNO₃. To an aliquot of the sample (~4*M* in HNO₃) 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 4*M* HNO₃, and discard the wash.

Step 2. To the organic phase, add ~50 mg of solid NH₂OH•HCl and then one-half volume of NH₄I-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 H₂O 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 HNO₃ 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}Pu standardized tracer solution, in 3*M* HCl
HCl: 9*M*; 4*M*
 CrO_3 : solid
 NH_4I : saturated aqueous solution
 $\text{NH}_4\text{I-HCl}$: one volume of saturated NH_4I solution
to eight volumes of 9*M* HCl
 $\text{NH}_2\text{OH}\bullet\text{HCl}$: 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 4*M* HCl into an erlenmeyer flask and add a few crystals of CrO_3 . 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. \sim 1 cm), the tip of which has been plugged with glass wool. Wash the column with 2 ml of 4*M* 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 4*M* HCl and then with 2 ml of 9*M* HCl. Discard the washings. Add a few crystals of $\text{NH}_2\text{OH}\bullet\text{HCl}$ to the top of the column.

Step 5. Add 2 ml of $\text{NH}_4\text{I-HCl}$ 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 3*M* in HCl by addition of the appropriate quantity of H_2O . 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 6*M* 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}Pu tracer is added; NaNO_2 is used to ensure that all the plutonium is converted to the +4 state to effect complete exchange.

2. Reagents

^{236}Pu standardized tracer solution in 3*M* HCl

HDEHP solution: 0.75*M* solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane

DBHQ solution: 0.2*M* solution of 2,5-di-tertiary butylhydroquinone in 2-ethyl-1-hexanol

HCl: 6*M*; 3*M*

NaNO_2 : 10*M*

3. Procedure

Step 1. Pre-equilibrate the 0.75*M* HDEHP solution with an equal volume of 3*M* HCl in a separatory funnel. (The size of the funnel should be about twice that of the sample aliquot.) Add sufficient 10*M* 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 10*M* 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 6*M* HCl, and discard the wash.

Step 2. To the organic phase add one-third volume of the 0.2*M* DBHQ solution and shake for ~ 10 s. Add one-half volume of 6*M* HCl, shake for ~ 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 H_2O to make the solution 3*M* 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 LaF₃ by stirring with 2 to 3 drops of saturated H₃BO₃ 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⁺ 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 H₂O 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}Am tracer: standardized by counting a known volume or known weight of solution

^{244}Cm tracer: standardized by counting a known volume or known weight of solution

Lanthanum carrier: 5 mg lanthanum/m ℓ , added as $\text{La}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ in H_2O

HCl: 1M; 2M; 6M; conc

HNO_3 : conc

HF: conc

H_3BO_3 : saturated aqueous solution

HF-HCl wash solution: 1M in each component

NH_4OH : 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-m ℓ erlenmeyer flask, add amounts of ^{243}Am and ^{244}Cm tracers approximately equal to those of the ^{241}Am and ^{242}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 m ℓ of conc HCl and 3 drops of conc 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-m ℓ long-taper glass centrifuge tube. Wash the column with 4 to 5 m ℓ 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_3BO_3 solution and adding an equal volume of conc HCl. Dilute to 4 to 5 ml with H_2O , and precipitate $La(OH)_3$ by the dropwise addition of conc NH_4OH . 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_2O , 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_3BO_3 solution; then add 10 drops of conc HCl and ~0.02 ml of conc HNO_3 .

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 μ 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_4OH , and then make barely acidic with 1M HCl. Electroplate onto a 1-in. platinum disk for 20 min at 2 A. The ^{241}Am and ^{242}Cm are related to the ^{243}Am and ^{244}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. Efurd 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, HNO_3 , and 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}Am tracer: standardized by alpha-counting known weights of solutions and by isotope dilution mass spectrometry

^{244}Cm tracer: standardized by alpha-counting known weights of solutions and by isotope dilution mass spectrometry

Lanthanum carrier: 1 mg lanthanum/ml, added as $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ in H_2O

HCl: conc; 6M; 3M; 0.05M

HF: conc

HCl-HF: 3M HCl-3M HF

HClO_4 : conc

HNO_3 : 90% HNO_3 ; conc; 10M; 0.1M; 0.01M

H_3BO_3 : saturated aqueous solution

NaOH: 6M

NH_4OH : 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

AgNO_3 : 10% AgNO_3 by weight in H_2O

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}Am and ^{244}Cm tracers in amounts equal to those of the ^{241}Am and ^{242}Cm expected. Add 1 ml of lanthanum carrier. To equilibrate the sample and tracer, add 20 ml of HClO_4 and 10 ml of 90% 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 H_3BO_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 H_2O , stir, and centrifuge. Discard the supernate.

Step 4. Dissolve the sample in 3 ml of 6M HCl. Add 10 ml of H_2O and make the solution

alkaline with NH_4OH . Place in a heating block at 80°C for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 10 mL of H_2O that contains 1 drop of NH_4OH . 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°C heating block for 30 min. Make the solution alkaline with NH_4OH . Place in a heating block for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 10 mL of H_2O that contains 1 drop of NH_4OH . Centrifuge and discard the supernate.

Step 7. Dissolve the precipitate in 10 mL of conc HCl that contains 1 drop conc 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 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 HNO_3 ; collect the wash in the same tube. Evaporate the solution to dryness. Add 1 mL of 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 HNO_3 and 3 drops of conc HClO_4 to the quartz test tube that contains the americium and curium; heat at 130°C for 1 h. Raise the temperature of the heating block to 180°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 HNO_3 and evaporate the sample to dryness. Add 10 mL 0.01M HNO_3 , 1 drop of 10% 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°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 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 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 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 5*M* 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 0.1*M* HNO₃.

References

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(October 1989)

SEPARATION OF AMERICIUM AND CURIUM FROM TRANSURANIUM 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(ϕ P)A].

2. Reagents

HClO₄: conc

HCl: 4M; 1M

2-EH(ϕ P)A: 1M in *n*-heptane [29 ml of 2-EH(ϕ 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(ϕ P)A reagent and 5 ml of 1M HCl.

3. Preparation of 2-Ethylhexylphenylphosphonate [2-EH(ϕ 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 H₂O. Add a Teflon stirring bar, cover with a watch glass, and heat on a heater-stirrer for \sim 72 h. The saponification reaction is complete when the volume of the organic phase has increased by \sim 50%. Remove the watch glass and continue heating to permit the 2-ethylhexanol formed to evaporate; add H₂O, 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 HClO₄.

Step 2. Take up the sample in 100 λ of 1M HCl and allow the solution to run into the column. Wash the sample tube with 50 λ 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 HNO₃; (d) back-extraction of only the lighter lanthanides and actinides into 0.8M HNO₃; (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 ²⁴⁰Am and ²⁴¹Am can be effected by gamma-ray counting in the presence of curium.

2. Reagents

HNO₃: fuming; conc; 4M; 0.8M; 0.05M

HClO₄: conc

HF: conc

HCl: conc

HCl-HF: 4M in each acid

H₃BO₃: saturated aqueous solution

NaOH: 6M

NH₄OH: conc

NH₂OH•HCl: solid

Tellurium(IV) carrier: 10 mg tellurium/ml, added as Na₂TeO₃ in 6M HCl

Tellurium(VI) carrier: 10 mg tellurium/ml, added as Na₂TeO₄•2H₂O in 3M HCl

Neodymium carrier: 5 mg neodymium/ml, added as NdCl₃•6H₂O

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% NH₂OH•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⁺ form), nominal minus 400 mesh; batch selected to give satisfactory separation

Cation-exchange resin: Bio-Rad AG 50W-X4, 200 to 400 mesh (H⁺ 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⁺ 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 HNO₃, 20 ml of conc HClO₄, and 25 ml of conc HF. Boil to heavy fumes of HClO₄. Repeat treatment and boiling once or twice. Add 40 ml of 4M HNO₃, 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 H_3BO_3 and 2 ml of conc HNO_3 , and boil. If the sample is not dissolved, add 2 ml of H_3BO_3 and 1 ml of 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 H_2O 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 H_2O . Discard the washes.

Step 5. Dissolve the precipitate in ~3 ml of conc HCl , dilute to 20 ml with H_2O , and make alkaline with conc NH_4OH . Centrifuge, wash the precipitate with H_2O , and discard the wash.

Step 6. Dissolve the precipitate in ~1 ml of conc 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 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 ~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 HNO_3 . Back-extract the americium and the lighter tripositive lanthanides and actinides with two 10-ml portions of 0.8M 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 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 inesh 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 ~2 ml, add 10 to 20 mg of neodymium carrier (or any tripositive lanthanide carrier), and dilute to ~20 ml with H_2O . 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 H_3BO_3 and conc HCl . Dilute the solution to 15 ml with H_2O , and make alkaline with 6M $NaOH$. Centrifuge and discard the supernate. Wash the precipitate with 15 ml of H_2O and discard the wash.

Step 10. Dissolve the precipitate in 1 ml of conc HCl , add ~100 mg of $NH_2OH \cdot HCl$, dilute to 15 ml with H_2O , and reprecipitate the hydroxides with conc NH_4OH . Centrifuge and discard the supernate. Wash the precipitate with 15 ml of H_2O and discard the wash.

Step 11. Dissolve the precipitate in 3 to 5 drops of conc HCl and dilute to ~30 ml with H_2O . Add the equivalent of 1 to 2 ml of centrifuged Bio-Rad AG 50W-X4, 200 to 400 mesh cation resin (H^+ form) in water-slurry form, stir for 1 min, and centrifuge. Discard the supernate, wash the resin with 30 ml of H_2O , and discard the wash.

Step 12. Slurry the resin from *Step 11* in 1 to 2 ml of H_2O ; transfer to the top of the cation-exchange column prepared in *Step 1*. Complete the transfer with a small H_2O wash. Allow the resin to settle and draw off the H_2O . Start eluting with $EtOH-HCl$ reagent (Note 3) under ~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 ~2 min. Centrifuge, discard the supernate, and wash the precipitate with H_2O ; discard the wash. Treat the solid with 2 to 5 ml of saturated H_3BO_3 and 2 ml of conc 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 $\text{NH}_2\text{OH}\bullet\text{HCl}$ 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.

(October 1989)

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 NH_4NO_3 solution and the elements are back-extracted into H_2O . To keep the volumes of TBP and H_2O 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 ~ 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 ℓ

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 H_2O to produce ~ 2400 ml of solution; 1.9M, made by diluting three volumes of saturated $\text{Al}(\text{NO}_3)_3$ with one volume of H_2O

NH_4NO_3 - HNO_3 reagents: 10M in NH_4NO_3 and 0.2M in HNO_3 , made by dissolving 7 lb of NH_4NO_3 in H_2O , adding 50 ml of conc HNO_3 , and diluting to 4 ℓ with H_2O ; 0.65M NH_4NO_3 -0.05M HNO_3 , made by combining 28 ml of conc HNO_3 and 570 ml of saturated NH_4NO_3 and making up to 9 ℓ with H_2O

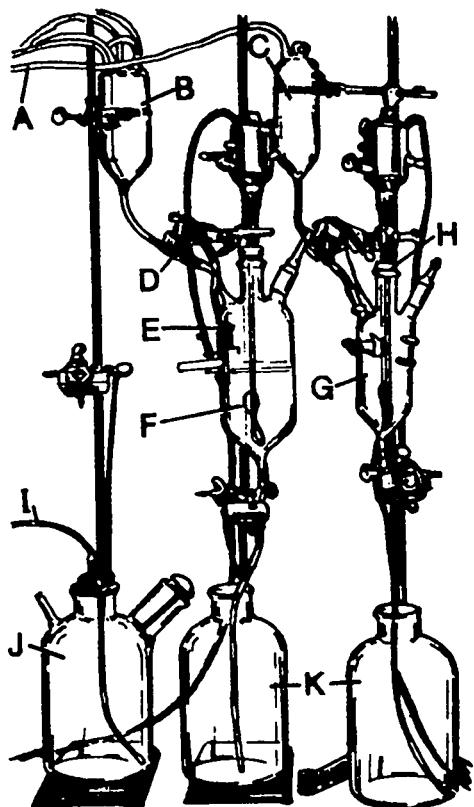


Fig. 1. TBP and HDEHP extraction apparatus. (A) lines to $\text{Al}(\text{NO}_3)_3$, NH_4NO_3 , and HNO_3 wash solutions and to H_2O ; (B) TBP transfer vessel; (C) HDEHP transfer vessel; (D) typical solenoid valve; (E) TBP mixing vessel; (F) stainless steel centrifugal stirrer; (G) HDEHP mixing vessel; (H) Teflon gland; (I) air pressure line; (J) feed solution vessel; and (K) vessels for receiving waste solutions or product.

LiOH : 4*M*, made by dissolving 671 g of $\text{LiOH} \cdot \text{H}_2\text{O}$ in H_2O and diluting to 4 ℓ

Buffer solution: (pH 1) for standardizing pH meter

HCl : 10*M*

Tri-*n*-butylphosphate (TBP)

HDEHP: 0.5*M*, made by diluting 645 g of di-2-ethylhexyl orthophosphoric acid to 4 ℓ with *n*-heptane

Decanol

HCl-HF : 4*M* in each acid

Tellurium(IV) carrier: 10 mg tellurium/ $\text{m}\ell$, added as Na_2TeO_3 in 6*M* HCl

Tellurium(VI) carrier: 10 mg tellurium/ $\text{m}\ell$, added as $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ in 3*M* HCl

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

n-heptane

EtOH-HCl : 20% absolute ethanol-80% conc HCl -0.1% $\text{NH}_2\text{OH} \cdot \text{HCl}$, 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^+ form), nominal minus 400 mesh; batch-selected to give satisfactory separations.

4. Procedure

The ground-up sample is dissolved in a mixture of conc HNO_3 , HClO_4 , and HF and is boiled to fumes of HClO_4 after each addition. The solution is made 4*M* in HNO_3 and then 4*M* in HF ; the insoluble fluorides (including the tripositive actinide fluorides) are filtered. The precipitate is washed twice with 4*M* HF -4*M* HNO_3 , dissolved in conc HClO_4 , and diluted to make a solution 1 to 2*M* in 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 4*M* LiOH to make the solution 1.7 to 1.9*M* in $\text{Al}(\text{NO}_3)_3$ and $\sim 0.1\text{M}$ in H^+ (pH 1). This is done by pouring the sample into a 9- ℓ bottle and adding first $\sim 4000\text{ ml}$ of saturated $\text{Al}(\text{NO}_3)_3$ and then 4*M* LiOH slowly from a dispensing burette while stirring the solution vigorously. Stop the addition of 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 1.9*M* ($\sim 75\%$ saturated; Note 2).

Step 2. Pour 1 kg of TBP into the extraction vessel. Then add 500 ml of 1.9*M*- $\text{Al}(\text{NO}_3)_3$ 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(NO₃)₃ and stir for 2 min; wash with five 500-ml portions of 10M NH₄NO₃-0.2M HNO₃ and stir for 5 min each time. Discard the washings.

Step 5. Back-extract the lanthanides and actinides with three 500-ml portions of H₂O; 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 NH₄OH 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 NH₄NO₃-0.05M HNO₃ 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 HNO₃. Dissolve the sample from *Step 9* in 10 ml of conc HCl. Add 1 drop each of conc HNO₃, 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 HNO₃; collect the eluates in the same flask.

Step 11. Boil the sample to ~2 ml; dilute with H₂O 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 H₃BO₃ and conc HCl; dilute the solution to 15 ml with H₂O and make the solution alkaline with 6M NaOH. Centrifuge and discard the supernate. Wash the precipitate with H₂O and discard the washings. Dissolve the precipitate in 1 to 2 ml of conc HCl, dilute to ~20 ml with H₂O, and add ~100 mg of NH₂OH•HCl. Warm the solution gently, make alkaline with conc NH₄OH, and centrifuge. Discard the supernate, wash the precipitate with H₂O, and discard the washings.

Step 12. Dissolve the precipitate in 3 to 5 drops of conc HCl and dilute to ~30 ml with H₂O. 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 H₂O.

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 H₂O) 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 H₂O and transfer to top of the cation-exchange column. Complete the transfer with a small H₂O wash. Allow the resin to settle and draw off the H₂O. Start eluting with EtOH-HCl under ~10 psi air pressure at a flow rate of $\sim 0.1 \pm 0.015$ 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(NO₃)₃.

In *Step 3*, wherever 500 ml is indicated, replace with 300 ml.

In *Step 4*, use three 300-ml portions of NH₄NO₃-HNO₃ wash.

In *Step 5*, use three 300-ml portions of H₂O.

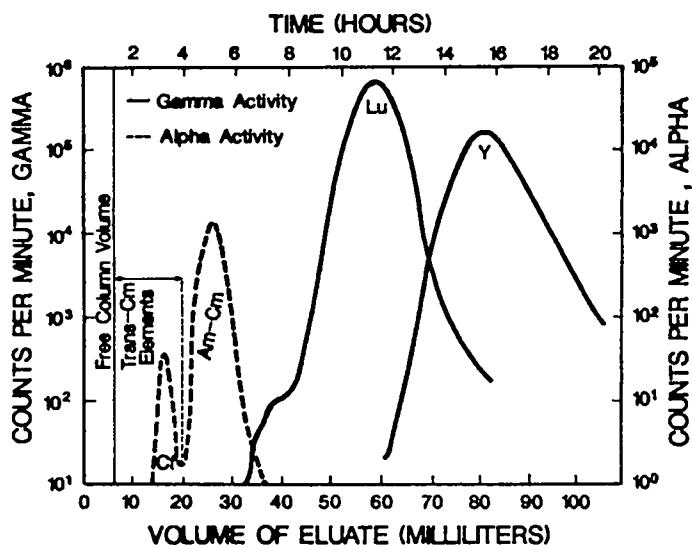


Fig. 2. Elution curve for transplutonium actinides.

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 H₂O. Add 100 mg of NH₂OH•HCl, warm the solution gently, make alkaline with conc NH₄OH, and centrifuge. Discard the supernate, wash the precipitate with H₂O that contains a few drops of conc NH₄OH, 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 H₂O. 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 H₂O.

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 H_2O , 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 <u>Extractions</u> | 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 $\sim 10\%$ fractionation of the actinides.

4. The americium-curium fraction from the column is suitable for the determination of americium by gamma-counting.

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SEPARATION OF TRACE AMOUNTS OF TRANSPLUTONIUM ELEMENTS FROM FISSION PRODUCTS

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H.L. Smith, and W. R. Daniels

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 $\text{La}(\text{OH})_3$ 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 $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

Lanthanum carrier: 5 mg lanthanum/ml, added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

Zirconium carrier: 10 mg zirconium/ml, added as $\text{ZrO}(\text{NO}_3)_2$ in 1M HNO_3

Tellurium carrier: 10 mg tellurium/ml, added as Na_2TeO_3 in 1M HCl

Strontrium carrier: 10 mg strontium/ml, added as $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 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-HNO₃: 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

$$K_1 = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})} \sim \frac{10^{-\text{pH}}(\text{A}^-)}{(\text{M}_{\text{HA}}) - (\text{A}^-)} ,$$

or

$$10^{-\text{pH}} \sim \frac{K_1 [(\text{M}_{\text{HA}}) - (\text{A}^-)]}{(\text{A}^-)} ,$$

where

$$K_1 \sim 10^{-3.9} ,$$

(M_{HA}) = 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 .

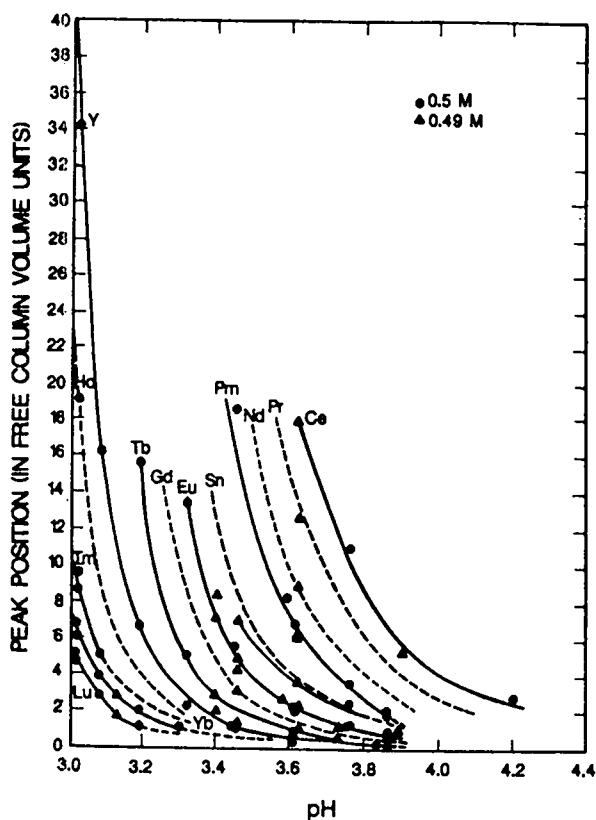


Fig. 1. Lanthanide elution positions *vs* pH with 0.5M α -hydroxy isobutyric acid.

Cation-exchange resin: Bio-Rad AG 50-X4, 400 mesh or finer. The resin is prepared by washing successively with H_2O , NH_4OH , H_2O , and three times with conc HCl. For the ethanol-HCl columns, the resin is stored as an HCl slurry. For the slurry in H_2O , the resin should be washed an additional three times with H_2O .

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

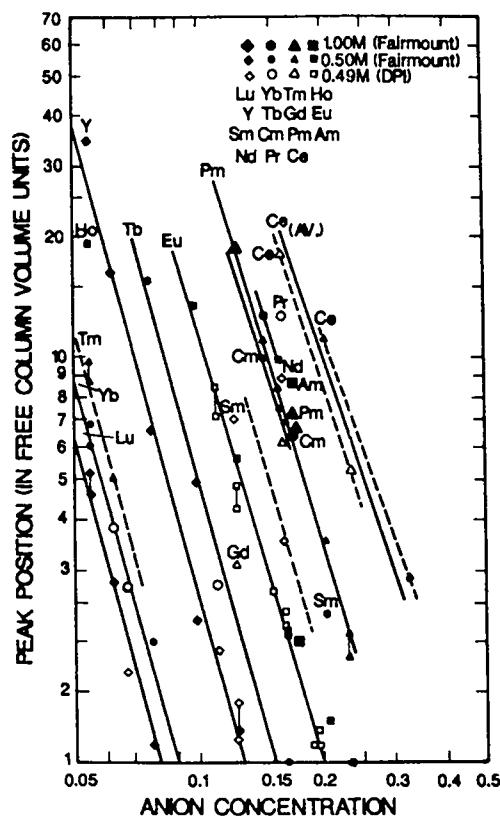


Fig. 2. Lanthanide and actinide elution positions *vs* hydroxy isobutyrate anion concentration.

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_4SCN , 6M NH_4OH , H_2O , and HCl, and then stored as the ammonium form in H_2O . (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 NH_4OH to precipitate the $\text{Y}(\text{OH})_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 to 1.0 ml H_2O .

Step 2. Dissolve the precipitate in a mimimum 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 HNO_3 solution.

Step 3. Dissolve the fluoride precipitate by adding 1 drop of saturated H_3BO_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 NH_4OH , centrifuge, discard the supernate, and wash the precipitate twice with 0.1 to 1.0 ml of H_2O .

Step 4. Dissolve the precipitate in 3 ml of 10M HCl. Add 1 drop of conc 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 NH_4OH 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 H_2O .

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 H_2O , 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 H_2O 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.).

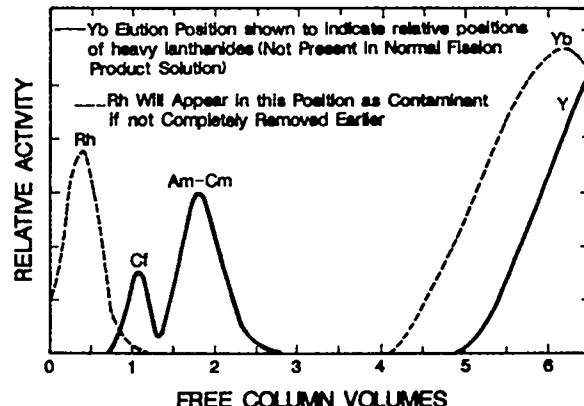


Fig. 3. Twenty percent ethanol-saturated HCl elution from AG 50-X4 cation resin.

Step 8. Place the tube that contains the sample in an oil or steam bath and evaporate to $\sim 0.5\text{ ml}$; 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 NH_3 or carbonate-free NH_4OH . Centrifuge, discard supernate, and wash the precipitate with 0.5 ml of H_2O .

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-hydroxisobutyrate 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 HNO_3 and HClO_4 .

Notes

1. TABLE I
Separation Factors with Ammonium
Alpha-Hydroxisobutyrate
($\text{Cm} = 1.0$)

| Element | Relative Peak Position |
|-------------|------------------------|
| 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}Cm present to the known quantity of added ^{244}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 NH_4SCN 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 NH_4SCN solutions. The curium is finally removed from the column by elution with a more dilute NH_4SCN 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 H_2O

^{244}Cm standard solution: 100 to 1000 counts/ min/mL

HClO_4 : conc

HCl : conc; 3M

HNO_3 : conc

NH_4OH : 3M

NH_4CNS : 5M; 1M in a 3:1 ethanol-to- H_2O mixture

Solution A: a mixture that contains 2 to 3 drops of conc 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}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 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 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 NH_4CNS . Add 2 mL of 5M NH_4CNS to the dry residue in the erlenmeyer flask and swirl to obtain solution. Use Hydrion paper (pH range 1.2 to 2.4), 3M NH_4OH , and 3M HCl to adjust the pH to ~ 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 NH_4CNS that has been adjusted to pH 1.5 with 3M HCl , and push this solution through at the same rate. Make up a 1M NH_4CNS solution in a 3:1 ethanol-to- H_2O 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 NH_4CNS solution with an equal volume of H_2O , 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 NH₄CNS. 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 ²⁴⁴Cm tracer employed is 3 to 5 times that of the estimated ²⁴²Cm 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 ~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 NH₄CNS 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 TRANSURANIUM 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 10*M* 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 6*M* 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; 10*M*; 6*M*; 0.1*M*

HNO₃: conc; 0.05*M*

Lanthanum carrier: 10 mg lanthanum/ml, added as La(NO₃)₃•6H₂O in H₂O

NH₃: gas

NH₄OH: 6*M*

Ethanol-HCl solution (EtOH-HCl): 20% absolute ethanol-80% conc HCl (by volume); saturated with HCl gas at room temperature

0.5*M* 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 H₂O

Cation-exchange resin: Bio-Rad AG 50W-X4, 200 to 400 mesh; slurry in H₂O

Cation-exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh; slurry in H₂O

3. Procedure

Step 1. Pass gaseous NH₃ 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 H₂O that contains a small amount of NH₄OH. Centrifuge and discard the washings. Repeat the washing process.

Step 2. Dissolve the precipitate in 20 to 25 drops of conc HNO₃, and adjust the pH to 1.2 to 2.0 by the dropwise addition of 6*M* NH₄OH. Dilute to ~10 ml with H₂O and add the solution to a 60-ml separatory funnel. Add 10 ml of 0.5*M* 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 0.05*M* HNO₃; 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 6*M* 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 NH_3 gas until precipitation is complete. Centrifuge and discard the supernate. Wash the precipitate with $\sim 2\text{ ml}$ of H_2O , centrifuge, and discard the washings.

Step 5. Dissolve the hydroxide precipitate in 1 ml of 10*M* HCl and 1 drop of conc 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 10*M* HCl that contains 1 drop of conc HNO_3 .) Collect the eluate in a 40-ml long-taper Pyrex centrifuge tube.

Step 6. Dilute the eluate to $\sim 8\text{ ml}$ with H_2O . Bubble in NH_3 gas until precipitation is complete, centrifuge, and discard the supernate. Wash the precipitate with $\sim 2\text{ ml}$ of H_2O , centrifuge, and discard the washings.

Step 7. Dissolve the precipitate in 1 drop of conc HCl, dilute the solution to 12 ml with H_2O , 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 0.1*M* HCl and add the washings to the column. Elute with three 1-ml portions of 6*M* HCl; catch the eluates in a clean long-taper centrifuge tube.

Step 8. Bubble 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 ~ 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 ~ 40 s/drop. Collect dropwise in fractions and alpha-count. The transcurium elements elute first, followed by americium and curium (~ 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)

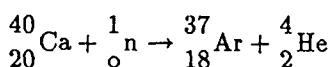
II. Separation of Products from Irradiated Targets

THE SEPARATION OF ^{37}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}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}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}Cl , formed from ^{37}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).

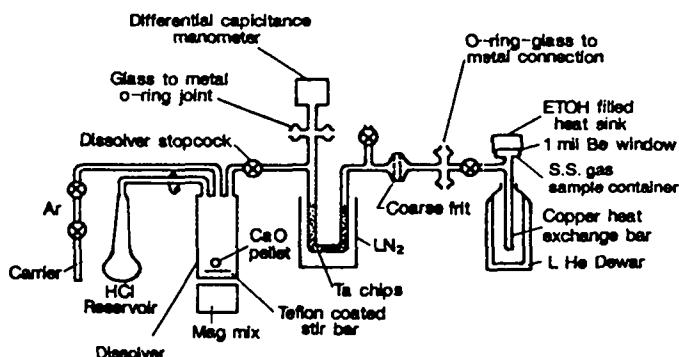


Fig. 1. Dissolver apparatus.

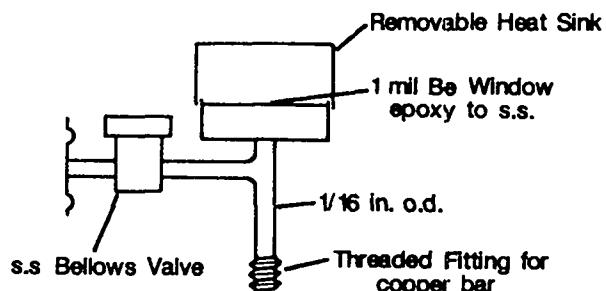


Fig. 2. Stainless steel sample container.

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 CaCl₂ remains. (The argon is not condensed by the liquid nitrogen, but the distillation permits complete mixing between carrier gas and the ³⁷Ar 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 CaCl₂ in the dissolver and stir for ~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 ~10 min. Disconnect the sample container and count the 2.62-keV x-ray from ³⁷Cl 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 ³⁷Ar 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 HNO_3 and thallium is precipitated as TII. The target metals are left in solution as iodocomplexes, PbI_4^{2-} and BiI_4^- . In each case, the thallium is purified by La(OH)_3 scavenges and then precipitated as Tl_2CrO_4 . Chemical yields are $\sim 50\%$.

2. Reagents

Thallium carrier: 10 mg thallium(I)/ml, made by dissolving the pure metal in 6M 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 $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$

HNO_3 : conc; 6M; 2M

NH_4OH : conc

NaI: solid

NaI reagent: 3M in NaI and 2M in HNO_3

Na_2CrO_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 HNO_3 . Evaporate the solution to $\sim 2\text{ml}$, and then use 2M 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 HNO_3 (the thallium remains in the +1 state) and heat over a burner to volatilize any I_2 present. Dilute the solution to $\sim 20\text{ml}$ with H_2O and reprecipitate TII, this time with NaI reagent. Centrifuge and discard the supernate. Redissolve the TII in a minimum of 6M HNO_3 and dilute to 20 ml with H_2O . Add 4 drops of lanthanum carrier and precipitate La(OH)_3 with an excess of conc NH_4OH . 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 HNO_3 and repeat the La(OH)_3 scavenging.

Step 4. To the supernate add 2 ml of 10% Na_2CrO_4 solution; place on a steam bath for a few minutes to permit the Tl_2CrO_4 to coagulate. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H_2O , centrifuge, and discard the wash. Slurry the Tl_2CrO_4 in 10 ml of H_2O , filter through a weighed filter circle, dry, weigh, and mount for counting. Without the heating and washing, the small Tl_2CrO_4 crystals would pass through the filter paper; the Tl_2CrO_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 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 HNO_3 to transfer the solution to a 40-ml glass centrifuge tube. Add 10 g of NaI to precipitate TII. (Some 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 BiI₃ and I₂ from the TlI.)

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 HNO_3 , excess nitrate is removed with $\text{NH}_2\text{OH} \bullet \text{HCl}$, and the astatine is reduced to the -1 oxidation state by SnCl_2 in $8M$ HCl . The astatine (with traces of polonium and iodine) is then adsorbed on a coarse-grain tellurium column under an N_2 atmosphere. Following acid and H_2O rinses of the column to remove unwanted radioactive entities, the astatine is eluted with 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 ~ 20 to 40 min and typical chemical yields range from 25 to 50% .

2. Reagents

HNO_3 : conc

HCl : conc; $8M$; $1.5M$

NaOH : $2M$

$\text{NH}_2\text{OH} \bullet \text{HCl}$ solution: $0.1\text{ g of compound}/\text{ml H}_2\text{O}$

SnCl_2 solution: $1M$ compound in $8M$ HCl

Silver foil: 1 mil; precleaned with CCl_4 and dilute HNO_3

Tellurium powder: ~ 30 mesh; purity 99.999%

3. Procedure

A. Column Preparation

In distilled H_2O , sediment the tellurium to be used for the column packing (Note). Decant the H_2O and wash the tellurium with hot $1.5M$ HCl and H_2O . Sediment the tellurium again and place in a glass column; be sure that the element remains under H_2O . 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 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 H_2O until it is needed. Typically, columns with active regions of ~ 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 HNO_3 . Remove excess NO_3^- ion from solution by the dropwise addition of the $\text{NH}_2\text{OH} \bullet \text{HCl}$. Reaction occurs with vigorous bubbling and the $\text{NH}_2\text{OH} \bullet \text{HCl}$ should be added carefully. When reaction is complete, add conc HCl to the solution until the concentration of that acid is $\sim 8M$. Add a few milliliters of 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 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 $8M$ HCl and then with H_2O 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 > 2×10^3 ; 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 ~ 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}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}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}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 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 HNO_3 , and then with 1M HCl; the latter removes NO_3^- ion, a biological poison. Potassium is eluted from the column with 12M 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 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: KCl in H_2O ; of known concentration

Scandium carrier: ScCl_3 in very dilute HCl; of known concentration

HCl: 12M; 8M; 1M

HNO_3 : 8M; 4M

NH_4OH : 6M

H_2O_2 : 30% aqueous solution

$\text{NH}_4\text{OH-NH}_4\text{Cl}$ buffer: 0.1M in both NH_4OH and NH_4Cl ; 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 H_2SO_4

Hydrated antimony pentoxide (HAP)-exchanger: source: Carlo Erba, Industrial Chemicals Division, Milan, Italy; washed with distilled H_2O 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 HNO_3 and dilute with H_2O to make the solution 4M in acid. Add 150 μg 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 HNO_3 and discard the washes. Wash the column with 1M HCl until the effluent gives a negative test for NO_3^- ion with carbazole reagent. (If NO_3^- is present, a deep green color will form.) Discard the effluent.

Step 3. Elute potassium with several column volumes of 12M HCl. Add 2 ml of 30% H_2O_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 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 NH₄OH. 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 NH₄OH-NH₄Cl buffer (pH 9.4) to effect quantitative elution of potassium. Combine the effluents.

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RECOVERY OF RADIOHAFNIUM FROM A TANTALUM TARGET

R. J. Daniels, P. M. Grant,
and H. A. O'Brien, Jr.

1. Introduction

This procedure was designed to isolate ^{172}Hf produced by the bombardment of tantalum foils with 800-MeV protons. The tantalum targets had a purity of >99.9%, weighed ~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 HNO_3 ; coprecipitation of hafnium (presumably as anionic fluorocomplexes) on CaF_2 ; extraction of hafnium from HClO_4 solution into thenoyltrifluoroacetone (TTA); and back-extraction into conc HCl. The overall chemical yield is $93 \pm 5\%$.

The ^{172}Hf decays (with a half-life of 1.87 y) to ^{172}Lu and the latter isotope transforms (with a half-life of 6.70 d) to stable ^{172}Yb . The ^{172}Hf - ^{172}Lu combination offers a possible medical generator system, in which the ^{172}Lu has potential applications in compound labeling and biodistribution studies in animal models. The availability of millicurie quantities of ^{172}Hf should serve to stimulate preclinical investigations of the lanthanide compounds in nuclear medicine.

2. Reagents

Hafnium carrier: 500 to 600 μg of metal in hafnium solution

HF: conc

HNO_3 : conc

HClO_4 : conc

HCl: conc

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 μg of hafnium carrier and 2 to 3 mL of conc HF/g of the target. Then add conc HNO_3 (dropwise initially) until dissolution is complete. The dissolution process usually requires ~3 h and a volume of HNO_3 that is slightly under half that of the HF.

Step 2. Dropwise, add 45 mg of Ca^{2+} as CaCl_2 solution (Note 1) and an additional mL of conc HF. Permit the fine white 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 Ca^{2+} to the supernate and repeat the coprecipitation procedure. Combine the CaF_2 precipitates (Note 2).

Step 3. Dissolve the CaF_2 precipitate in conc HClO_4 (~0.25 mL of acid/mg of Ca^{2+} precipitant), and dilute the solution to 2M in 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 Ca^{2+} added in the coprecipitation procedure and to ensure its complete removal from the final product.

2. Coprecipitation of hafnium with 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 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 CaF_2 to precipitate; sometimes only the addition of more Ca^{2+} will effect the complete removal of ^{172}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 $\text{Al}(\text{NO}_3)_3 \bullet 9\text{H}_2\text{O}$ added depends upon the amount of fluoride in the CaF_2 precipitate; 2.5 g of $\text{Al}(\text{NO}_3)_3 \bullet 9\text{H}_2\text{O}$ 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

P. M. Grant, M. Kahn,
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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% H_2O_2 to give a solution of molybdic acid, H_2MoO_4 . Following removal of excess H_2O_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 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}Sr and ^{85}Sr isotopes are obtained from the irradiation process. Because ^{82}Sr has a reasonably long half-life (25.55 d) and decays to an alkali metal of very short half-life (^{82}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 Sr^{2+}/ml , added as $\text{Sr}(\text{NO}_3)_2$ solution

HNO_3 : 7 to 8M

HCl : 0.12M

H_2S : gas

H_2O_2 : 30% aqueous solution (unstabilized)

NH_4OH : conc; 3.7M

NH_4Cl : 0.1M aqueous solution

$\text{Pb}(\text{NO}_3)_2$: 5 mg of Pb^{2+}/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 H_2SO_4

HDEHP solution: 50% solution by volume of di-2-ethylhexyl orthophosphoric acid in toluene

Hydrous 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_2O_2 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_2O_2 .

Step 2. By a careful combination of evaporation with gentle heating and the addition of conc NH_4OH , make the solution $\sim 1M$ 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 $Pb(NO_3)_2$ solution (5 mg of Pb^{2+}). A white precipitate of $PbMoO_4$ forms immediately. Stir the suspension, heat on a steam bath for 1 to 2 h, centrifuge, decant the supernate, and set aside. Wash the $PbMoO_4$ precipitate several times with a 0.1M NH_4Cl solution that has been made slightly alkaline by the addition of NH_4OH . 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 $PbMoO_4$ 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_4OH . A white precipitate, probably $Pb(OH)_2$, forms. Bubble H_2S 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_3 , 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_3 .

Step 6. Heat the filtrate to drive off any excess H_2S and adjust the pH to ~ 6.0 by the dropwise addition of conc NH_4OH . If necessary, add a few milligrams of strontium carrier in the form of $Sr(NO_3)_2$ 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_2 -exchange crystals (HZO-1) at a rate of ~ 0.1 ml/min. Collect the strontium-containing effluent.

(B) SEPARATION OF YTTRIUM

V. R. Casella, P. M. Grant,
and H. A. O'Brien, Jr.

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 12*M* 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}Sr with prominent gamma emissions of 898.04 keV (93.4%) and 1836.13 keV (99.4%). The latter photon will interact with ^9Be to produce monoenergetic neutrons of \sim 150-keV kinetic energy. The properties of ^{88}Y make it attractive for use with ^9Be as a photoneutron source in nuclear safeguards and other areas of research.

2. Reagents

HCl: 12*M*; 8*M*; 0.12*M*

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 0.12*M* 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 8*M* 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 12*M* 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

R. E. Whipple, P. M. Grant, R. J. Daniels, W. R. Daniels, and H. A. O'Brien, Jr.

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 8*M* HCl. Subsequent treatment of the organic phase with 30% H₂O₂ extracts molybdenum into the aqueous phase but has no effect on the zirconium. Extraction of the organic phase with 3.5*M* 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 5.8*M* in both HF and H₂SO₄. The overall yield of zirconium is 96 \pm 6%.

Zirconium-88 (half-life, 83.4 d) is the precursor of ^{88}Y . There would be advantages to incorporating the parent isotope into an ^{88}Y -Be photoneutron source as well. A combined ^{88}Y - ^{88}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; 3.5*M*

H₂SO₄: conc

H₂O₂: 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% H₂O₂. 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 H₂SO₄ 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.

(October 1989)

SEPARATION OF IRON AND SCANDIUM FROM A NICKEL TARGET

B. P. Bayhurst

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 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 H_2O 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 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 ScF_3 is precipitated. The latter is converted to the hydroxide and ignited to the oxide. The chemical yields are $\sim 85\%$ for iron and $\sim 95\%$ 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 Sc_2O_3 /ml, added as 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 HNO_3

HCl: conc; 10M; 7.9M; 5.5M; 0.1M

HNO_3 : conc

NH_4HF_2 -HF reagent: 4M in NH_4HF_2 and 1M in HF

Aqua regia: 3:1 conc HCl and HNO_3

NH_4OH : 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 H_2O and add an excess of conc NH_4OH . [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 H_2O and reprecipitate the hydroxides with conc NH_4OH . 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 H_2O 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 H_2O 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_2O layer with the previous one. To the aqueous extract, add an excess of conc NH_4OH to precipitate $Fe(OH)_3$, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 5. Dissolve the $Fe(OH)_3$ 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_4OH to precipitate $Fe(OH)_3$, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl , add 6 ml of filter paper pulp slurry, and reprecipitate $Fe(OH)_3$ with conc NH_4OH . 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_2O_3 .

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 $Sc(OH)_3$, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of conc HCl and reprecipitate the hydroxide with conc NH_4OH . Centrifuge and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 8. Dissolve the $Sc(OH)_3$ 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_4OH to precipitate $Sc(OH)_3$. Centrifuge and discard the supernate. To the precipitate add 3 ml of NH_4HF_2 -HF reagent (the scandium is converted to ScF_6^{3-}), and bring the solution to a methyl red end point with conc NH_4OH . Add 2 drops of lanthanum carrier, centrifuge, and transfer the supernate to a clean plastic tube. Discard the precipitate. Repeat the LaF_3 scavenge twice. To the supernate add 1.5 ml of conc NH_4OH 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_3 precipitate coagulates. Centrifuge and discard the supernate.

Step 10. Add 1 ml of 10M $NaOH$ to the ScF_3 and heat, while stirring, on a steam bath for a few minutes. Add 9 ml of H_2O , centrifuge, and discard the supernate. Dissolve the $Sc(OH)_3$ formed in a minimum of conc HCl , and reprecipitate the hydroxide with conc NH_4OH . Dissolve the precipitate in a minimum of conc HCl , add 6 ml of filter paper pulp slurry, and reprecipitate $Sc(OH)_3$ with conc NH_4OH . 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_2O_3 .

(October 1989)

SEPARATION OF CARRIER-FREE ALUMINUM FROM SILICON TARGETS

K. W. Thomas

1. Introduction

This procedure separates carrier-free ^{26}Al from a large silicon target (~ 100 g) that has been bombarded by 750-MeV protons. The target is dissolved in a mixture of equal volumes of conc HF and HNO_3 , and the silicon distills as SiF_4 during the dissolution process. After successive evaporation to dryness with conc HF, fuming HNO_3 , and conc 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}Na and ^7Be , 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}Al from ^{22}Na and ^7Be 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
 HNO_3 : fuming; conc
 HClO_4 : conc
 H_2O : 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, H_2O , 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 HNO_3 and HF at $\sim 100^\circ\text{C}$. The dissolution is carried out in a closed system; the 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 HNO_3 , and finally with conc HClO_4 . Slurry the residue with conc HClO_4 and transfer to a 40-ml Vycor centrifuge tube. Heat the slurry to dryness in an open furnace at 200°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, ~ 40 ml/h). Discard the effluent. (It contains large amounts of ^7Be and ^{22}Na .) Wash the column with 10 ml of the $\text{H}_2\text{C}_2\text{O}_4$ -HCl solution, 70 ml of H_2O , and 60 ml of $0.1M$ HCl. (These washes remove significant amounts of ^{22}Na and ^7Be .) Discard the washes.

Step 4. Elute the aluminum with 150 ml of $6M$ HCl. Carefully take the solution to dryness (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 1*M* 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 1*M* 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 HNO₃ and conc HClO₄ and then pass through an AG-MP1 column as in *Steps 2 and 3*, but use 50 mL of 0.25*M* H₂C₂O₄-0.1*M* HCl (rather than 10 mL) as a wash. (Use of the larger amount improves the separation of ⁷Be.)

Reference

E. S. Gureev, V. N. Kosyakoz, and G. N. Yakovlev, *Radiochimiya* **6**, 655 (1964).

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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 ~ 800 -MeV protons. The targets were 8-cm-square, 32-mm-thick slabs of tantalum metal (weight ~ 250 g). After irradiation, a target is dissolved in a mixture of conc HF and HNO_3 ; calcium carrier is added to precipitate CaF_2 , which carries hafnium and the lanthanides. The precipitate is dissolved in a H_3BO_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 10*M* 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-HNO_3 mixture: a 4:1 mixture by volume of the conc acids

HCl : conc; $10M$; $0.4M$

HNO_3 : fuming

H_3BO_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 (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 ℓ of HF-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 ~ 250 mg of calcium carrier and allow the CaF_2 precipitate that forms to settle. Decant the clear solution and centrifuge the remaining slurry. Wash the precipitate twice with H_2O . If more than one target slab is used, combine all CaF_2 precipitates.

Step 3. To the precipitate add H_3BO_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 H_2O to make the HCl concentration $<0.5M$. (If three slabs of tantalum target are used, the volume of solution is now ~ 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 10*M* 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 HNO_3 and boil to near dryness. Add 10 ml of conc HCl and boil to a volume of ~ 0.5 ml. Dilute to ~ 20 ml with H_2O . Add a slurry containing 1.5 ml of cation-exchange resin in H_2O , centrifuge, and discard the supernate. Wash the resin with 10 ml of H_2O 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 H₂O. 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}Br , ^{82}Sr , ^{85}Sr , AND ^{88}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 HNO_3 - H_3PO_4 plus Cl^- carrier mixture. Bromine and chlorine are evolved as gaseous species and are trapped as AgX in a AgNO_3 solution. The silver halide is dissolved in aqueous NH_3 and the silver is adsorbed as $\text{Ag}(\text{NH}_3)_2^+$ on a cation-exchange resin; the radioactive Br^- and carrier 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 6*M* HCl. The effluent, made ~9*M* in HCl, is passed through an anion resin column; those ions that give relatively stable anionic chloro complexes (for example, Zn^{2+} and 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 6*M* 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 0.5*M* 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: 0.1*M*; 0.5*M*; 6*M*; conc

HNO_3 - H_3PO_4 reagent: 550 ml of conc HNO_3 , 250 ml of conc H_3PO_4 , 200 ml of H_2O , and 2 mg of Cl^- carrier, added as NH_4Cl

NaOH: 0.1*M*; 4*M*; 50 wt% aqueous solution

NH_4OH : 3*M*

AgNO_3 : 0.01*M*

1,4-Dioxane

Toluene

HDEHP (di-2-ethylhexyl orthophosphoric acid)

2,4-Pentanedione (acetylacetone)

Cation-exchange resin: Dowex 50-X4, 100 to 200 mesh, NH_4^+ form

Cation-exchange resin: Dowex 50-X4, 100 to 200 mesh, 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 ~40 mA•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-l erlenmeyer flask, add 50- to 75-ml increments of HNO_3 - H_3PO_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 ~500 ml.) Bromine and carrier chlorine are absorbed in the trap containing AgNO_3 solution (0.01*M*). Other gases (for example, oxides of nitrogen) collect in the NaOH (4*M*) trap.

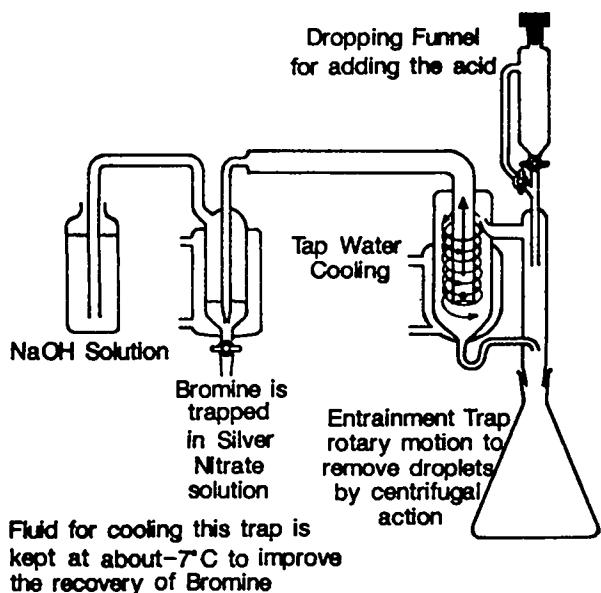


Fig. 1. Schematic of hot-cell equipment for recovering radioactive bromine from molybdenum.

Step 2. Centrifuge the silver halides in the AgNO_3 trap and discard the supernate. Wash the precipitate with ~ 4 ml of H_2O , centrifuge, and discard the wash. As quickly as possible, dissolve the precipitate in 5 ml of 3M NH_4OH . (Radiation reduces AgBr and 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 (NH_4^+ form; 4-mm i.d. by 50-mm length) with 3M NH_4OH . 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 NaOH . The $\text{Ag}(\text{NH}_3)_2^+$ ion is adsorbed on the column. Wash the column with 1 ml of H_2O and combine effluents.

Step 4. Heat effluents to drive off NH_3 . The solution contains radioactive bromine as 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 H_2O ; then add two volumes of 1,4-dioxane. Pass the solution through a Dowex 50-X4, 100 to 200 mesh, cation resin column (H^+ form; 30-mm i.d. by 100-mm length; preconditioned with a mixture of $\text{HNO}_3\text{-H}_3\text{PO}_4$, H_2O , 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, 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 HCl through the column to elute Sr^{2+} , 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 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 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 9. Use a volume of 6M 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% 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_2O 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}Sr , ^{85}Sr , ^{88}Y , AND ^{88}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% H_2O_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 6*M* HCl. The effluent, made $\sim 9\text{M}$ 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 3*M* 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 6*M* 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 0.5*M* 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; 0.1*M*; 0.5*M*; 3*M*; 6*M*; conc

NaOH: 50 wt% aqueous solution

H_2O_2 : 30% aqueous solution (unstabilized); 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 $\text{A}\cdot\text{h}$. The irradiation produced ~ 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 H_2O_2 . Then add sufficient H_2O_2 to make the color of the solution yellow. A total of ~ 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% H_2O_2 and then with 100 ml of H_2O 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 6*M* 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 3*M* 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-pantanenedione, and toluene. (The 2,4-pantanenedione 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 H₂O 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 HNO_3 and H_3PO_4 or in 30% H_2O_2 . The former method of dissolution is preferred.

The dissolved sample is passed through a cation-exchange resin column; MoO_4^{2-} and other anions formed in the solution process pass through the column. The resin is then washed with 0.5M NH_4Cl solution to elute rubidium, the resin being converted to the 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 H_2O and the resin is then converted to the H^+ form with 0.5M HCl, a process that removes more manganese. Strontium is finally eluted from the resin by 6M HCl. (If H_2O_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}Sr and ^{85}Sr is obtained; chemical yields are as high as 90%.

2. Reagents

HCl: 0.5M; 6M; conc

$\text{HNO}_3\text{-H}_3\text{PO}_4$ solution: 500 ml of conc HNO_3 , 250 ml of conc H_3PO_4 , and 200 ml of H_2O

Aqueous H_2O_2 solutions: 10%; 30%

NH_4Cl : 0.5M

Dioxane

Dioxane- H_2O : 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% H_2O_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% H_2O_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 ~50 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- H_2O solution and then with 250 ml of H_2O . If H_2O_2 was the solvent, wash the column with 250 ml of 10% H_2O_2 solution followed by 250 ml of H_2O . Discard all effluents.

Step 3. To the column, add successively 500 ml of 0.5M NH_4Cl solution, 500 ml of alpha-HIB solution (0.5M; pH 5), 100 ml of H_2O , and 250 ml of 0.5M 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 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 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 H_2O . 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 1*M* HCl until the eluate, which contains the zirconium, shows no activity.

Step 4. Make the effluents from *Step 2* 1*M* in HCl and pass the solution through a fresh AG 50-X8 cation-exchange resin column. The ^{88}Y , which has grown in from ^{88}Zr , is adsorbed on the column and rubidium passes through.

(October 1989)

SEPARATION OF CURIE QUANTITIES OF IRON FROM AN IRRADIATED NICKEL TARGET

H. A. O'Brien, Jr., P. M. Grant, G. E. Bentley,
J. W. Barnes, and H. M. Zacharis

1. Introduction

Curie quantities of ^{52}Fe are produced through spallation of a nickel target by 800-MeV protons. Following the irradiation process, the target is dissolved in conc HNO_3 , the solution is made 6*M* in HCl , and the iron is extracted into methylisobutylketone (MIBK). Two washings of the organic layer with a mixture 6*M* in HCl and 3% in H_2O_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}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

HNO_3 : 10*M*

HCl : conc

H_2O_2 : 3%

MIBK (methylisobutylketone; 4-methyl-2-pentanone): equilibrated with 6*M* HCl just before use

3. Procedure

The nickel target (~ 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 $\sim 50 \text{ ml}$ of 10*M* HNO_3 , and make the solution 6*M* 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 6*M* in HCl and 3% in H_2O_2 . (The H_2O_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 H_2O 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)

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}U and of plutonium with ^{242}Pu ; (2) extraction of these elements as nitrates into ethyl acetate from a 1M HNO_3 solution saturated with NH_4NO_3 ; (3) back-extraction into H_2O ; (4) adsorption of the uranium and plutonium on an anion-exchange resin column; (5) washes with 0.1M H_2SO_4 and 10M HCl, followed by elution of plutonium(III) by means of an HI-HCl mixture and uranium by HNO_3 after washes with 0.1M H_2SO_4 and 8M HCl; and (6) separate treatment of the uranium and plutonium on macroporous anion-exchange resins; the elements are adsorbed from a H_2O_2 -HCl solution, and after appropriate washes of the resins, the uranium is eluted with H_2O and the plutonium with 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}Zr and ^{97}Zr , ^{95}Nb , ^{99}Tc , ^{103}Ru , ^{229}Th , ^{131}Te , and ^{132}Te remain with the uranium. Relatively large amounts of the salting out agent, NH_4NO_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 H_2SO_4 wash. Large amounts of H_2SO_4 and 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}Tc and ^{95}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 ~80% and plutonium recovery ~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}U tracer: source, National Bureau of Standards (NBS)
 ^{242}Pu tracer
 HClO_4 : conc
 HNO_3 : conc; 8M; 2M; 1M
 HBr : 47%; source, MCB Reagents
 HCl : 10M; 8M; 6M; 1.5M
 H_2SO_4 : 0.1M
Aqua regia: 3:1 mixture, by volume, of 10M HCl and conc HNO_3
HI-HCl mixture: 1:9 mixture, by volume, of 48% HI and 10M HCl
 H_2O : Type 1 reagent-grade water (deionized)
 H_2O_2 -HCl reagent: 1 drop of 30% H_2O_2 to 9 ml of 10M HCl
 NH_4NO_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 HCl and 50% H_2O . It is washed 20 times with deionized H_2O and stored as an H_2O 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}U tracer in amount to provide approximately equivalent ratios of $^{233}/^{235}$ and $^{238}/^{233}$, and then add ^{242}Pu tracer equal to the estimated quantity of ^{239}Pu . Add 2 ml of conc HClO_4 and evaporate to dryness (Note 2).

Step 2. Add 5 ml of 2M HNO_3 and sufficient solid NH_4NO_3 to saturate the solution, and warm to room temperature. (The addition of the NH_4NO_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 HNO_3 that has been saturated with NH_4NO_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 H_2O , 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 NH_4NO_3 . Add 1 ml of 10M HCl and evaporate to dryness. Add 1 ml of 0.1M H_2SO_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 H_2O washes and one 1-ml 0.1M H_2SO_4 wash. Discard the effluent. Wash the tube with 1 ml of 0.1M H_2SO_4 and add the wash to the resin column (Note 5). Discard the effluent. Add 1 ml of 10M HCl containing a trace of HNO_3 (10 ml of HCl + 1 drop of conc HNO_3) to the column and discard the effluent. Rinse the tip of the column with a stream of deionized H_2O .

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 H_2O .

Step 6. Elute uranium with 1 ml of 1M HNO_3 and 1 ml of conc 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 I^- , add 1 drop of conc 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 H_2O_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 H_2O washes and three 1-ml H_2O_2 -HCl reagent washes. Use one additional portion of 1 ml of the H_2O_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 H_2O and elute the uranium with three successive 1-ml portions of deionized H_2O ; 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 HNO_3 and 3 drops of conc HClO_4 and heat to 130°C for 1 h. Evaporate to dryness at a temperature >180°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}U to affect the determination of ^{238}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 HNO_3 (Note 7). Wash the tip of the column with a stream of deionized H_2O and elute the plutonium with three 1-ml portions of 47% 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 HBr solution of plutonium to dryness in a heating block. Destroy the traces of HBr and organic material from the remaining macroporous anion resin by adding 3 drops of conc HNO_3 and 3 drops of conc HClO_4 and heating to 130°C for 1 h in a heating block. Evaporate to dryness at a temperature greater than 180°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 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 ~110°C) followed by at least one strong fuming (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: ~95% of the uranium, ~80% of the plutonium, ~50% of the neptunium, 60 to 80% of the zirconium, and traces of niobium, technetium, ruthenium, tellurium, and iron; of course, NH_4NO_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}U with a radiation meter, if possible.

5. The H_2SO_4 is effective in the removal of the remaining ^{239}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 H_2SO_4 , but uranium sticks quantitatively. In *Step 4* when the uranium and plutonium are being dissolved in the warm 0.1M H_2SO_4 , care must be taken to avoid concentration of the H_2SO_4 by evaporation. A 0.5M H_2SO_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}Pu mass peak.

6. The final solution is assayed for ^{233}U by alpha-counting to determine chemical yield. Also, at this point an aliquot may be removed for ^{237}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 HNO₃ needed here and in the quantities of 6M HCl required on the macroporous anion resin cleanup column. Therefore, the relative amount of ⁹⁵Zr (by means of its 724- and 756-keV gammas) and of ²³⁷U (by means of its 208-keV gamma) should be ascertained with a multichannel pulse height analyzer and the amount of ²³⁹Pu 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 HNO₃ and HClO₄, and the residue is dissolved in 9M HCl that contains enough H₂O₂ 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 HClO₄ 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% H₂O₂ is warmed at ~90°C for 20 to 30 min to ensure the presence of a small amount of free Cl₂, which prevents reduction of plutonium on the column.

HNO₃: conc; source: NBS

HClO₄: 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

H₂O: Use only H₂O that has been deionized by passing through a Milli-Q H₂O system.

3. Ion-Exchange Column Preparation

Disposable plastic pipette tips are used for ion-exchange columns. These are cleaned by immersion in 8M HNO₃ at 80°C for 48 h. The tips are then rinsed thoroughly with Milli-Q H₂O 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 HNO₃ at ~80°C for 48 h. After thorough rinsing in Milli-Q H₂O, 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 HNO₃ (as previously described for the disposable pipette tips).

All transfers are performed using transfer pipettes, which are cleaned by immersion in 8M HNO₃ for 48 h at 80°C. After thorough rinsing with Milli-Q H₂O, 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 HNO₃ for 48 h at 80°C. After thorough rinsing with Milli-Q H₂O, 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 ~ 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.

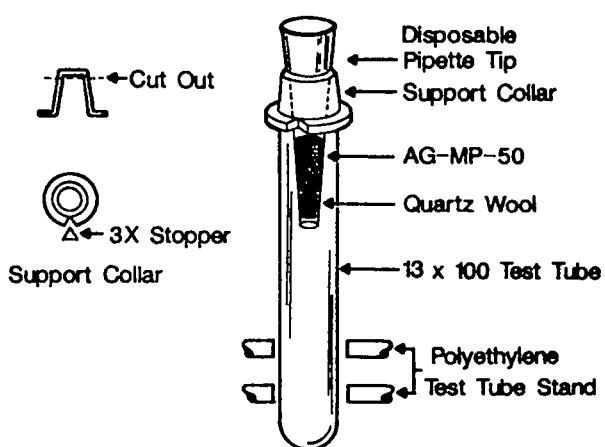


Fig. 1. Details of micro ion-exchange column.

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 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 HNO_3 and evaporate the solution to a small volume. Then add a few drops of conc HClO_4 and fume to dryness.

Step 3. To the dry Pyrex tube containing the recovered plutonium, add ~ 1 ml of 9M HCl containing a trace of free 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 H_2O and fume to $\sim 0.5\text{ ml}$. Add 3 to 4 drops of conc HNO_3 and fume to dryness. Add 3 drops of conc HClO_4 and evaporate to fumes at 130°C . Increase the temperature to 180°C and fume for 1 h, adding 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 HNO_3 for 48 h and rinsed with Milli-Q H_2O). 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)

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. Knobeloch

1. Introduction

The successful dissolution of underground nuclear debris samples depends basically on repeated evaporations with conc HF to convert SiO_2 and silicates to volatile 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

HNO_3 : fuming
 HClO_4 : conc
HF: conc
 HCl : 3M
 NaOH : 6M

3. Procedure

Step 1. Place the dried, pulverized sample in a cylindrical Teflon vessel of $\sim 700\text{-mL}$ capacity. Add 25 mL of fuming HNO_3 , 100 mL of conc HClO_4 , and, with care, 50 mL of conc HF. Heat to strong fumes of 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 HClO_4 .

Step 3. Repeat *Step 2* twice. (If 10 g of debris are being dissolved, repeat *Step 2* four times; add HClO_4 as necessary to prevent the sample from becoming dry.)

Step 4. Evaporate until the volume is ~ 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 H_2O . Rub the inner surfaces well and flush them with H_2O to remove adhering 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 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 HClO_4 . Cool, add 50 mL of conc HF, and evaporate the solution until the volume is ~ 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 ≤ 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 SiO_2 by reaction with HF at ~ 0.25 atm of pressure and a temperature near the boiling point of H_2O . 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 HNO_3 and conc HClO_4 , and the mixture is evaporated to dryness. The residue is dissolved in dilute HNO_3 .

All operations are carried out in a hot cell by using manipulators.

2. Reagents

HF: conc; gas

HNO_3 : 90% (yellow fuming); 1M

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 H_2O to remove drilling mud, (2) selection of the portions of high specific activity, and (3) drying and grinding.

Step 1. Add the sample (~ 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 (H_2O aspirator.)

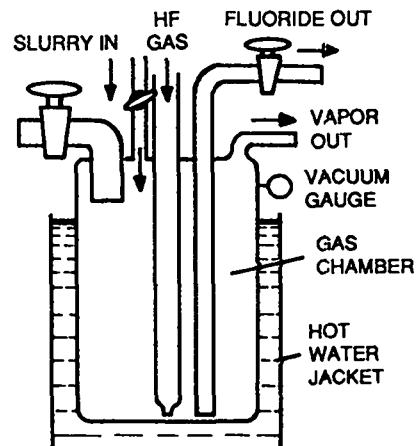


Fig. 1. Dissolver and gas chamber.

Step 2. After 15 minutes, begin to heat the H_2O jacket surrounding the chamber and decrease the pressure to ~ 0.25 atm. While the HF flow is maintained, rapidly raise the temperature of the H_2O 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 H_2O 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 ~ 10 min (Note 4). Pour off the supernate containing the zirconium and niobium into a 2-l Teflon beaker. Wash the precipitate twice with ~ 0.75 l of H_2O ; 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).

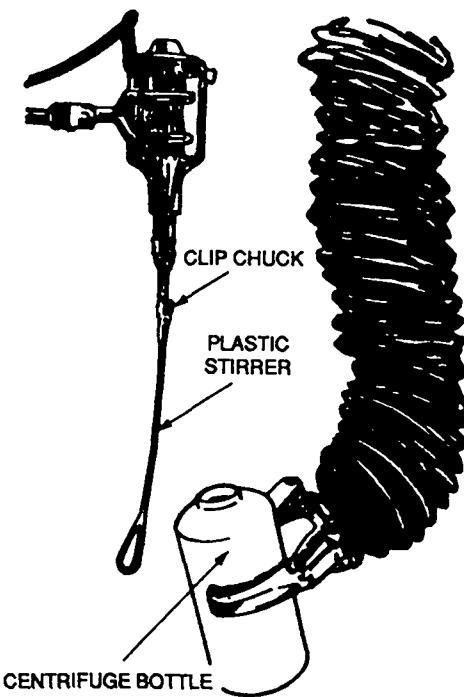


Fig. 2. Centrifuge bottle and stirrer.

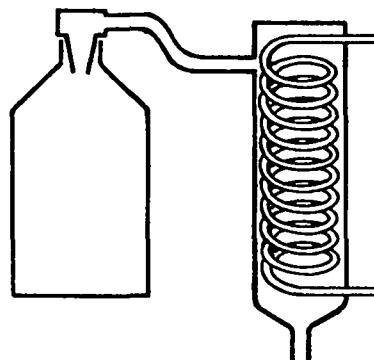


Fig. 3. Teflon evaporation equipment.

Step 4. Add 160 ml of 90% HNO₃ and 240 ml of 70% HClO₄ to the precipitate and stir. Pour the slurry into a 0.6-*l* 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 HNO₃ 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% HNO₃, and 70% HClO₄—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 ~6 in. from the top. It was equipped with a special head (source: International Equipment Company) for holding four 1-*l* bottles.

5. Bottles of 0.6- to 2-*l* 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% HClO_4 in the presence of a small amount of 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 CO_2 liberated in the dissolving process. This possibility is avoided through the use of a device for separating the droplets from the CO_2 and returning them to solution.

Activated charcoal is first partially ignited in O_2 and then dissolved in 90% HNO_3 and 70% 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% HNO_3 .

(A) Dissolution of Bulk Graphite That Contains Uranium and Niobium Carbides

1. Reagents

HClO_4 : 70%

HNO_3 : 90% (yellow fuming)

HF: conc

HCl : 6M

HCl-HF solution: 4M in HCl and 0.3M in HF

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.

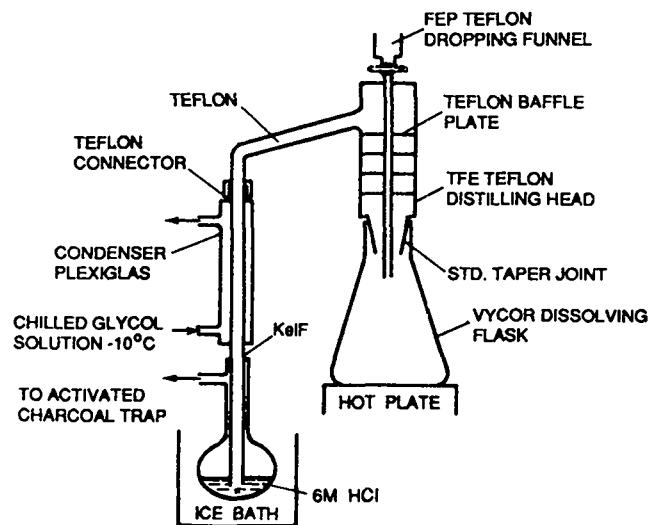


Fig. 1. Dissolution apparatus.

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 CrO_3 and 150 ml of 70% 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% 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 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 H_2O ; 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

HClO_4 : 70%

HNO_3 : 90% (yellow fuming)

HCl: 4M

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 O_2 tank. Heat the bottom of the beaker to raise the temperature of the sample to ~600°C. Pass O_2 slowly over the sample and continue heating for 2 h. (Too rapid an 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% HNO_3 and 100 ml of 70% HClO_4 . Boil on a hot plate while adding 50 ml of 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 H_2O to bring the volume to ~40 ml. Filter into a 500-ml volumetric flask and make up to volume with H_2O . The solution can now be analyzed for fission products.

Note

It would not be necessary to add the CrO₃ initially if it were possible to add the fuming HNO₃ at that time. If HNO₃ is added initially with the HClO₄, the reaction proceeds smoothly at first, but when the greenish fumes characteristic of Cl₂ are replaced by the white fumes of HClO₄, enough pressure is generated in the system to blow the sample into the condenser or explode the equipment.

(October 1989)

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 O₂ and N₂ 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 ⁸⁵Kr 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 ($\sim 2 \text{ l}$) obtained under vacuum at depth in a well or from the surface.

Carrier gas bulbs: A set of bulbs of known volume ($\sim 12 \text{ ml}$ each) filled sequentially with xenon and krypton at measured pressure and temperature.

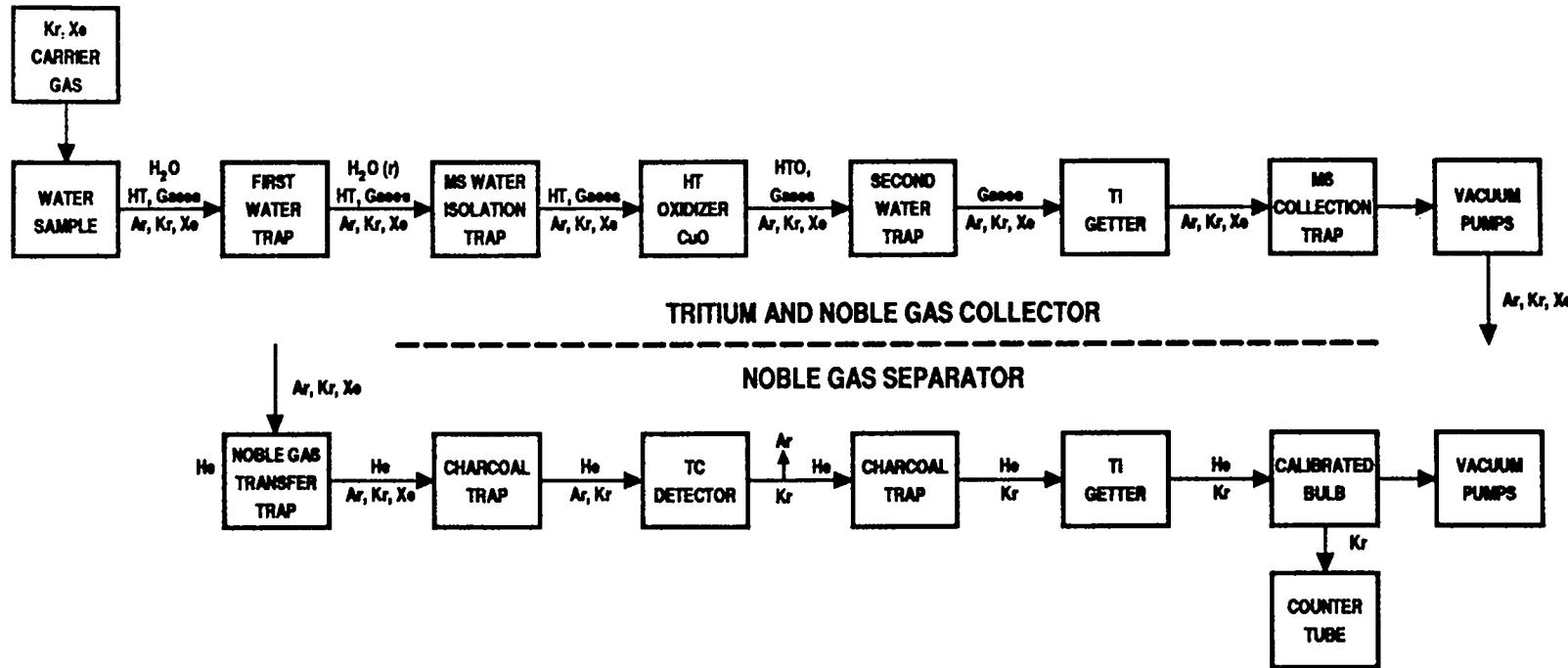


Fig. 1(a). Functional diagram of vacuum system.

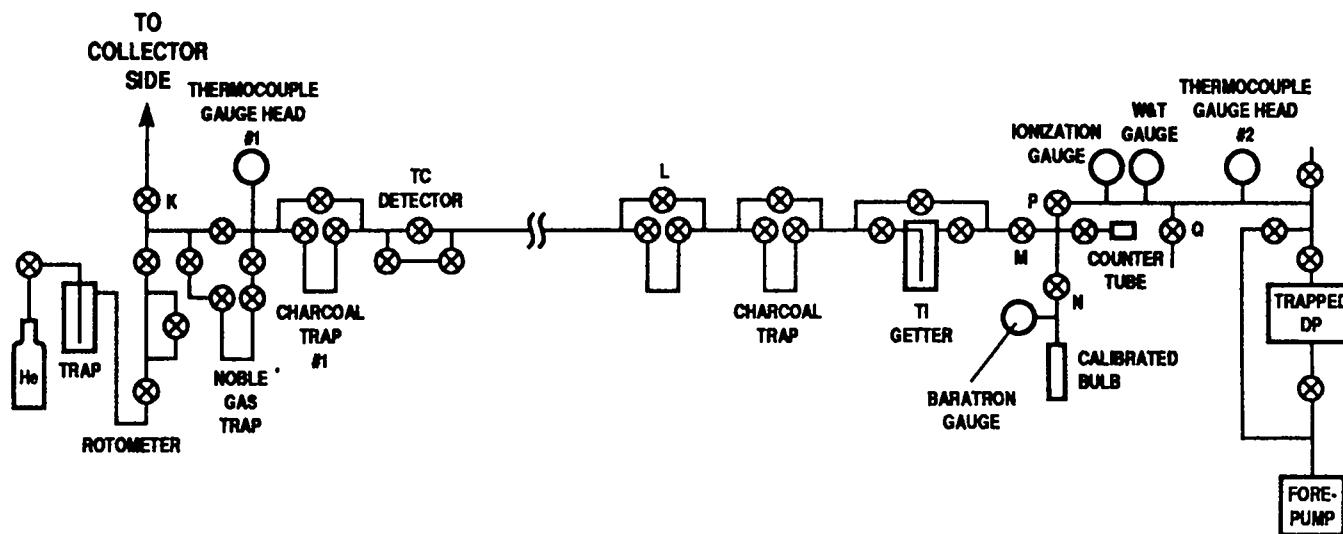
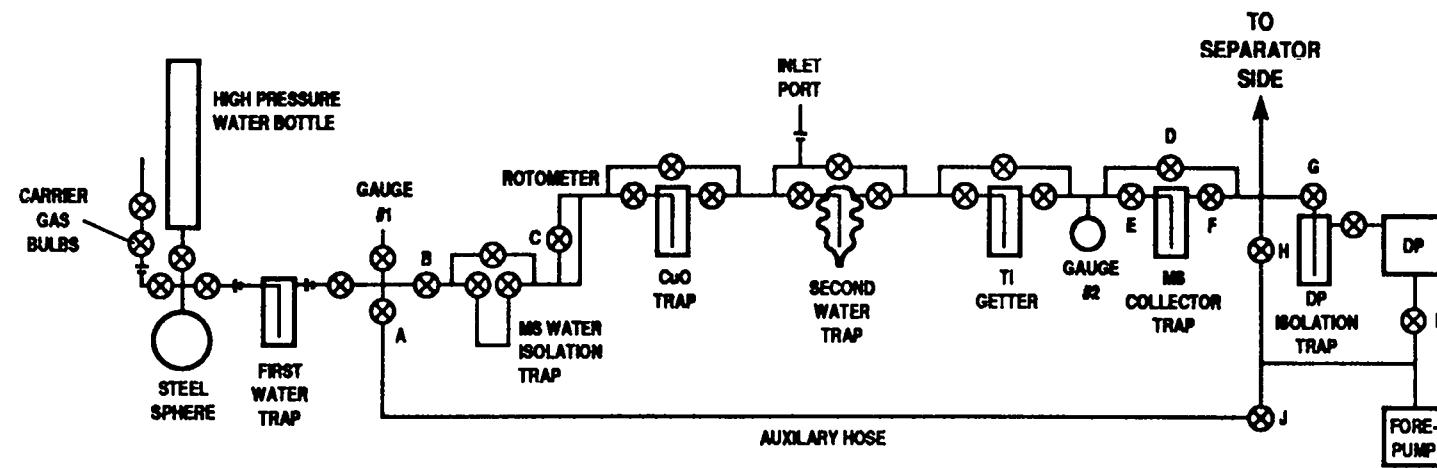


Fig. 1(b). Detailed scheme of both the collector side and the separator side of the vacuum system.

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 H₂O 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 N₂, O₂, 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 N₂ 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 N₂ 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 N₂, O₂, 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 N₂.

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 H₂O 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 4×10^{-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 N₂ 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 N₂

DP isolation trap: liquid N₂

Step 4. Isolate the second water trap by closing the appropriate valves. Add 500 λ 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 H₂O will be collected in the first H₂O 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 N₂ coolant from the MS collector trap, and place an auxiliary furnace (maintained at 450°C) on this trap. Precool the noble gas trap with liquid N₂, 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°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 H₂O 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 H₂O, 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 H₂O isolation trap. Momentarily close off the DP (valve G) and pump out the system through the forepump (open valve H). Heat the drop of H₂O in the first H₂O 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_2O 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_2O bottle. (This bottle should be rinsed with deionized H_2O before reuse.) Measure the volume of H_2O in the sphere and transfer the H_2O to a labeled bottle. Rinse the sphere thoroughly with deionized H_2O , and leave $\sim 1\ell$ of H_2O 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_2O and steam to escape. Collect a sample of the H_2O 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 5×10^{-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 chlorothene- N_2 slush bath (-33°C) and place liquid N_2 coolants on the two charcoal traps. (Chlorothene is 1,1,1 trichloroethane, also known as methyl chloroform.) Turn on the two furnaces set to operate at 450°C , the furnace for the titanium getter trap for 900 to 1000°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_2 on charcoal trap No. 1 with the chlorothene-liquid N_2 slush; mark the time on the chart paper. Argon will be eluted in ~ 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.

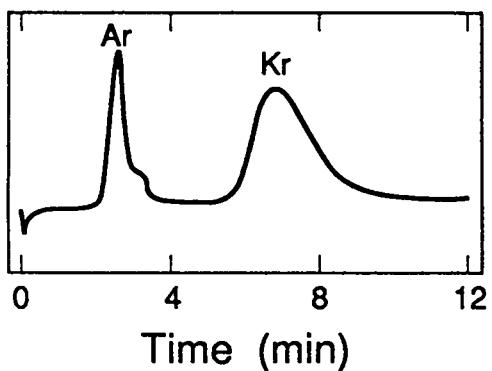


Fig. 2. Elution curve for argon and krypton.

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 N₂ 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 H₂O 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 N₂. 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 $<10^{-4}$ 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 $<300^\circ\text{C}$.

(October 1989)

THE SEPARATION OF IODINE FOR NEUTRON ACTIVATION ANALYSIS OF IODINE-129 IN LARGE AQUEOUS SAMPLES

K. Wolfsberg, K. S. Daniels, and S. Fraser

1. Introduction

The following are the major chemical steps in the measurement of trace quantities of ^{129}I in large aqueous samples. After the addition of 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 I^- carrier, is first adsorbed on an anion-exchange resin, from which it is removed as IO_3^- by oxidation with NaClO in conc HNO_3 . Any Br_2 is removed by extraction with CCl_4 , and IO_3^- is reduced to I_2 by $\text{NH}_2\text{OH} \cdot \text{HCl}$. Following a cycle of reduction (to I^-), oxidation (to I_2), and reduction, I^- is again adsorbed on an anion-exchange resin. The resin is then irradiated.

Iodide is removed from the irradiated resin by treatment with NaClO . The IO_3^- formed is reduced to I_2 by $\text{NH}_2\text{OH} \cdot \text{HCl}$ and then to I^- by NaHSO_3 . Finally, the I^- is converted to I_2 (with acidic NaNO_2), again reduced to 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
 HNO_3 : conc; 6M
 NH_4OH : 0.3M
 NaClO : ordinary bleach solution, fresh or stored cold
 $\text{NH}_2\text{OH} \cdot \text{HCl}$: 1M
 NaHSO_3 : 1M
 NaNO_2 : 1M
 KBr : 1M
 AgNO_3 : 1M
 CCl_4 : cold

Ethanol
Toluene
Acetone
 SO_2 : gas

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh (HSO_4^- form)

3. Procedure

Step 1. To the sample (up to 12 ℓ), add 30 mg of iodine carrier. Wait ~ 24 h and pump the sample through a 1- by 10-cm column of the Bio-Rad AG 1-X8 resin.

Step 2. Use ~ 10 mL of distilled H_2O to rinse the resin from the column into a beaker, and add 3 mL of NaClO . Heat on a steam bath for 5 min, remove from the bath, and add 3 mL of conc HNO_3 and 1 mL of 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 CCl_4 to the solution and extract any Br_2 present. If the CCl_4 extract is yellow, repeat the extraction. Discard the CCl_4 phases.

Step 4. To the aqueous phase add 3 mL of $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution, extract the I_2 with 15 mL of toluene, and discard the aqueous phase. Wash the toluene layer twice with 10- mL portions of H_2O and discard the washes.

Step 5. Add 10 mL of H_2O to the toluene layer and then 1M 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 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 NaNO₂ to convert I⁻ to I₂. Shake the funnel to extract the I₂ into the toluene and discard the aqueous layer. Wash the toluene with two 10-ml portions of H₂O and discard the washes.

Step 8. Bubble SO₂ through H₂O; maintain at ice-bath temperature until a saturated solution of the gas is formed. Add the SO₂ solution dropwise to the toluene until the color of I₂ 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 SO₂.

Step 10. Adjust the pH to ~6 with 0.3M NH₄OH, 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 H₂O 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 H₂O, 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 Br₂ in solution by shaking with 10 ml of CCl₄. Discard the CCl₄. 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 NH₂OH•HCl and 15 ml of toluene. Extract I₂ into the toluene and discard the aqueous phase. Wash the toluene layer twice with 10 ml of H₂O and discard the washes.

Step 16. To the toluene add 10 ml of H₂O, convert I₂ to I⁻ as in *Step 5* by the dropwise addition of 1M NaHSO₃, 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 H₂O layer add 1 ml of 6M HNO₃ and boil vigorously for 15 to 30 s. If I₂ appears, reduce it by the dropwise addition of 1M NaHSO₃.

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 AgNO₃. Stir and heat on a steam bath for 5 min. Cool and centrifuge for 5 min.

Step 22. Decant the supernate. Add H₂O and break up the precipitate. Using a stream of H₂O, filter the precipitate on a preweighed filter paper. Wash the precipitate three times with 5-ml of H₂O 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. Cappis

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_2O was purified by passing "house" deionized H_2O through a Milli-Q H_2O purification system.

HF: conc (NBS)

HClO_4 : conc (NBS); 1.2M

HNO_3 : conc (NBS)

Lead spike: lead enriched in ^{208}Pb ; source: Oak Ridge National Laboratory

Uranium spike: ^{233}U

HCl: conc (NBS); 8M; 1.5M

H_2SO_4 : 0.1M; made from Suprapur MCB reagent

H_3PO_4 : 10 g of sublimed high-purity P_4O_{10} dissolved in 250 ml of H_2O . (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

$\text{HCl-H}_2\text{SO}_4$ mixture: 8M in HCl and 3M in H_2SO_4

$\text{HNO}_3\text{-H}_2\text{O}_2$ mixture: 2M in HNO_3 and 2% in H_2O_2

HCl-NH₄Cl solution: pH 2.8

NH_4OH : prepared by bubbling high-purity anhydrous NH_3 through H_2O

Anion-exchange resin: Bio-Rad AG 1-X8, 100 to 200 mesh (Cl^- form). Resin and Milli-Q H_2O 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: $\frac{1}{2}$ in. by $\frac{1}{8}$ 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 H₂O. The equipment is then placed in a solution of equal volumes of reagent grade HCl and Milli-Q H₂O 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 H₂O. The heating treatment is repeated, first in aqua regia, next in a mixture of equal volumes of analytical reagent HNO₃ and Milli-Q H₂O, and finally in Milli-Q H₂O that contains a trace of HNO₃. After the cleaning processes, the pieces of equipment are covered with Milli-Q H₂O.

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 HNO₃ in a weighed bottle. The resulting solutions are made to volume with Milli-Q H₂O 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 HNO₃ and diluting with Milli-Q H₂O 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 SiO₂ 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 SiF₄.) 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_4 (1:1 by volume) and again take the sample to dryness. Fume the residue to dryness with conc HClO_4 to remove fluorides. This treatment may have to be repeated. If insoluble carbonaceous material remains, dissolve it by fuming with a conc HClO_4 -conc HNO_3 mixture (1:1 by volume). Convert the residue to nitrates by multiple fumings with conc HNO_3 .

Take up the residue of nitrates in a mixture of equal volumes of conc HNO_3 and H_2O , and centrifuge the solution to remove any insoluble minerals remaining. Transfer the supernate to a clean, weighed Teflon bottle and make up with H_2O 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 1*M* 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^- 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_2O 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 1*M* HBr . Discard

all effluents. Add two 1-ml portions of 1.5*M* 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_4 , and take the solution to dryness. Repeat the HClO_4 treatment. Add 50 μl of 1.2*M* HClO_4 and then 7 ml of H_2O 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_4OH 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 1.5*M* HCl that is delivered dropwise on the anode by means of a pipette. Add 10 μl of H_3PO_4 to the solution to prepare it for mass spectrometric analysis.

Mix another aliquot of sample solution with a weighed aliquot of the ^{208}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 ^{233}U spike. (If only the isotopic composition is of interest, no spike is added.) Dry the sample at low heat and take up in 8*M* HCl . Prepare an anion-exchange resin column as described in Sec. 6B, but use 8*M* HCl rather than HBr for the final rinse. Load the sample on the column and add 1 ml of 8*M* HCl to rinse the sides of the reservoir. Discard the effluent. Add successively to the resin 2 ml of 8*M* HCl , 1 ml of $\text{HCl-H}_2\text{SO}_4$ mixture (8*M* in HCl and 3*M* in H_2SO_4), 3 ml of 0.1*M* H_2SO_4 , and 3 ml of 8*M* HCl . Discard all effluents. Then add 1 ml of H_2O to elute uranium, and collect the eluate in an electroplating cell. Add 2 ml of $\text{HNO}_3\text{-H}_2\text{O}_2$ mixture (2*M* in HNO_3 and 2% in H_2O_2) 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-NH₄Cl 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 H₃PO₄ 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 ~ 90 V. The total sample should contain ~ 100 ng of lead. The loading process is described here.

Rinse a Teflon tube in H₃PO₄; draw the acid into the tube farther than the 5- μl sample will reach. Repeat the rinse three times and discard all rinsings. Pick up 5 μl 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 H₃PO₄ and use it to load 5 μl 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

H₃PO₄ begins to fume (~ 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 ~ 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 ~ 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).

$$\text{fractionation factor} = \frac{(A/B)_{\text{Known}} - 1}{(A/B)_{\text{Meas}} - 1} \quad (1)$$

$$\frac{(A/B)_{\text{Known}} - 1}{(A/B)_{\text{Meas}} - 1} \quad .$$

A and B are the isotopes of the element of interest, and ΔM 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).

$$(A/B)_x = (A/B)_{\text{Meas}} + B_{Bl}/B_x[(A/B)_{\text{Meas}} - (A/B)_{Bl}] \quad (2)$$

B_{Bl} is the quantity of isotope B in the blank and $(A/B)_{Bl}$ 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).

$$A_x = \frac{(A/B)_{\text{Meas}} - (A/B)_{Sp}}{1 - [(A/B)_{\text{Meas}} / (A/B)_x]} B_{Sp} \quad . \quad (3)$$

$(A/B)_{\text{Meas}}$ 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. $(A/B)_{Sp}$ is the isotope ratio in the spike, $(A/B)_x$ is the corrected isotope ratio in the unspiked sample, and B_{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}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}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).

$$(A/B)_x = (A/B)_{\text{Meas}} - B_{Sp}/B_x[(A/B)_{\text{Meas}} - (A/B)_{Sp}] \quad (4)$$

$$- B_{Sp}/B_x[(A/B)_{\text{Meas}} - (A/B)_{Sp}]$$

$(A/B)_x$ 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.

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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

H₂SO₄: 6M

H₃BO₃: solid

KI: solid; 10% aqueous solution

KIO₃: solid; 2.5×10^{-3} M; standardized

(NH₄)₂SO₄•FeSO₄•6H₂O: primary standard

CCl₄

2. Preparation of ICl reagent

Add 10 g of KI and 6.44 g of KIO₃ to 150 mL of H₂O 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 CCl₄ and, while stirring, add 10% KI dropwise until the color of I₂ appears in the CCl₄ (lower) layer. Remove the CCl₄ 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 CCl₄ and shake vigorously for 3 h on a wrist-action shaker. Use a transfer pipette to remove the pink CCl₄ 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 KIO₃ solution

In a 1-L volumetric flask, dissolve 7.002 g of (NH₄)₂SO₄•FeSO₄•6H₂O (primary standard) and combine with sufficient H₂SO₄ 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 KIO₃ 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 CCl₄. 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 CCl₄ 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 I₂. The latter dissolves in the CCl₄.

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 H₃BO₃. With the stopper attached to the centrifuge tube, centrifuge the oxidized sample from *Step 1* to remove any trapped CCl₄ 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 H₃BO₃. To prevent loss of I₂ to the air, take great care to ensure that some of the

aqueous phase is on both sides of the CCl_4 in the transfer pipette. While stirring, titrate the I_2 with the standardized KIO_3 solution; disappearance of the pink I_2 color in the CCl_4 layer indicates that titration is complete. Calculate the amount of iron(II) present in terms of percent FeO .

(B) Determination of Total Iron

1. Reagents

HClO_4 : conc

HF: conc

HNO_3 : conc

HCl: conc; 6M; 0.1M

Aqua regia

NH_4OH : conc

NaOH : 10M

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

$(\text{NH}_4)_2\text{SO}_4 \bullet 6\text{H}_2\text{O}$: 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 ethylenediaminetetraacetic acid; 4.0000 g in 1 L of H_2O ; 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 HNO_3 . Repeat the HCl treatment. Make the solution up to 1 L so that it is ~0.1M in HCl.

Dissolve 4.0000 g of the disodium salt of ethylenediaminetetraacetic acid in H_2O and dilute to 1L (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 ~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 Fe_2O_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 HClO_4 , 2 mL of conc HNO_3 , and 4 mL of conc HF. Evaporate on a hot plate to HClO_4 fumes. Cool, carefully add 4 mL of conc HF, and again evaporate to HClO_4 fumes. Repeat the HF treatment. Fume off all but ~1 mL of the 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 NH_4OH , then add 4 drops more of the conc NH_4OH . 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 Fe(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 ~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 Fe_2O_3 .

To determine the original percentage of Fe_2O_3 , multiply the percentage of FeO [see Sec. (A)] by 1.1115 and subtract from the total Fe_2O_3 .

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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, O₂ and CO₂ 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 H₂O 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-μm 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 ~ 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 $0.05\text{-}\mu\text{m}$ 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 (~ 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 $\sim 20\text{ mL/g}$ 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 ~ 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 H₂O. The mixture is then shaken for a few days and passed through a 0.05- μ 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 UO₂(NO₃)₂•6H₂O in H₂O that has been purified with a Millipore deionizing system (Milli-Q system) and filtered through a 0.05- μ 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- μ 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 ²³⁷U, 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}Sr , ^{137}Cs , ^{133}Ba , ^{152}Eu , ^{141}Ce , ^{95m}Tc , ^{131}I , and ^3H (the ^3H 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 $\sim 2\text{ mL}$ of conc HCl, and evaporate again. Then add $\sim 0.5\text{ mL}$ 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}Tc (which is obtained in alkaline solution) to $\sim 0.5\text{ mL}$ 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}I and tritiated water to $\sim 5\text{ mL}$ of groundwater for a final concentration of $\sim 10^4\text{ dpm}/50\text{ }\lambda$. (These solutions are used to measure the free column volume.)

3. Preparation of Pretreated Groundwater

Add 50 g of crushed rock to 1 L 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 $\sim 5\text{ g}$ of crushed rock to particles of $<250\text{ }\mu\text{m}$ in diameter. Combine with $\sim 100\text{ mL}$ 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 $106\text{ }\mu\text{m}$ and for argillite, 180 to $250\text{ }\mu\text{m}$. 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 H_2O 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}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}I is sorbed by the rock, measure the free column volume with both tritiated water and ^{131}I solution.)

Step 3. Prepare a beaker of boiling H_2O . Place a Luer fitting that contains a frit in the boiling H_2O 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 H_2O , shake off excess H_2O , 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 Ge(Li) detector to count the sample if more than one isotope has been loaded, and a 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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