

LA-1721, 4th Ed. (7-79, Rev.)

U. 3069
UC-4, Chemistry
Issued: April 1975

MASTER

Collected Radiochemical Procedures
(Radiochemistry Group CNC-11)

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Revisions and Additions

Issued: July 1979

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

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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 on pp. 407 and 408 of "Ion Exchange Separations in Analytical Chemistry" by O. Samuelson, published by John Wiley & Sons, Inc., New York, 1963. The bismuth, in solution in a minimum of concd 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 . The procedure was checked with carrier-free ^{207}Bi and a chemical yield of 99% was obtained.

2. Reagents

HCl: concd; 0.5M

H_2SO_4 : 1M

Anion exchange resin: Bio-Rad AG 1-X8, 100-200 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 1-3/4 to 2 in. of resin. Before using, wash the resin column with concd HCl.

3. Procedure

Step 1. Dissolve the ore sample and make up to 3M HCl so that there are 5 mg of ore/ml of solution. Evaporate 1-2 ml of sample solution nearly to dryness, take up in 1 ml of concd 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 concd 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.

June 1979

SEPARATION OF MILLIGRAM AMOUNTS OF COBALT AND MANGANESE FROM 100 GRAMS OF IRON

R. J. Prestwood

1. Introduction

This procedure was developed for possible use in the Apollo Space Program. Its major steps include (1) extraction of Fe(III) into isopropyl ether from a solution 7.9M in HCl; (2) passage of the aqueous layer from the extraction onto an anion exchange resin column, with the manganese passing through and the cobalt staying on the column; and (3) elution of the cobalt by means of 4M HCl. Chemical yields are 98% for cobalt and 80% for manganese.

2. Reagents

HCl: concd; 7.9M; 6M; 4M

HNO₃: concd

Isopropyl ether

Anion exchange resin: Bio-Rad AG 1-X8, 100-200 mesh (wash the resin column with 7.9M HCl before using)

3. Procedure

Step 1. Dissolve 100 g of iron in a minimum of 6M HCl in a 1-ℓ Erlenmeyer flask. Evaporate the solution to about 300 ml, then add the appropriate amount of concd HNO₃ to oxidize the iron to the +3 state. With the use of a hot plate and a magnetic stirrer, reduce the volume to about 150 ml. (The solution is quite viscous at this stage.) Cool and transfer the solution to a 2-ℓ separatory funnel with 850 ml of 7.9M HCl.

Step 2. Add 1 ℓ of isopropyl ether and shake thoroughly. Draw off the aqueous (lower) layer but


do not discard because it contains the cobalt and manganese. Extract the iron from the ether layer with 1000-, 500-, and 200-ml portions of H₂O. Combine the aqueous layers in a 4-ℓ bottle. Return the original water layer containing the cobalt and manganese to the ether in the separatory funnel and add 200 ml of concd HCl to bring the acid concentration back to 7.9M. Shake thoroughly and drain the aqueous layer into a 1-ℓ Erlenmeyer flask. Remove the ether in this layer with an air bubbler. Back-extract the ether layer again, this time with 500- and 100-ml portions of H₂O. Add the aqueous layers to the original back-extracts of iron in the 4-ℓ bottle. Remove the ether from the back-extracts with an air bubbler.

Step 3. Boil down the aqueous layer containing the cobalt and manganese to a few milliliters. Add 2 ml of concd HNO₃ and evaporate to a small volume. Repeat the HNO₃ treatment. Add 5 ml of concd HCl and evaporate the solution to about 2 ml. Repeat the HCl treatment. Adjust the volume to 25 ml and the HCl concentration to 7.9M. Extract with 30 ml of isopropyl ether in a 60-ml separatory funnel.

Step 4. Drain the aqueous layer onto the top of a 5-in. Bio-Rad AG 1-X8, 100-200 mesh, anion exchange resin column. Collect the effluent, which contains Mn²⁺. Wash the column with 20 ml of 7.9M HCl to remove any remaining manganese and combine the wash with the previous effluent. The cobalt remains on the column as a green band about 1 in. wide.

Step 5. Add sufficient 4M HCl to remove the green band containing the cobalt from the column and collect the eluate in an Erlenmeyer flask. Any residual iron that has collected on the column remains there. (Note: The cobalt can be precipitated and weighed as the anthranilate and the manganese as MnNH₄PO₄·H₂O.)

June 1979

germanium, gold, hafnium 

RECOVERY OF RADIOHAFNIUM FROM TANTALUM

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 approximately 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 consisted of (1) dissolution of the target in a mixture of concd HCl and HNO_3 ; (2) coprecipitation of hafnium (presumably as anionic fluorocomplexes) on CaF_2 ; (3) extraction of hafnium from HClO_4 solution into thenoyltrifluoroacetone (TTA); and (4) back-extraction into concd HCl. An overall chemical yield of $93 \pm 5\%$ was obtained for radiohafnium.

The ^{172}Hf decays to ^{172}Lu with a half-life of 1.87 yr, and the latter isotope transforms to stable ^{172}Yb with a half-life of 6.70 days. The ^{172}Hf - ^{172}Lu combination offers a possible medical generator system, with the ^{172}Lu having 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 rare-earth compounds in nuclear medicine.

2. Reagents

Hf carrier: 500-600 μg of metal in HF solution
HF: concd
 HNO_3 : concd
 HClO_4 : concd
HCl: concd
 CaCl_2 : a solution of known concentration
 $^{45}\text{Ca}^{2+}$ tracer (optional): obtained from Oak Ridge
National Laboratory
 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: 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 500-600 μg of hafnium carrier and 2-3 ml of concd HF per gram of the target. Then add concd HNO_3 , dropwise initially, until dissolution is complete. The dissolution process usually requires about 3 h and a volume of HNO_3 slightly under half that of the HF.

Step 2. Slowly add in dropwise fashion 45 mg of Ca^{2+} as CaCl_2 solution (Note 1) and an additional milliliter of concd 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 concd HClO_4 (approximately 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. [Fluoride ion interferes with the TTA extraction process. The quantity of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ added depends upon the amount of fluoride in the CaF_2 precipitate; 2.5 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is typical, although up to 15 g did not adversely affect the extraction.] Transfer the solution to a separatory funnel along with 25-30 ml of TTA reagent. Equilibrate the mixture on a Burrell wrist-action shaker for 1 h. If it is determined that the radiohafnium did not extract quantitatively into the organic phase, add additional $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and repeat the extraction.

Step 4. Dilute the organic phase from the TTA extraction tenfold with benzene. Extract twice with 25-ml volumes of concd HCl and combine the aqueous phases. These contain the radiohafnium.

Notes

1. Calcium-47 tracer was added 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. Occasionally, when less than quantitative coprecipitation of radiohafnium occurs, it generally is associated with the presence of appreciable residual Ca^{2+} in solution, as indicated by the added $^{47}\text{Ca}^{2+}$. Volume reduction

and addition of concd 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.

4. Primary Literature Reference

R. J. Daniels, P. M. Grant, and H. A. O'Brien, Jr., *Int. J. Nucl. Med. Biol.* 5, 11 (1978).

June 1979

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, *Anal. Chem.*, **46**, 782 (1974), on the direct determination of ferrous iron in silicate rocks and minerals by iodine monochloride; and the other, by K. L. Cheng, R. H. Bray, and T. Kurtz, *Anal. Chem.*, **25**, 347 (1953), on the determination of total iron by disodium dihydrogen ethylenediaminetetraacetate titration. Major modifications of the former procedure include the preparation method of the iodine monochloride solution, elimination of the necessity for blanks, and some technique changes. The main modification in the reported method for the determination of total iron is in the preparation of the sample for analysis. The sample preparation method reported herein improves the consistency of the analytical results.

2. Reagents

Analysis for ferrous iron

HF: concd

HCl: concd; 9M; 6M

H₂SO₄: 6M

H₃BO₃: solid

KI: solid; 10% aqueous solution

KIO₃: solid; $2.5 \times 10^{-3}M$ (standardized)

(NH₄)₂SO₄·FeSO₄·6H₂O: primary standard

Carbon tetrachloride (CCl₄)

Analysis for total iron

HClO₄: concd

HF: concd

HNO₃: concd

HCl: 6M; 0.1M

NH₄OH: concd

NaOH: 10M

NaC₂H₃O₂: 6M

(NH₄)₂SO₄·FeSO₄·6H₂O: primary standard

Fe: National Bureau of Standards standard sample 55e, open-hearth iron (99.8% pure)

Salicylic acid: 1 % of acid in 100 ml of ethanol

EDTA reagent: disodium salt of ethylenediaminetetraacetic acid; 4.0000 g in 1 l of H₂O (standardized)

3. Determination of Ferrous Iron

(a) Preparation of ICl reagent.

Add 10 g of KI and 6.44 g of KIO₃ to 150 ml of water in a 1-l bottle that contains a Teflon-coated magnetic stirrer. Stir until the salts have dissolved; then, with continued stirring, add 450 ml of concd HCl. Add 20 ml of CCl₄ and, while stirring, 10% KI dropwise until the color of I₂ appears in the CCl₄ (lower) layer. Remove the CCl₄ layer with a transfer pipet 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 Model DD Burrell wrist-action shaker. Use a transfer pipet to remove the pink CCl₄ layer and discard. Dilute the 30 ml of ICl solution to 100 ml with 9M HCl.

(b) Standardization of the $2.5 \times 10^{-3}M$ (approx) 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 Fe(II) standard of 1 mg/ml of solution. For standardization of the KIO₃ solution, proceed as described below for the determination of ferrous iron but substitute 3 ml (3 mg) of the Fe(II) standard for the iron-containing sample.

(c) Analytical procedure.

Step 1. Weigh out 50-70 mg of sample (minus 200 mesh) into a Tefzel 50-ml Nalgene centrifuge tube fitted with a specially machined male Teflon stopper. (Two-ounce Teflon bottles with caps may be used for holding the sample.) Carefully cover the sample with 3 ml of CCl₄. To a polyethylene 50-ml graduated cylinder, add 20 ml of 6M HCl, 3 ml of the diluted ICl reagent, and 2 ml of concd HF. Pour the solution into the mixture of sample and CCl₄.

and stopper *immediately*. Place on a Burrell shaker and shake for *at least* 4 h. As the sample slowly dissolves, the Fe(II) is oxidized to the ferric state by ICl, which then is reduced to I₂. The latter dissolves in the CCl₄.

Step 2. Prepare a 125-ml Erlenmeyer flask containing a Teflon-coated magnetic stirring bar, 10 ml of 6*M* 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 pipet transfer the contents of the tube to the 125-ml Erlenmeyer flask containing the HCl and H₃BO₃. Take great care to ensure that some of the aqueous phase is on both sides of the CCl₄ in the transfer pipet to prevent loss of I₂ to the air. While stirring, titrate the I₂ with the standardized KIO₃ solution; disappearance of the pink I₂ color in the CCl₄ layer indicates titration is complete. Calculate the amount of ferrous iron present in terms of percent FeO.

4. Determination of Total Iron

(a) Standardization of EDTA reagent.

Accurately measure 1.0000 g of National Bureau of Standards standard 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 oxidized to Fe(III). Add 10 ml of concd HCl and evaporate the solution to a small volume to remove excess HNO₃. Repeat the HCl treatment. Make the solution up to 1 ℓ so that it is about 0.1*M* in HCl.

Dissolve 4.0000 g of the disodium salt of ethylenediaminetetraacetic acid in H₂O and dilute to 1 ℓ (EDTA reagent). Add 3 ml (3 mg) of standard

Fe(III) solution to a 100-ml beaker containing a magnetic stirrer, then add 3-4 drops of concd HCl. Use a 6*M* NaC₂H₃O₂ solution to adjust the pH to 2.5 (use pH meter) so that the volume of the solution is about 20 ml. Add 5 drops of salicylic acid indicator solution and titrate *immediately* with the EDTA reagent.

We found that 1.62 ml of EDTA solution is equivalent to 1.00 mg of Fe(III) or 1.43 mg of Fe₂O₃.

(b) Analytical procedure.

Step 1. Weigh out 50-100 mg of sample (minus 200 mesh) into a 75-ml Teflon beaker. Add 7 ml of concd HClO₄, 2 ml of concd HNO₃, and 4 ml of concd HF. Evaporate on a hot plate to HClO₄ fumes. Cool, carefully add 4 ml of concd HF, and again evaporate to HClO₄ fumes. Repeat the HF treatment. Fume off all but about 1 ml of the HClO₄.

Step 2. Use 10-15 ml of 0.1*M* HCl to transfer the solution to a 40-ml glass centrifuge tube. Carefully neutralize the solution with concd NH₄OH, then add 4 drops more of the concd NH₄OH. Add 4 drops of 10*M* 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 concd HCl. Use 0.1*M* HCl to transfer the solution to a 100-ml beaker containing a magnetic stirrer. The volume of solution should be about 20 ml. Adjust the pH to 2.5 with 6*M* NaC₂H₃O₂, add 5 drops of salicylic acid indicator solution, and titrate with standard EDTA reagent. Calculate the total iron present as percent Fe₂O₃.

To determine the original percentage of Fe₂O₃, multiply the percentage of FeO (Sec. 3 above) by 1.1115 and subtract from the total Fe₂O₃.

June 1979

SEPARATION OF IRON AND SCANDIUM FROM A NICKEL TARGET

B. P. Bayhurst

1. Introduction

After the metal target is dissolved in aqua regia, Fe(III) and scandium are separated from the nickel by precipitation of the hydroxides with concd aqueous ammonia and the nickel is converted to the $\text{Ni}(\text{NH}_3)_6^{2+}$ ion. The Fe(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 concd HCl medium. After removal of adsorbed cobalt from the column, the Fe(III) is eluted by 0.1M HCl and finally converted to the oxide.

The scandium, which remains in the aqueous layer from the isopropyl ether extraction, is, after preliminary treatment, dissolved in concd 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, while in this form, fluoride and hydroxide scavengers are performed in the presence of lanthanum carrier and Fe(III) holdback carrier. The fluorocomplex is then destroyed and ScF_3 is precipitated. The latter is then converted to the hydroxide and ignited to the oxide. The chemical yields are ~85% for iron and ~95% for scandium.

2. Reagents

Standard Fe(III) carrier: 10 mg Fe/ml, made up from pure Fe wire (NBS standard)

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

Sc carrier: 20 mg Sc_2O_3 /ml, added as ScCl_3 in very dilute HCl; standardized (see original SCANDIUM procedure)

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

HCl: concd; 10M; 7.9M; 5.5M; 0.1M

HNO_3 : concd

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

NH_4OH : concd

NaOH: concd

Isopropyl ether

Methyl red indicator solution

Anion exchange resin: Bio-Rad AG 1-X8, 100-200 mesh (wash the resin column with 7.9M HCl before using)

3. Procedure

Step 1. To a sample of metal target in a 40-ml glass centrifuge tube, add 2 ml of standard Fe(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 concd NH_4OH . [Fe(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 concd HCl to dissolve the precipitate. Dilute to 30 ml with H_2O and reprecipitate the hydroxides with concd NH_4OH . Centrifuge, and discard the supernate. Repeat the dissolution and precipitation processes three more 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 concd HCl and evaporate the solution to <1 ml. Add 10 drops of concd HCl and 10 ml of 7.9M HCl and 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 containing 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 Fe(III). Transfer the aqueous layer to a clean glass centrifuge tube. Repeat the back-extraction of the ether layer and combine the water layer with the previous one. To the aqueous extract, add an excess of concd NH_4OH

to precipitate $\text{Fe}(\text{OH})_3$, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 5. Dissolve the $\text{Fe}(\text{OH})_3$ in a minimum of concd HCl and add the solution to a 13- by 1-cm Bio-Rad AG 1-X8, 100-200 mesh, anion exchange resin column that has just been washed with 7.9M HCl. Discard the effluent. Wash the column with 10 ml of 7.9M HCl, and then with a total of 30 ml of 5.5M HCl to remove the cobalt. Discard the washes.

Step 6. Elute the $\text{Fe}(\text{III})$ with 30 ml of 0.1M HCl, collecting the eluate in a clean glass centrifuge tube. Add an excess of concd NH_4OH to precipitate $\text{Fe}(\text{OH})_3$, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of concd HCl, add 6 ml of filter paper pulp slurry, and reprecipitate $\text{Fe}(\text{OH})_3$ with concd NH_4OH . Filter through a 9-cm Whatman No. 541 filter paper, transfer to a Coors 00 porcelain crucible, and ignite in a furnace that is brought slowly to 1000°C . Maintain at 1000°C for 1 h, then cool, weigh, and mount the Fe_2O_3 .

Step 7. Wash the aqueous layer containing 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 about 5 ml. Add an excess of 10M NaOH to precipitate $\text{Sc}(\text{OH})_3$, centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of concd HCl and reprecipitate the hydroxide with concd NH_4OH . Centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 8. Dissolve the $\text{Sc}(\text{OH})_3$ in a minimum of concd 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 about 5 ml and transfer to a clean polyethylene centrifuge tube.

Step 9. Add an excess of concd NH_4OH to precipitate $\text{Sc}(\text{OH})_3$. 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 concd NH_4OH . Add 2 drops of lanthanum carrier, centrifuge, and transfer the supernate to a clean polyethylene tube. Discard the precipitate. Repeat the LaF_3 scavenge twice. To the supernate, add 1.5 ml of concd NH_4OH and 2 drops each of $\text{Fe}(\text{III})$ holdback and lanthanum carriers, centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate. Add 6 ml of concd 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 $\text{Sc}(\text{OH})_3$ formed in a minimum of concd HCl and reprecipitate the hydroxide with concd NH_4OH . Dissolve the precipitate in a minimum of concd HCl, add 6 ml of filter paper pulp slurry, and reprecipitate $\text{Sc}(\text{OH})_3$ with concd NH_4OH . Filter onto 9-cm Whatman No. 541 filter paper, transfer the paper to a Coors 00 porcelain crucible, and ignite at 1000°C for 15 min. Cool, weigh, and mount the Sc_2O_3 .

June 1979

THE LANTHANIDES

K. Wolfsberg and D. Handel

1. Introduction

After the radiochemical purification of the lanthanides (rare earths) as a group, the individual lanthanides are separated on a cation column of low cross linkage and fine particle size at room temperature by eluting with α -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 eluent continuously. Individual or small groups of lanthanides also may be separated by elution at only 1 pH or by making a step change in concentration or pH of the α -hydroxyisobutyric acid.

2. Reagents

HClO₄: concd
HCl: concd
HNO₃: concd
H₃BO₃: saturated
H₂C₂O₄: saturated; 0.5%
HF: concd
H₃PO₄: concd
H₂SO₄: concd
H₂O₂: 30%
NH₄OH: concd
NH₂OH·HCl: 5M aqueous solution
Ethanol: 95%
Zr carrier: 10 mg Zr/ml, added as ZrO(NO₃)₂·2H₂O in 1M HNO₃
Te carrier: 10 mg Te/ml, added as Na₂TeO₃ in H₂O
Ba carrier: 10 mg Ba/ml, added as Ba(NO₃)₂ in H₂O
 α -Hydroxyisobutyric acid reagent: made from a 50% aqueous solution; supplied as Con-O by the Continental Chemical Company, San Francisco, prepared as described in Sec. 5 and diluted as necessary
Dowex AG 50W-X4 or AG 50W-X8 cation resin: minus 325 wet mesh, NH₄⁺ form

Dowex AG 1-X8 anion resin: 50-100 mesh
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, and Y carriers: 5 mg of oxide/ml, standardized, 99% pure

¹⁴⁶Pm tracer: produced by ¹⁴⁴Sm(n, γ) ¹⁴⁶Sm—¹⁴⁶Pm, standardized

0.01M EDTA: 3.743 g disodium (ethylene dinitrolo) tetra-acetate (direct from bottle) per liter

0.01M La³⁺ in 1M HCl: prepared from La₂O₃

NH₄Cl: 25% wt/vol in H₂O

pH 10 buffer: 61.5 g of NH₄Cl dissolved in 400 ml of concd NH₄OH

Arsenazo indicator: 3-(2-arsenophenylazo)-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 about 100 mg of phenolphthalein in 100 ml of ethanol

8-Quinolinol reagent II: a mixture of 10 ml of quinolinol reagent I and 5 ml of concd NH₄OH diluted to 200 ml with H₂O

Filter aid: for preparation, disintegrate in a blender ten 18.5-cm circles of Whatman No. 42 filter paper in water, dilute to 2 l with H₂O, and add 1 ml of concd HCl

HCl rinse solution for anion resin column: 10 ml of concd HCl and 1 drop of concd HNO₃, freshly prepared

3. Preparation and Standardization of Carriers

Dissolve approximately 5 g of the desired lanthanide oxide in about 50 ml 6M HCl. Heat, or add a few drops of concd HNO₃ if dissolution is difficult. Filter and dilute to 1 l, adjusting the HCl concentration to 2 or 3M. Any pure soluble Ce(III) salt may be used for cerium carrier.

The lanthanides may be standardized by pipetting 6 ml of carrier solution directly into a tared porcelain crucible that has been fired for 2 h. Evaporate the solution gently under a heat lamp, add 3 ml of concd HNO₃, and 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, pipet three 2-ml portions of the carrier into 125-ml

Erlenmeyer flasks and titrate with EDTA solution, as described in Sec. 10. The titrations should agree within 0.5%.

4. Standardization of ^{149}Pm

The solution should contain 800-1200 counts/min of ^{149}Pm /ml. Pipet 5 ml of the solution and about 20 mg of standardized neodymium carrier into each of four centrifuge tubes. Dilute to about 20 ml, heat on a steam bath, and add approximately 6 ml of concd NH_4OH . Centrifuge. Dissolve the precipitate in 1 ml of concd HCl , dilute to 20 ml, heat on a steam bath, and add 10 ml of saturated $\text{H}_2\text{C}_2\text{O}_4$. Digest the precipitate, centrifuge, filter, ignite to the oxide, and mount as in Step 10A of Sec. 11. Count the samples for several days 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. 10). 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. α -Hydroxyisobutyric Acid Reagent

Dilute 400 ml of Con-O liquid (see Sec. 2, Reagents) to 4 l with H_2O and add concd NH_4OH to obtain solutions of desired pH. Several batches of solution, similarly prepared, are combined and stored in 6.5-gal Nalgene dispenser bottles. The solution is approximately 0.5M α -hydroxyisobutyric acid. Solutions of acid concentration 0.06 and 0.08M are made up by appropriate dilution with H_2O .

6. Treatment of Resins

Bio-Rad Laboratories will prepare cation resin according to the following specifications: Dowex AG 50-X4 or X8, "minus 325 wet mesh"; the actual range is 24 to 45 μm . The resin is washed successively with 6M HCl , 1M NH_4CNS , 6M HCl , 1M NH_4OH , and H_2O . The Bio-Rad Dowex AG1 resins need no further purification. Because of the variations among various batches of the cation exchange

resin, they should be evaluated before routine use; also, the pH of eluent, eluent concentration, and/or flow rate should be adjusted for the particular separation.

7. Preparation of Cation Exchange Columns

Select a 70-cm length of 8-mm-i.d. Pyrex tubing. Draw one end out to a drip 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 polyethylene wash bottle. The settling rate of the resin may be increased by using air pressure. Resin should be added to a height of about 65 cm. Care should be taken that no part of the resin goes dry. Columns prepared in this manner may be stored by sealing both ends with dropper bulbs or by storing the columns in a cylinder of water.

8. Preparation of Anion Columns

A 15-ml centrifuge tube is blown out at the bottom and a 15-cm length of 6-mm-i.d. glass tubing is attached to the column. The end of the glass tubing is drawn to a 1-mm-i.d. drip tip. Load the glass tubing part of the column with anion resin in the same manner that 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.

9. Gradient Elution Equipment

A schematic diagram of the pH gradient elution equipment is shown in Fig. 1. Several columns may be operated from one setup by delivering the eluent 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.

Elution is begun with the levels of the two solutions at the same height. One-half of the volume that is removed from the flask containing the low pH solution is replaced continuously by high pH

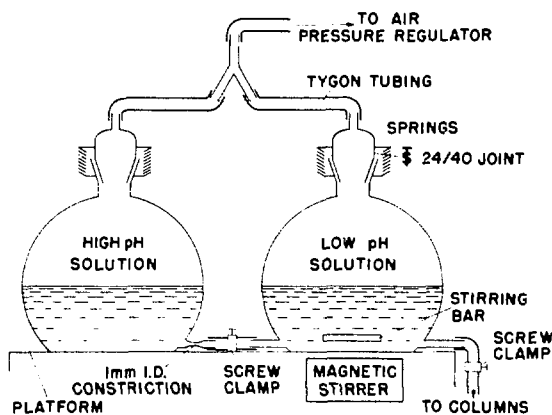


Fig. 1. Gradient elution equipment.

solution by gravitational leveling. Thus, the pH of the eluent 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 change the rate of change in pH or concentration of the α -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 eluent requires only one reservoir. If a stepwise change in eluent is desired, it can be achieved with a manual changeover. If the step change is to occur during nonworking hours, it can be made by connecting lines from both reservoirs to the column through solenoid valves actuated by an electric timer. Several plastic solenoid valves are available commercially.

10. 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 of lanthanide oxide.

Dilute the sample to about 30 ml in a 125-ml Erlenmeyer flask and add an excess of 0.01M EDTA from a 10-ml buret (0.6-0.7 ml for each milligram of rare-earth oxide and about 0.9 ml for each milligram of yttrium oxide). Add about 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 or 2 drops of arsenazo indicator and back titrate with 0.01M La^{3+} solution from another 10-ml buret while the solution is still hot. The end point is reached when the solution turns from salmon to violet or red-violet when approximately 1/2 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 about 6 ml 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 ml of carrier. For thickness corrections, the weight of the sample can be calculated from the titration of the sample, the titration of 2 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 rare-earth oxide that has been ignited at 950°C (Note 1).

11. 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, pipet 2 ml of desired carrier and the active sample, as well as 4 ml of concd HClO_4 and 1 ml of concd HNO_3 , and fume to near dryness. Add 3 ml of concd HNO_3 and enough H_2O to transfer the solution to a 40-ml

polycarbonate centrifuge tube. Add H₂O to bring volume to about 15 ml, then add 2-5 ml of concd HF, digest on a steam bath for 30 min, and centrifuge for 15 min. Decant the supernate and wash the precipitate with about 20 ml of H₂O containing a few drops of concd HF. Centrifuge, and discard the supernate (Note 2).

Step 2. Slurry the precipitate with 2 ml of saturated H₃BO₃ and add 2 ml of concd HNO₃, 10 ml of H₂O, and 2 drops of zirconium carrier. Heat to dissolve any precipitate. Add 2-5 ml of concd HF, heat on a steam bath for a few minutes, and centrifuge (Note 3). Wash the precipitate with H₂O containing a few drops of HF. Centrifuge, and discard the supernate.

Step 3. Slurry the precipitate with 2 ml of saturated H₃BO₃, add 2 ml of concd HNO₃, and heat on a steam bath, if necessary, to dissolve the precipitate. Add 15 ml of H₂O.

Step 4. Add 8 ml of concd NH₄OH, heat for 1 min on a steam bath, digest, and centrifuge. Discard the supernate. (The anion resin column may be prepared at this time.) Wash the precipitate with 15 ml of H₂O to which a few drops of concd NH₄OH has been added. Centrifuge, and discard the supernate.

Step 5. Dissolve the hydroxide precipitate in 4 ml of concd HCl and 1 drop of concd HNO₃ 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 resin column and collect the eluate in a 125-ml Erlenmeyer flask. Rinse the column with one 4- and one 6-ml HCl rinse solution (see Sec. 2, Reagents), 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 4-5 ml. Transfer the solution to a long, tapered centrifuge tube with 15 ml of H₂O. Add 8 ml of concd NH₄OH and 3 drops of 5M NH₂OH·HCl. Heat on a steam bath for about 1 min, digest, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of H₂O containing a few drops of NH₄OH.

Step 7. Dissolve the precipitate in 6 drops of concd HCl and dilute the solution to about 30 ml with H₂O. Add about 30 drops (transfer pipet) of minus 400 mesh or 200-400 mesh cation resin slurry in H₂O. Stir or shake for about 5 min and centrifuge for 5 min, letting the centrifuge stop without the use of the brake (Note 4). (The centrifuged resin has a volume of about 1 ml.) Discard the supernate.

Step 8. Slurry the resin with about 1 ml of H₂O and, with a transfer pipet, transfer it to the top of a previously prepared cation resin column. After the resin settles, remove the H₂O. Rinse the centrifuge tube with 1-2 ml of H₂O, add the rinsings to the column, allow to settle, and remove the H₂O. (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 (Fig. 1) with 150 ml of α -hydroxyisobutyric acid reagent solution of pH 3.34 on the low side and 150 ml of reagent solution of pH 3.73 on the high side. If several columns are operated from one set of flasks, the volumes of eluents are increased proportionally. A small additional volume of solution of low pH 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. Collect the eluate in 15-min fractions with a fraction collector.

The lutetium-thulium elution is performed in a similar manner except that the concentration of the α -hydroxyisobutyric acid solution is changed rather than the pH, which is maintained at 5.5. The concentration of the acid solution may be changed by using a gradient setup with 150 ml of 0.06M acid solution on the low side and 150 ml of 0.08M acid solution on the high side. Alternatively, the concentration of the acid solution may be changed by using solenoid valves actuated by an electric timer. For this method, the column is connected by a Y-tube to two 2- ℓ flasks, one containing 0.06M α -hydroxyisobutyric acid solution and the other 0.08M solution. The solenoid that regulates delivery of the 0.06M acid is turned on first, then the electric timer

is set to deliver the 0.08M acid solution approximately 16 h later (Notes 5, 6, and 7).

Step 10A. For the light lanthanides and yttrium, add a few drops of saturated $\text{H}_2\text{C}_2\text{O}_4$ to each fraction to precipitate and locate the individual lanthanides. Promethium is located by measuring the activity in the tubes between samarium and neodymium. Combine the individual lanthanide fractions in centrifuge tubes. To the promethium fraction, add 2 ml of neodymium carrier. Add 5 ml of saturated oxalic acid to the centrifuge tubes and digest the oxalates for 15 min on a steam bath. Centrifuge, suspend the oxalates in about 5 ml of H_2O , and filter on a 2.5-cm circle of Whatman No. 42 paper using a filter chimney assembly. Ignite the oxalates in a Coors 00 porcelain crucible for approximately 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 about 0.5 ml of 8-quinolinol reagent I to each fraction. Add concd NH_4OH to make each fraction basic (red) and combine the fractions containing an individual element in a 250-ml beaker. (At least 10 ml of reagent I should be used in those tubes containing the element.) Add about 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 Whatman No. 42 paper using a large Millipore filter chimney assembly. Wash with 8-quinolinol reagent II. Ignite the quinolate for 1.5 h at 950°C (Note 8).

Step 10C. If a given light lanthanide is to be recycled through a second cation exchange column when a separation of 10^3 from other lanthanides is required, the oxalate may be dissolved and destroyed by heating it in a centrifuge tube with about 1 ml of concd HNO_3 containing about 100 mg of KClO_3 . For heavy lanthanides, the 8-quinolate is ignited and dissolved in about 2 ml of concd HCl and 0.5 ml of concd HNO_3 . Then one performs Step 6 for the hydroxide precipitation before the cation 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, the oxide formed by ignition of the 8-quinolate is dis-

solved in 2 ml of concd HCl and 1 drop of concd HNO_3 . The solution is heated on a steam bath and cooled. Then 6 ml of concd HCl is added and the procedure taken up 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 Whatman No. 42 paper using a filter assembly with an 11-mm-i.d. glass chimney. 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, the circle of paper on which the sample is mounted should be washed, dried, and tared before the mounting operation. The papers and samples should be cooled for 20 min before weighing.

Step 12. After sample counting is completed, yield determination by EDTA titration may be performed. Remove the sample, filter paper, and tape cover from the counting plate by cutting around the outside of the filter paper with a sharp blade. Place this sandwich in a 125-ml Erlenmeyer flask. Add 10 ml of H_2O and 2 ml of concd HCl . Bring to boiling and place the flask on a hot plate set to maintain the temperature just below boiling for about 20 min. The filter paper may disintegrate, but this does not interfere. Titrate the sample in the manner described in Sec. 10.

The CeO_2 does not dissolve with the HCl treatment described above. After the sample sandwich is placed in the flask, add about 2 ml of concd H_2SO_4 and heat the mixture to SO_3 fumes over a flame. Then cautiously add a mixture of 2 parts of concd H_2SO_4 and 1 part of 30% H_2O_2 dropwise to destroy the charred paper and tape. Fume the clear solution down to about 0.25 ml. Dilute to 30 ml, add 0.1-0.2 g of ascorbic acid, and proceed with the EDTA titration as described in Sec. 10.

Notes

1. Consult the following references for general information on EDTA titrations.

G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, New York (1955).

H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, *Chemist Analyst* **46**, 106 (1958).

A review of EDTA methods for the lanthanides is given by H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, *Chemist Analyst* **47**, 78 (1959).

This procedure was adapted from J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, *Anal. Chem.* **30**, 1111 (1958).

2. If cerium is to be determined, steps must be made 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 6*M* 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 about 10 ml of 6*M* NaOH and then with H₂O before carrying out Step 2. The same treatment may be used after Step 2. Precipitation of hydroxides with 6*M* 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 6*M* NaOH and then with H₂O.

4. The 200-400 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 eluent (α -hydroxyisobutyric acid reagent) is 3.40 and the pH is changed at an average rate of approximately 0.025 pH unit per hour. For the operation of one column, this condition is met by starting with 144 ml of 0.394*M* α -hydroxyisobutyric acid, pH 3.40, in the first flask and with 144 ml of eluent, pH 4.20, in the

second flask. If several columns are operated from one set of flasks, the volumes of eluents 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. Collect the eluate in 15-min fractions using a fraction collector.

When this step is performed, the lanthanides elute in the following manner.

<u>Element</u>	<u>Time that element starts eluting off column (h)</u>
Y	3.1
Gd	6.5
Eu	8.2
Sm	10.5
Pm	13.2
Nd	16.5
Pr	19.5
Ce	22.5
La	28.0

Those lanthanides that are present in 6- to 9-mg quantities have elution widths 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 elute with an eluent at a single pH. For Dowex AG 50W-X8, the following approximate values of pH or α -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 0.08*M*; and lutetium 0.06*M*. (For thulium at 0.08*M* and lutetium at 0.06*M* the pH of the eluent is ≈ 5.5 .)

7. Some elements elute very closely to each other. Such cases are 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 about 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. Ten milligrams of a lighter lanthanide carrier usually are added for hydroxide precipitation before the cation column separation. The activity peaks are located by gross γ -counting. About 3 mg of the appropriate carrier are then added to the α -hydroxyisobutyrate solution containing the activity of interest, and the element is precipitated and ignited as in Step 10.

After the sample has been ignited, transfer the oxide into a long, tapered centrifuge tube. Add 2 ml of concd HCl and 3-5 drops of concd HNO₃. Heat 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.) Place the centrifuge tube in an oil bath and evaporate to a volume of a drop or two using an air jet. Transfer the drops in 20- λ portions to the appropriate end of a quartz vial that contains quartz wool that has been weighed previously. Dry for about 8 min under a heat lamp after each transfer. Rinse the centrifuge tube with 1 drop of concd HCl and transfer the rinse to the quartz vial. Heat the vial at 600°C for 20 min, cool for 20 min, and weigh.

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 about 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.

ADDENDUM I TO THE LANTHANIDE PROCEDURE

1. Alternative Group Purification

The steps described below are alternatives for Steps 1 through 7 of Section 11 of THE

LANTHANIDES procedure. They can be used only for light rare earths (cerium-terbium) and yttrium. Heavy rare earths do not back-extract readily from HDEHP. (See CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM NEVADA SOIL SAMPLES.)

The lanthanides are extracted from a dilute nitric acid solution into *n*-heptane containing di-2-ethylhexyl orthophosphoric acid (HDEHP), and the resulting organic phase is scrubbed with dilute nitric acid. 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 nitric acid, and the aqueous phase is scrubbed with a solution of HDEHP in trichloroethylene. The distribution coefficient, $K(o/a)$, 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 in obtaining the distribution ratios.

2. Special Reagents

HNO₃: 0.05M; 4M

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

0.1M HDEHP: a solution of the acid in trichloroethylene. (The HDEHP used is assayed at >94% pure by the supplier, the Victor Chemical Division of the Stauffer Chemical Co. If highly purified HDEHP is used, some loss of the lighter lanthanides may occur because $K(o/a)$ 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, about 0.3 mg each of carriers of the other lanthanides may be added. If promethium is to be determined, add ¹⁴⁵Pm tracer. The maximum quantity of carrier that can be used is 60 mg.

Step 2. Add 3 ml of concd 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 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 6-8 ml of concd NH_4OH . Heat for 2 min on a steam bath, centrifuge, and discard the supernate. Wash the precipitate in 1-2 ml concd HNO_3 and wash down the sides of the tube with a small volume of water. Evaporate the sample to dryness under a heat lamp or by boiling gently over a burner.

Step 4. Dissolve the residue in 10 ml of 0.05M HNO_3 . Transfer the solution to a 60-ml separatory funnel, add 10 ml of 0.5M HDEHP in *n*-heptane, and shake. (Shake for 1 min if done manually and 2 min if done on a Burrell shaker.) Discard the aqueous (lower) layer.

Step 5. Scrub the organic phase with two 10-ml portions of 0.05M HNO_3 and discard the lower phase after each scrubbing.

Step 6. Back-extract the lanthanides by shaking the organic phase with two 5-ml portions of 4M HNO_3 . Drain the aqueous (lower) phase after each extraction into the same clean 60-ml separatory funnel. If either yttrium or terbium is to be determined, use four, rather than two, 5-ml portions of 4M HNO_3 . Discard the organic phase.

Step 7. Scrub the combined aqueous extracts with two 10-ml portions of 0.1M HDEHP in trichloroethylene. Discard the lower phase after each scrubbing.

Step 8. Scrub the aqueous solution once with 10 ml of *n*-heptane to remove most of the dissolved HDEHP. Drain the HNO_3 solution (lower phase) into a 40-ml centrifuge tube and discard the heptane.

Step 9. Add 6-8 ml of concd NH_4OH , centrifuge, and discard the supernate. Wash the precipitate with H_2O and discard the washings.

Step 10. Continue with the separation of the individual lanthanides as in Steps 7, 8, 9, 10, and 11 of the LANTHANIDE procedure. Addendum II gives methods for sample mounting and yield determination as alternatives for Steps 10 and 11 of the LANTHANIDE procedure.

Note

Yttrium can be separated from the lighter lanthanides by slightly modifying the above procedure. Instead of scrubbing with 0.05M HNO_3 in Step 5, scrub with four 10-ml portions of 0.75M HNO_3 . With this operation, >99.9% of the neodymium (and lanthanides of lower atomic number) and about 93% of the europium are removed into the aqueous scrubs. Eighty-eight percent 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 can be mounted directly as the oxalate or oxide and counted. To do this, dissolve the $\text{Y}(\text{OH})_3$ from Step 9 in about 4 drops of concd HCl , add 20 ml of H_2O , and proceed as in Step 10 of the LANTHANIDE procedure or as in Alternative Step 10 of Addendum II.

ADDENDUM II TO THE LANTHANIDE PROCEDURE

Alternative Procedures for Sample Mounting and Determination of Chemical Yield

Given below are alternatives for Steps 10 and 11 for the lighter lanthanides of Sec. 11 of the LANTHANIDE 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 the fractions making up the activity of each lanthanide in a centrifuge

tube. 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 $\text{H}_2\text{C}_2\text{O}_4$ and digest the oxalate precipitates for 15 min on a steam bath. Centrifuge, and discard the supernates. Suspend each precipitate in 5 ml of H_2O , break up the lumps, and filter onto a 1-in.-diam circle of Whatman No. 42 filter paper using a ground-off Hirsch funnel and a filter chimney setup. Wash each oxalate with three successive 5-ml portions of H_2O , then ethanol, and finally ether. Dry the sample for 10 min at 110°C , then 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 around the outside of the filter paper with a sharp blade. Place the sandwich in the titration vessel, and add 10 ml of H_2O and 2 ml of concd HCl . Pipet in an excess of EDTA solution. Heat the solution on a hot plate for about 20 min and adjust the pH to 8 or 9 as described in Sec. 10 of the LANTHANIDE procedure. Back titrate the excess EDTA with La^{3+} 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 \AA , and $0.0125M$ EDTA and $0.025M$ La^{3+} solutions are used.

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palladium, phosphorus, plutonium, potassium, protactinium 

An Additional Note

When the plutonium sample is from soil 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 regular PLUTONIUM procedure is performed.

Add the recommended amount of lanthanum carrier, 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 H₂O, stir, centrifuge, and discard the supernate. Dissolve the precipitate in 1-2 drops of concd HCl and dilute to 2-3 ml with 3M HCl. Continue with Step 2 of the procedure, omitting addition of lanthanum carrier.

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ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING

D. C. Hoffman

1. Introduction

The procedure described below is an adaptation of one by R. F. Mitchell, Anal. Chem., 32, No. 3, 326 (1960). The plating setup is the same as that used in the Uranium-235 procedure.

2. Reagents

HCl: concd; 1M
HNO₃: concd
NH₄OH: concd
Ethanol: absolute
NH₄Cl: solid
Methyl red indicator solution

3. Procedure

Step 1. In a graduated centrifuge tube, collect the eluate from Step 9 of the PLUTONIUM procedure. (The

same amount of eluate as would normally be collected on the Pt disk for pulse analysis is collected). To the eluate add 2-3 drops of concd HNO₃ and place the tube in an oil bath which is maintained at about 100°. With the aid of an air jet, evaporate the solution to dryness. Add 3 drops of concd 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 concd HCl and transfer to the electroplating cell. Use a 1" Pt plating disk, a thin-walled chimney, and a plastic gasket. Wash the centrifuge tube with two 0.5-ml portions of distilled H₂O, transferring the washings to the plating cell (vol. ~1.5 ml). Add two small spatulafuls of NH₄Cl and 2 drops of methyl red indicator solution. Make the solution basic with concd NH₄OH and then add 1M HCl dropwise until the solution is barely acidic.

Step 3. Electroplate at 2 amp and about 6.8 v for 15 min while the solution is stirred with a graphite rod. Just before plating is completed, add 0.5 ml of concd 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 Pt disk, first with H₂O and then with ethanol. Flame the plate and count for 1 min on an alpha counter.

Step 4. By means of Duco cement, mount the Pt plate on a standard fission mount.

REMOVAL OF PLUTONIUM-239 FROM RARE EARTHS, CESIUM, AND ZIRCONIUM

B. E. Cushing

1. Introduction

Plutonium(IV) can be quantitatively removed from the rare earths, cesium, and zirconium by extraction with trioctylamine. The separation is not satisfactory if the plutonium is in an oxidation state other 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, then this element is employed as carrier.

2. Reagents

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

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

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

HCl: 5M; concd

H_2SO_4 : concd

NaNO_2 : 0.1M

Triisooctylamine: 20% by volume in Amsco-95

3. Procedure

All operations are performed in a glove box.

Step 1. Pipet an aliquot of the sample into a 50-ml erlenmeyer flask and add 1 ml each of the desired carriers. Add 10-20 drops of concd H_2SO_4 and heat to fumes of SO_3 .

Step 2. Cool the solution and transfer to a 40-ml centrifuge cone with 5-10 ml of 5M HCl. Add about 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 cone with a minimum amount of 5M HCl, adding the rinsings to the separatory funnel. Add an equal volume of 20% (by volume) triisooctylamine in Amsco-95 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 it was found that three extractions were sufficient to completely remove 47 mg of plutonium in the sample.

2. The procedure does not remove ^{241}Am activity. Americium activity may be separated from the plutonium-free aqueous solution in the following manner:

(a) Precipitate hydroxides by means of ammonia gas. Centrifuge, discard the supernate, and wash the precipitate with H_2O . Centrifuge and discard the supernate.

(b) Dissolve the precipitate in 1-2 drops of concd HCl and add 1 ml of 5M NH_4CNS buffered at pH 1.2. Put the solution on an AG 1-X8 anion column (100-200 mesh and 1 cm \times 6 cm) which has been previously equilibrated with the 5M NH_4CNS solution.

(c) Elute with 10 ml of the cold 5M NH_4CNS solution. This procedure gives a decontamination factor of about 5×10^3 and should be repeated to ensure removal of americium.

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 utilized for the back-extraction of plutonium (IV) from solutions of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The use of DBHQ as a reagent for this purpose was suggested in the May 31, 1968, annual progress report of the Chemical Technology Division of ORNL, ORNL-4272.

Work in our laboratory has shown that treatment with DBHQ reagent followed by contact with 6M HCl will back-extract both plutonium-(IV) and (VI) quantitatively from HDEHP-*n*-heptane solutions. It should be noted that 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 solutions) for plutonium (IV) are very much higher than for plutonium (VI) and 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 and sodium nitrite 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; source: Eastman Organic Chemicals

DBHQ solution: 0.2M solution of 2,5-di-tertiary butylhydroquinone in 2-ethyl-1-hexanol; Source: Eastman Organic Chemicals.

HCl: 6M; 3M

NaNO_2 : 10M

3. Procedure

Step 1. Pre-equilibrate the 0.75 M HDEHP solution with an equal volume of 3M HCl in a separatory funnel. (The size of the funnel should be about twice that of the aliquot of sample that will be used.) Add sufficient 10M NaNO_2 to an aliquot of the sample and the Pu tracer (in either a narrow-necked conical centrifuge tube or an erlenmeyer flask) to make the final concentration of the salt about 0.2M (for example, 1 ml of 10M 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, centrifuging if necessary (Note). Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 6M HCl and discard the wash.

Step 2. To the organic phase, add one-third volume of the 0.2M DBHQ solution and shake for about 10 sec. Add one-half volume of 6M HCl, shake for about 2 min, and allow 5 min for the separation of the two phases. Drain and save the aqueous (lower) phase and discard the organic layer.

Step 3. If the volume of the aqueous phase is less than 5 ml, add H_2O to make the solution 3M in acid and proceed to Step 2 of the PLUTONIUM procedure. If the volume of the aqueous phase is greater than 5 ml, transfer the solution to a 125-ml erlenmeyer flask and evaporate to 2-5 ml over a burner. Transfer the solution to a 40-ml conical centrifuge tube, dilute to make the solution 3M in acid by means of water washes from the erlenmeyer flasks, and then continue with Step 2 of the PLUTONIUM procedure.

Note

If very large aliquots (150-200 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 TO PROCEDURE FOR THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION. II

F. O. Lawrence and D. C. Hoffman

If large amounts of thorium are present, complete the above procedure and then carry out Steps 2, 3, and 4 of the regular PLUTONIUM procedure. Then dissolve the LaF_3 by stirring with 2-3 drops of saturated H_3BO_3 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 concd HCl, collecting the effluents in the Erlenmeyer flask. Boil down the combined effluents to a small volume (0.5-2 ml) and transfer the solution to a 40-ml glass centrifuge tube. Dilute with sufficient H_2O to make the solution 3M in HCl and proceed with Step 2 of the regular PLUTONIUM procedure.

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EXTRACTION OF PLUTONIUM FROM PHOSPHORIC ACID SOLUTIONS BY OCTYLPYROPHOSPHORIC ACID

S. DeVilliers, F. O. Lawrence,
and D. C. Hoffman

1. Introduction

This procedure for extracting plutonium from phosphoric acid solutions is a modification of one developed by S. Amiel of the Israel Atomic Energy Commission, Soreq Nuclear Research Centre. Plutonium in the +3 or +4 condition in 53% phosphoric solution is extracted into a solution of 0.2M octylpyrophosphoric acid (OPPA) in kerosene. The plutonium is back-extracted into concentrated hydrofluoric acid solution and is then coprecipitated on lanthanum fluoride. After dissolution of the

fluoride in boric acid solution, further purification of the plutonium is effected by proceeding with the regular PLUTONIUM procedure at the appropriate place. Between 70-75% of the plutonium activity is recovered by the extraction procedure, provided the OPPA reagent is less than 30 days old.

2. Reagents

Preparation of ^{236}Pu tracer solution.

Take standardized ^{236}Pu tracer in 3M HCl to dryness and dissolve the residue in 10 ml of 42.5% H_3PO_4

La carrier: 5 mg La^{3+} /ml, added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in H_2O

H_3PO_4 : 53% by weight

HF: concd

HCl: concd

H_3BO_3 : saturated aqueous solution

NaNO_2 : 1M aqueous solution

Preparation of octylpyrophosphoric acid (OPPA) reagent.

Introduce 500 ml of kerosene into a 2-l externally cooled reaction vessel. Add 142 g (0.5 mole) of P_2O_5 with constant stirring. Then slowly (30 min) add 260 g (2 moles) of octanol and continue stirring for about 1 h, taking care that the temperature does not rise above 40°C. Make up to a volume of 1 l with kerosene. Prepare 0.2M OPPA reagent by appropriate dilution of the 1M solution with kerosene.

3. Procedure

Step 1. To 1 ml of the ^{236}Pu tracer solution in a 40-ml glass centrifuge tube, add 25 ml of the plutonium sample in 53% H_3PO_4 solution (Note 1). (Samples containing as much as 20 nCi of plutonium have been used successfully in the procedure.) Add 1 ml of 1M NaNO_2 solution, warm in a water bath, and cool (Note 2).

Step 2. In a 60-ml separatory funnel, equilibrate 5 ml of 0.2M OPPA reagent with an equal volume of 53% H_3PO_4 . Centrifuge, and discard the aqueous (lower) layer.

RECOVERY OF RADIOPOTASSIUM FROM VANADIUM

V. R. Casella, P. M. Grant,
and H. A. O'Brien, Jr.

Step 3. To the OPPA layer in the separatory funnel, add the sample solution and shake the mixture for 2 min. Transfer to a 40-ml glass centrifuge tube, centrifuge for 10 min, transfer the OPPA layer to a 40-ml polyethylene centrifuge tube, and discard the aqueous layer.

Step 4. Add 0.5 ml of concd HF, shake the mixture for 2 min, and centrifuge. Transfer the lower layer to a clean polyethylene tube and dilute to 5 ml with distilled H₂O.

Step 5. Extract the OPPA layer a second time with 0.5 ml of concd HF and again dilute the aqueous layer to 5 ml with distilled H₂O. Discard the organic phase.

Step 6. To the combined aqueous layers, add 10 drops of La³⁺ carrier. Centrifuge, and transfer the supernate to a clean polyethylene tube. Add La³⁺ carrier dropwise to the supernate until no more precipitate is formed, centrifuge, and discard the supernate. Combine the fluoride precipitates.

Step 7. Dissolve the combined precipitates in a mixture of 2 drops of saturated H₃BO₃ and 1 ml of concd HCl and perform Steps 6-10 of the regular PLUTONIUM procedure.

Notes

1. Samples of different volumes may be processed by making appropriate adjustments in the amounts of reagents used. The volume ratio of OPPA reagent to H₃PO₄ is maintained at 1:5 and that of concd HF to OPPA reagent in the back-extraction is maintained at 1:10.

2. Sodium nitrite treatment ensures reduction of any Pu(VI) to Pu(IV) and oxidation of Pu(III) to Pu(IV). If the plutonium is known to be in the +4 state, do not carry out the NaNO₂ treatment. If the treatment is used, extraction with the OPPA reagent is performed as soon as the solution has cooled.

1. Introduction

This procedure describes the recovery of potassium-43 produced by the bombardment of vanadium targets with 800-MeV protons. The targets were 0.25 mm thick and had a purity of about 99.9%. Typical proton bombardments were for a duration of approximately 3 μ A-h integrated intensity.

An irradiated foil was dissolved in 8M HNO₃, the solution diluted to 4M in acid, and scandium and potassium carriers added. The solution was 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 was washed with 4M HNO₃, and then with 1M HCl; the latter removed nitrate ion, a biological poison. Potassium was eluted from the column with 12M HCl. The concentrated acid also carried some antimony from the HAP, and it was removed by adsorption on an anion exchange resin from a solution 8M in HCl. The final decontamination step consisted of passing the eluant, adjusted to pH 10, through a chelating ion exchange resin and washing the resin with NH₄OH-NH₄Cl buffer of pH 9.4. The chelating resin has little affinity for alkali metal cations. An overall chemical yield of potassium of 91 \pm 3% was obtained.

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. It is used in diagnostic nuclear medicine for body electrolyte and cardiovascular studies.

2. Reagents

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K carrier: KCl in H₂O; of known concentration

Sc carrier: ScCl_3 in very dilute HCl; of known concentration

HCl: 12M; 8M; 1M

HNO_3 : 8M

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: 2-3 mg of carbazole ($\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, diphenylimide) per 1 ml of concd H_2SO_4

Hydrated antimony pentoxide (HAP) exchanger: source, Carlo Erba, Industrial Chemicals Division, Milan, Italy; washed with distilled water before using to remove fine particulates

Bio-Rad AG 1-X8: 50-100 mesh, anion exchange resin

Bio-Rad Chelex-100: 100-200 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-long) of hydrated antimony pentoxide (HAP) exchanger at a rate of about 0.2 ml/min. Discard the eluant. Wash the column with

several column volumes of 4M HNO_3 and discard the washes. Wash the column with 1M HCl until the eluant gives a negative test for NO_3^- ion with carbazole reagent. (If NO_3^- is present, a deep green color will form). Discard the eluant.

Step 3. Elute potassium with several column volumes of 12M HCl. Add 2 ml of 30% H_2O_2 to the eluant to enhance the Sb(V) oxidation state and evaporate to near dryness. Take up the residue in 15 ml of 8M HCl and pass the solution at a flow rate of about 0.3 ml/min through a column (0.8-cm-i.d. and 10-cm-long) of Bio-Rad AG 1-X8 anion exchange resin to remove any antimony present. Collect the eluant.

Step 4. Adjust the pH of the eluant to 10 by evaporation and addition of NH_4OH . Pass the solution through a column (0.8-cm-i.d. and 10-cm-long) of Bio-Rad Chelex-100 cation exchange resin. Collect the eluant. Wash the column with several column volumes of $\text{NH}_4\text{OH-NH}_4\text{Cl}$ buffer (pH 9.4) to effect quantitative elution of potassium. Combine the eluants.

4. Primary Literature Reference

V. R. Casella, P. M. Grant, and H. A. O'Brien, Jr., *J. Radioanal. Chem.* **36**, 337 (1977).

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rhenum, rhodium, rubidium, ruthenium 

RHENIUM

B. P. Bayhurst

1. Introduction

This procedure was designed for the separation of rhenium from soil 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 $\text{Re}(\text{VII})$ in 0.1M HCl solution through a cation exchange resin column, (4) $\text{Cu}(\text{II})$ - and $\text{Fe}(\text{III})$ -8-hydroxyquinolate scavenges, and (5) removal of $\text{Ru}(\text{III})$ 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 about 50%.

2. Reagents

$\text{Re}(\text{VII})$ carrier: KReO_4 in H_2O , corresponding to about 15 mg of $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4/\text{ml}$; standardized (see procedure for THE SEPARATION OF RHENIUM FROM TUNGSTEN)

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

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

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

$\text{Ru}(\text{III})$ carrier: 10 mg Ru/ml, added as RuCl_3 in 0.1M HCl; probably contains some $\text{Ru}(\text{IV})$

HNO_3 : fuming; concd

HCl: concd; 6M; 0.2M; 0.1M

HF: concd

HF-HCl solution: 5M in each

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

NH_4OH : concd

NaOH: 10M

H_2S : gas

H_2O_2 : 30%

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, 100-200 mesh (H^+ form)

Ethanol: absolute

Methyl red indicator solution

3. Procedure

Step 1. Dissolve about 2 g of soil sample in a Teflon beaker by the successive addition of fuming HNO_3 , concd HCl, and concd 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 about 4M in HF and transfer to a 40-ml polyethylene centrifuge tube. Centrifuge, transfer the supernate to a Teflon beaker, and discard the precipitate.

Step 2. To the supernate, add 20 ml of concd HCl and evaporate nearly to dryness. Add 20 ml of concd HF and again evaporate nearly to dryness. Repeat the HCl and HF treatments and then transfer the solution to a 40-ml polyethylene 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 polyethylene 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 polyethylene tube.

Step 4. Heat the solution on a steam bath and saturate with H_2S for about 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 , again saturate with H_2S , centrifuge, and discard the supernate.

Step 5. To the precipitate, add 1 ml of 10M NaOH and 5-6 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 about 2 ml and neutralize to a methyl red end point with concd

HCl. Add an equal volume of 0.2M HCl and pass the solution through a Dowex 50-X8, 100-200 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 about 2 ml and dilute to 15 ml with H₂O. Add 2 ml of 8-hydroxyquinoline reagent and adjust the pH to 6 with 10M NaOH. Add 2 drops of Cu(II) carrier and heat to coagulate the precipitate. [The Cu(II)-8-hydroxyquinolate carries down a substantial amount of contaminant activity.] Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate. Repeat the Cu(II)-8-hydroxyquinolate scavenge, but, after centrifugation, filter the supernate through a 9-cm Whatman No. 541 filter paper and collect the filtrate in a clean glass tube.

Step 8. To the filtrate, add 2 ml of 6M HC₂H₃O₂ and 2 drops of Fe(III) carrier and heat on a steam bath until the precipitate coagulates. [The precipitate of Fe(III)-8-hydroxyquinolate carries down molybdenum activity.] Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate. Repeat the Fe(III)-8-hydroxyquinolate scavenge twice more. After the last centrifugation, filter the supernate through a 9-cm Whatman No. 541 filter paper and collect the filtrate in a 40-ml polyethylene centrifuge tube.

Step 9. To the filtrate, add 5.5 ml of concd HF and 8 ml of concd HCl. Heat on a steam bath and saturate with H₂S for 15 min. Stopper the centrifuge tube and permit the Re₂S₇ to coagulate. Then treat the precipitate with HF-HCl solution and 6M HCl as described in Step 4.

Step 10. Dissolve the Re₂S₇ with 10M NaOH and 30% H₂O₂ as in Step 5. Use H₂O to transfer the perrhenate solution to a 125-ml Erlenmeyer flask. Boil the solution until all the H₂O₂ has been decomposed. Add 5 ml of absolute ethanol, 2 ml of 10M NaOH, heat on a hot plate, then add 2 drops of Ru(III) carrier. Boil on a hot plate until Ru(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 Ru(OH)₃ scavenge twice more, adding ethanol each time to ensure that any Ru(IV) in the carrier is reduced to Ru(III).

Step 11. Evaporate the perrhenate solution in a glass centrifuge tube to about 2 ml, make it 9-10M in HCl, and heat for 30 min on a steam bath (to convert any technetium to the +4 oxidation state). Saturate with H₂S for 15 min, centrifuge, and discard the supernate. Wash the Re₂S₇ precipitate with 20 ml of 6M HCl and discard the wash.

Step 12. Add 1 ml of concd NH₄OH and 5-6 drops of 30% H₂O₂ to the sulfide. Heat on a steam bath until the solution is completely clear and dilute it to 15 ml with H₂O. Add 4 ml of [(C₆H₅)₄As]Cl reagent, boil the mixture for 2 min, then cool in an ice bath. Filter the [(C₆H₅)₄As]ReO₄ through a tared No. 42 Whatman filter circle, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with cold H₂O and then with cold absolute ethanol. Dry in an oven at 110°C for 5 min, cool, weigh, and mount for counting.

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RHODIUM

J. S. Gilmore

1. Introduction

In the determination of radorhodium the principal decontamination steps include (a) removal of ruthenium as the volatile RuO_4 , (b) precipitation of RhI_3 , and (c) iron(III) hydroxide and acid sulfide scavenges from solutions containing the extremely stable $[\text{Rh}(\text{CN})_6]^{3-}$ complex ion. The rhodium is finally electroplated from sulfuric acid solution after destruction of the complex. The chemical yield is about 60%, and six samples can be analyzed in about one day.

2. Reagents

Rh carrier: 10 mg Rh/ml, standardized
Co carrier: 10 mg Co/ml, added as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ in 1M HCl
Mo carrier: 10 mg Mo/ml, added as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in H_2O
Ba carrier: 10 mg Ba/ml, added as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in H_2O
Sb(III) carrier: 10 mg Sb/ml, added as SbCl_3 in 1M HCl
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_4 in 1M HCl
HCl: 6M; concd
 HNO_3 : concd
 H_2SO_4 : concd
 HClO_4 : concd
 NH_4OH : concd
KCN: 3M
 NaNO_2 : 5M
 Na_2CO_3 : 0.5M
 $\text{Cu}(\text{NO}_3)_2$ solution: 100 mg Cu/ml
KI: solid
 H_2S : gas
Ethanol: 95%
Cation exchange column: 6 mm \times 6 cm Dowex 50-X8 (50-100 mesh) pretreated by washing with 3M NH_4OH

3. Preparation and Standardization of Carrier

Weigh out 27.34 g of $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ and make

up to 1 liter in 0.01M HCl. Pipet 3.0 ml of the solution into a 125-ml erlenmeyer flask and add 3 ml of concd H_2SO_4 , 2 ml of concd HClO_4 and 1 ml of concd HNO_3 . Heat until SO_2 fumes appear. Transfer the solution with 20 ml of H_2O to the plating cell having a weighed Pt disk as cathode. Electroplate at room temperature and 0.1 amp for 16 hr (Note). Wash the cathode with H_2O and then with 95% ethanol. Dry at 110° 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 Rh carrier and an aliquot of the sample.

Step 2. Add 3 ml of concd H_2SO_4 , 2 ml of concd HClO_4 , 1 ml of concd HNO_3 and heat until SO_2 fumes appear. Cool, add 2 ml of concd HClO_4 and evaporate to a volume of 1 ml.

Step 3. Add 3 ml of 6M HCl, 1 ml each of Mo and Co carriers, 1 to 2 g of solid KI and boil for 20 min, adding 6M 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 RhI_3 precipitate with 20 ml of warm 6M HCl and discard the supernate.

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

Step 5. Dilute to 20 ml with H_2O , add 3 drops of Fe carrier, and then concd NH_4OH 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 concd NH_4OH , 1 ml of Ba carrier, 3 ml of 0.5M Na_2CO_3 and warm on a steam bath for 5 min. Add 3 drops of Fe carrier, stir, and centrifuge. Transfer the supernate to a clean centrifuge tube and discard the precipitate.

Step 7. Add concd HCl dropwise until the

evolution of CO_2 ceases. Add 1 ml of 6M HCl, 1 ml each of Te(IV) and Sb(III) carriers, and saturate with H_2S . Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 8. Boil the solution for about 30 sec to remove H_2S . Add 7 ml of concd HCl, 2 ml of $\text{Cu}(\text{NO}_3)_2$ solution, and cool in an ice bath. (The Rh is precipitated, presumably as the compound $\text{Cu}_2[\text{Rh}(\text{CN})_6]_2$.) Centrifuge and discard the supernate.

Step 9. Dissolve the precipitate in 2 ml of concd NH_4OH and dilute to 10 ml with H_2O . Transfer to the Dowex 50 cation exchange column and allow the solution to pass through under gravity, catching the eluate in a 125-ml erlenmeyer flask. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is removed on the column, the $[\text{Rh}(\text{CN})_6]^{3-}$ passing through.

Step 10. Evaporate the solution nearly to dryness, add 3 ml of concd H_2SO_4 , and concen-

trate to a volume of 1 ml to remove Rh-cyanide complex.

Step 11. Repeat Steps 3 through 9, but collect the column eluate in a 40-ml centrifuge tube.

Step 12. Repeat Steps 6 through 10.

Step 13. Add 2 ml of concd HClO_4 , 1 ml of concd HNO_3 , and heat until SO_2 fumes are evolved. Transfer to the plating cell with 20 ml of H_2O . Electroplate at room temperature and 0.1 amp for 16 hr on a weighed Pt cathode disk. Wash the cathode with H_2O and then with 95% ethanol. Dry in an oven at 110° for 15 min. Cool, weigh, mount, and β -count.

Note

The components of the plating cell must be extremely clean in order to obtain a smooth, adherent cathode deposit.

ADDENDUM TO THE RHODIUM PROCEDURE

J. S. Gilmore

It has been found convenient to substitute for Step 9 the following method for the removal of Cu from the precipitate, which presumably has the formula $\text{Cu}_2[\text{Ru}(\text{CN})_6]_2$:

To the precipitate add 20 ml of H_2O , warm the mixture, and then add sufficient 6*M* NaOH to convert all the copper to the insoluble oxide, leaving 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 clean centrifuge tube, and discard the precipitate. Proceed to Step 10.

May 1968

SCANDIUM II

B. P. Bayhurst

1. Introduction

In the analysis for scandium in soil samples, the three major decontamination steps are (1) removal of iron and some zirconium on a Dowex AG 1-X8 anion exchange resin from a solution 10M in HCl, (2) $Zr_3(PO_4)_4$ scavenges, and (3) LaF_3 scavenges from solutions containing scandium in the form of fluorocomplexes. Following the decontamination steps, scandium is precipitated as the fluoride and converted to the hydroxide. It is then placed on a Bio-Rad AG 50W-X4 cation exchange resin from dilute HNO_3 solution. Elution from the column is effected with α -HIB (α -hydroxyisobutyric acid) and the scandium is finally precipitated as the hydroxide and ignited to the oxide. The chemical yield is 60-70%.

2. Reagents

Sc carrier: 20 mg Sc_2O_3 /ml, added as $ScCl_3$ in very dilute HCl; standardized (see original SCANDIUM procedure)

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

La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3

HCl: concd; 10M

HNO_3 : concd

$HClO_4$: concd

NH_4OH : concd

NaOH: concd

$NH_4H_2PO_4$: 1.5M

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

$NH_2OH \cdot HCl$: solid

Methyl red indicator solution

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

Anion exchange resin: Dowex AG 1-X8, 50-200 mesh (washed with 10M 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 centrifuge tube, add 1.0 ml of standard scandium carrier and 5 ml of concd $HClO_4$, and fume nearly to dryness. Dilute to 20 ml with H_2O and precipitate $Sc(OH)_3$ with 10M NaOH. Centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of concd HCl, dilute to 20 ml with H_2O , and precipitate $Sc(OH)_3$ with concd NH_4OH .

Step 2. Dissolve the precipitate in a minimum of concd 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 concd HCl and place the solution on a Dowex AG1-X8 anion exchange resin column (50-200 mesh). Collect the effluent in a 125-ml Erlenmeyer flask. Pass 15 ml of 10M HCl through the column and combine the effluent with the previous one.

Step 4. Add 2 drops of zirconium holdback carrier and evaporate to about 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 2-3M in HCl. Add 5 drops of 1.5M $NH_4H_2PO_4$ 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 polyethylene centrifuge tube.

Step 5. Add 3 ml of NH_4HF_2 -HF reagent and neutralize the solution to a methyl red end point with concd NH_4OH . (The scandium is now in the form of fluorocomplexes.) Add 100 mg of $NH_2OH \cdot HCl$, 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 polyethylene tube, and discard the precipitate. Repeat the LaF_3 scavenge three times

and transfer the final supernate to a clean polyethylene tube.

Step 6. Add 6 ml of concd 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 concd HCl and precipitate Sc(OH)_3 by adding concd 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 4-6 drops of concd HNO_3 and dilute to 30 ml with H_2O . Add 2-3 ml of Bio-Rad AG 50W-X4, minus 400 mesh, cation exchange resin, stir for about 1 min, centrifuge, and discard the supernate. Use a small amount of H_2O and a transfer pipet 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 α -HIB, for which the pH has been adjusted to 5.2. Maintain an air pressure of 3 psi on the column and collect the effluent containing 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 approximately 25-40 tubes.

Step 8. To the effluent 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 containing 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 concd HCl, dilute to 20 ml with H_2O , and add concd NH_4OH to precipitate Sc(OH)_3 . Centrifuge, and discard the supernate. Dissolve the precipitate in a minimum of concd HCl, add filter paper pulp slurry, and again precipitate Sc(OH)_3 with concd NH_4OH . Filter through a 9-cm No. 541 Whatman filter paper. Transfer the paper to a porcelain crucible and ignite at 1000°C for 15 min. Weigh and mount the Sc_2O_3 .

June 1979

SEPARATION OF SCANDIUM FROM LARGE AMOUNTS OF TITANIUM METAL

B. P. Bayhurst

1. Introduction

In this procedure, the titanium metal is dissolved by treatment with H_2O , concd HF, and concd HNO_3 . (The quantities of these reagents are given for a 55-g metal sample; the same proportions of metal, H_2O , HF, and HNO_3 are maintained for larger, and smaller, sample sizes.) After dissolution of the titanium, standard scandium carrier is added to precipitate ScF_3 away from TiF_6^{3-} . The fluoride is then converted to $Sc(OH)_3$, and the latter is dissolved and reprecipitated. The hydroxide is finally ignited to Sc_2O_3 . The chemical yield is ~85%.

2. Reagents

Sc carrier: 20 mg Sc_2O_3 /ml, added as $ScCl_3$ is very dilute HCl; standardized (see original SCANDIUM procedure).

HNO_3 : concd

HF: concd

HCl: concd

HF-HCl reagent: 1.2M in HF and 2M in HCl

NaOH: 10M

NH_4OH : concd

3. Procedure

Step 1. To a 55-g sample of titanium metal in a 1000-ml Teflon beaker, add 180 ml of H_2O and place

on a hot plate. Add 145 ml of concd HF in 5-ml increments, heating after each addition until reaction ceases. Add 20 ml of concd HNO_3 and heat until reaction is no longer apparent. Then, with heating, add another 35 ml of HNO_3 in portions of 5 ml, each increment being added after the previous one is consumed. The metal should now be in solution.

Step 2. Dilute the solution to 500 ml with H_2O , add 4.0 ml of standard scandium carrier, and heat on a hot plate for 3 h. Let the mixture stand overnight, heat for 1 h, then cool in an ice bath. Transfer the mixture in portions to clean 40-ml polyethylene centrifuge tubes. Centrifuge, discard the supernates, and combine the precipitates in a single polyethylene tube with the aid of HF-HCl reagent (1.2M in HF and 2M in HCl). Wash the precipitate with 20 ml of the HF-HCl reagent and discard the wash.

Step 3. Add 40 drops of 10M NaOH to the precipitate, dilute to 10 ml with H_2O , and heat on a steam bath until the $Sc(OH)_3$ formed coagulates. Centrifuge, and discard the supernate.

Step 4. Dissolve the precipitate in 2 ml of concd HCl, add excess concd NH_4OH to precipitate $Sc(OH)_3$, centrifuge, and discard the supernate. Add 2 ml of concd HCl to dissolve the precipitate, then add 6 ml of filter paper pulp slurry and an excess of concd NH_4OH to reprecipitate $Sc(OH)_3$. Filter onto a 9-cm No. 541 Whatman filter paper, transfer the paper to a Coors 00 porcelain crucible, and ignite at 1000°C for 15 min. Cool, weigh, and mount the Sc_2O_3 .

June 1979

QUANTITATIVE CHEMICAL RECOVERY OF SPALLATION-PRODUCED ELEMENTS. 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 99.90% pure foils, usually 0.51 mm thick, and were irradiated for 1 to 2 μ A-h of integrated intensity. Following irradiation, a target was permitted to stand for several days to permit the activities to decay to reasonable levels. The target was then radiographed and the hot spot was cut away from surrounding inactive metal. The radioactive section was cleaned of surface contaminants by immersion in chromic acid cleaning solution for 1-2 min, rinsed with distilled water, dried, and weighed. Typical molybdenum weights ranged from 1-10 g.

A. SEPARATION OF STRONTIUM

P. M. Grant, M. Kahn,
and H. A. O'Brien, Jr.

1. Introduction

Strontium is quantitatively separated from the irradiated molybdenum by a six-step procedure consisting of 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 lead molybdate is precipitated. Extraction of the lead molybdate with a 0.12M HCl-50% solution of bis-(2-ethylhexyl)phosphoric acid (HDEHP) in toluene 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, based on radioactivity determinations, is $94 \pm 2\%$ and separation is effected from molybdenum, technetium, niobium, zirconium, yttrium, rubidium, selenium, arsenic, zinc, and cobalt.

The long-lived strontium isotopes 82 and 85 are obtained from the irradiation process. Because ^{82}Sr has a reasonably long half-life (25.55 days) 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 one is primarily interested in strontium activities 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

Sr carrier: 10 mg Sr^{2+}/ml , added as $Sr(NO_3)_2$ solution
 HNO_3 : 7-8M
HCl: 0.12M
 H_2S : gas
 H_2O_2 : 30% aqueous solution (unstabilized)
 NH_4OH : concd; 3.7M
 NH_4Cl : 0.1M aqueous solution
 $Pb(NO_3)_2$: 5 mg of Pb^{2+}/ml of aqueous solution
Chromic acid cleaning solution: 35 ml of saturated aqueous $Na_2Cr_2O_7$ in 1 l of concd H_2SO_4
HDEHP solution: 50% solution by volume of bis-(2-ethylhexyl)phosphoric acid (source: Eastman Organic Chemicals) 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, 10-20 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 concd NH_4OH , make the solution about $1M$ in molybdenum and $3\text{-}4M$ 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 Mo(V) or Mo(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 to a clean centrifuge tube, and set aside the precipitate.

Step 3. To the supernate, add 1 ml of $\text{Pb(NO}_3)_2$ solution (5 mg of Pb^{2+}). A white precipitate of PbMoO_4 forms immediately. Stir the suspension, heat on a steam bath for 1-2 h, centrifuge, decant the supernate, and set it aside. Wash the PbMoO_4 precipitate several times with a $0.1M$ NH_4Cl solution that has been made slightly basic 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 1-2 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 basic with 0.5 ml of $3.7M$ NH_4OH . A white precipitate, probably Pb(OH)_2 , forms. Bubble H_2S through the suspension for about 30 min. The white precipitate is converted to PbS (brownish black). Acidify the mixture with 0.5 ml of $7\text{-}8M$ HNO_3 , heat on a steam bath for 10-15 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 about 6.0 by the dropwise

addition of concd NH_4OH . If necessary, add a few milligrams of strontium carrier in the form of $\text{Sr(NO}_3)_2$ solution. (See Sec. 1, Introduction; milligram quantities of strontium are required to maintain a quantitative recovery of the element.) Pass the solution through a column (0.8-cm-diam, 4-cm-long) of untreated 100-200 mesh hydrous ZrO_2 exchange crystals (HZO-1) at a rate of about 0.1 ml/min. Collect the strontium-containing eluate.

4. Primary Literature Reference

P. M. Grant, M. Kahn, and H. A. O'Brien, Jr., J. Inorg. Nucl. Chem. **37**, 413 (1975).

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 of 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 added to that from the prior molybdenum-strontium HDEHP extraction (Procedure A). The combined organic phases are back-extracted with $8M$ HCl , and the aqueous phase from this extraction is converted to $12M$ HCl and passed through an anion exchange resin. The yttrium remains in solution and is found in the column eluant, thus completing the separation from molybdenum. The overall chemical yield of yttrium is $96 \pm 4\%$.

Yttrium-88 (half-life, 107 days) and yttrium-87 (half-life, 80.3 hours) are the main long-lived isotopes of the element 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 about 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: 12M; 8M; 0.12M

HDEHP solution: 50% solution by volume of bis-(2-ethylhexyl)phosphoric acid (source: Eastman Organic Chemicals) in toluene.

Anion exchange resin: Bio-rad AG 1-X10, 100-200 mesh; preconditioned with concd HCl; column parameters: 0.8-cm i.d., 9-cm length, 0.1-ml/min flow rate.

3. Procedure

Step 1. Dissolve the hydrous molybdenum oxides from Step 2 of Procedure A in 10 ml of 0.12M HCl. Add 10 ml of HDEHP solution and equilibrate the mixture on a Burrell shaker for 50 min. Combine the organic phase (upper layer) with that from Step 4 of Procedure A. (If radiozirconium is to be isolated later, repeat the HDEHP extraction and add the organic layer to the other two layers.)

Step 2. Back-extract the combined organic phase twice successively with equal volumes of 8M HCl on the Burrell shaker, each time for 50 min. Combine the aqueous phases and set aside the organic phase for the separation of zirconium.

Step 3. Evaporate the aqueous solution to near dryness, then dissolve the mixture in 10 ml of 12M HCl. Pass the solution through the Bio-Rad AG 1-X10 anion exchange resin and collect the eluant containing the yttrium.

4. Primary Literature Reference

V. R. Casella, P. M. Grant, and H. A. O'Brien, Jr., *Radiochim. Acta* **22**, 31 (1975).

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 (Step 1) of the yttrium procedure (Procedure B) is performed twice, 99% of the zirconium is taken into the organic phase and remains there after back-extraction of the yttrium with 8M HCl. Subsequent treatment of the organic phase with 30% H_2O_2 extracts molybdenum into the aqueous phase but has no effect on the zirconium. Extraction of the organic phase with 3.5M HF then removes the zirconium, as well as any niobium that is present. The latter is separated from the zirconium by extraction into diisobutylcarbinol (DIBC), after the aqueous phase has been made 5.8M in both HF and H_2SO_4 . The overall yield of zirconium is $96 \pm 6\%$.

Zirconium-88 (half-life, 83.4 days) is the precursor of ^{88}Y . There would appear to be advantages in the incorporation of 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 long storage time for the attainment of radioactive equilibrium, and increase the useful lifetime of the photoneutron source.

2. Reagents

HF: concd; 3.5M

H_2SO_4 : concd

H_2O_2 : 30% aqueous solution (unstabilized)

Diisobutylcarbinol (DIBC): source, Carbide and Chemicals Company, Division of Union Carbide and Carbon Corporation

3. Procedure

Step 1. Back-extract molybdenum from the HDEHP phase of Step 2 of the yttrium procedure (Procedure B) with an equal volume of 30% H_2O_2 . Discard the aqueous (lower) layer.

Step 2. Back-extract the HDEHP layer with an equal volume of 3.5M HF to remove zirconium. Discard the organic layer.

Step 3. Make the aqueous phase 5.8M in both HF and H₂SO₄ and extract twice with equal volumes of diisobutylcarbinol (DIBC), discarding 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.

4. Primary Literature Reference

R. E. Whipple, P. M. Grant, R. J. Daniels, W. R. Daniels, and H. A. O'Brien, Jr., Radiochem. Radioanal. Lett. 27, 137 (1976).

June 1979

SEPARATION OF MILLIGRAM QUANTITIES OF STRONTIUM AND ZIRCONIUM FROM 100 GRAMS OF YTTRIUM

R. J. Prestwood

1. Introduction

Yttrium metal was used on the Apollo space ship as a possible high-energy particle monitor. The potential reactions of interest were ⁸⁹Y(n,2n)⁸⁸Y, ⁸⁹Y(n,3n)⁸⁷Y, ⁸⁷Sr, ⁸⁹Y(n,p)⁸⁹Sr, and ⁸⁹Y(p,n)⁸⁹Zr. It was therefore necessary to be able to analyze for very small amounts of strontium and zirconium in the presence of 100 g of yttrium (the weight of the metal used as monitor).

In the procedure, the yttrium metal sample is dissolved in HNO₃ and strontium is precipitated as Sr(NO₃)₂ by means of yellow fuming HNO₃. After appropriate purification of the Sr(NO₃)₂ to remove yttrium contaminant, SrCO₃ is precipitated for counting. The chemical yield is ~75%.

Following removal of strontium, zirconium is converted to the insoluble Zr₃(PO₄)₄. Yttrium contaminant is removed from the precipitate by conversion

to the hydroxide and dissolution of the latter in HNO₃. The Zr₃(PO₄)₄ is treated with concd HF and HNO₃, and the resulting ZrF₆ is precipitated as the barium salt. Reaction of BaZrF₆ with concd H₂SO₄ removes barium as BaSO₄. Zirconium is then precipitated as Zr(OH)₄ and ignited to ZrO₂ for counting. The chemical yield is ~80%.

2. Reagents

Sr carrier: 65 mg of Sr, added as Sr(NO₃)₂

Zr carrier: 60 mg of Zr, added as ZrOCl₂·8H₂O in 1M HNO₃

HNO₃: yellow fuming; concd

H₂SO₄: concd

NH₄OH: concd

NaOH: 10M

(NH₄)₂CO₃: 10% aqueous solution

NH₄H₂PO₄: 1.5M

BaCl₂: 1M

3. Procedure

Step 1. Add 100 ml of H₂O to cover the 100-g sample of yttrium in a 2-ℓ beaker. Over a period of 1.5 h, slowly add 1 ℓ of concd HNO₃ to dissolve the metal. Transfer the solution to a 1-ℓ Erlenmeyer flask and evaporate to about 350 ml on a hot plate. Add 65 mg of strontium carrier, as Sr(NO₃)₂, and make the volume up to about 480 ml with concd HNO₃. Add 200 ml of yellow fuming HNO₃ and stir the solution with a magnetic stirrer on a hot plate at low heat. (The solution should be warm, but not hot, to the touch.) Filter the Sr(NO₃)₂ precipitate through a sintered glass filter (350-ml, medium) under vacuum and collect the filtrate in a 2-ℓ suction flask. The filtration process requires about 14 min.

Step 2. Dissolve the Sr(NO₃)₂ on the filter with H₂O and collect the solution in a 500-ml suction flask. Evaporate to 2-5 ml and transfer the solution to a clean 40-ml glass centrifuge tube. Neutralize with concd NH₄OH and add an excess of 10% (NH₄)₂CO₃ solution to precipitate strontium and any yttrium present, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate in a minimum of concd HNO_3 . Precipitate $\text{Sr}(\text{NO}_3)_2$ by adding 20 ml of yellow fuming HNO_3 . Centrifuge, and transfer the supernate to the original filtrate (Step 1). Dissolve the $\text{Sr}(\text{NO}_3)_2$ in a minimum of H_2O and again precipitate the nitrate with yellow fuming HNO_3 . Centrifuge, and discard the supernate.

Step 4. Dissolve the $\text{Sr}(\text{NO}_3)_2$ in a minimum of H_2O and make the volume up to 20 ml. Make the solution basic with concd NH_4OH to precipitate any yttrium present. Centrifuge, and transfer the supernate to a clean glass centrifuge tube and discard any $\text{Y}(\text{OH})_3$ that has formed. Add 10% $(\text{NH}_4)_2\text{CO}_3$ solution to precipitate SrCO_3 . Filter onto a 1-in. Whatman No. 42 filter paper. Transfer the SrCO_3 from the paper to a tared plastic tube and weigh for NaI well counting.

Step 5. Transfer the combined filtrate and supernate from the 2-l suction flask to a 1-l Erlenmeyer flask. Add 60 mg of zirconium carrier (as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 1M HNO_3) and evaporate the solution to a volume of 300 ml. Add 25 ml of 1.5M $\text{NH}_4\text{H}_2\text{PO}_4$ solution and dilute the mixture to 550 ml. [This treatment precipitates $\text{Zr}_3(\text{PO}_4)_4$ and large amounts of YPO_4 . It probably would be better to add the $\text{NH}_4\text{H}_2\text{PO}_4$ dropwise, while heating and stirring the solution, until just slightly more than the stoichiometric amount for precipitation of $\text{Zr}_3(\text{PO}_4)_4$ is added.] Centrifuge the mixture in portions in 40-ml polyethylene tubes and save the supernates for their yttrium content. Treat the $\text{Zr}_3(\text{PO}_4)_4$ precipitate with about 5 ml of 10M NaOH

to convert YPO_4 to $\text{Y}(\text{OH})_3$; the $\text{Zr}_3(\text{PO}_4)_4$ is not affected. The $\text{Y}(\text{OH})_3$ is dissolved away from the $\text{Zr}_3(\text{PO}_4)_4$ with a minimum of concd HNO_3 . Centrifuge the mixture and save the supernate for its yttrium content.

Step 6. To the precipitate of $\text{Zr}_3(\text{PO}_4)_4$ now in a single polyethylene centrifuge tube, add 2 ml of concd HF and 4 ml of concd HNO_3 and dilute to 20 ml with H_2O . Centrifuge out the small amount of YF_3 that forms and transfer the supernate to a clean polyethylene tube. Add 2 ml BaCl_2 to the supernate to precipitate BaZrF_6 . Heat on a steam bath to coagulate the precipitate, centrifuge, and discard the supernate. Wash the precipitate with H_2O and discard the wash.

Step 7. Add 2 ml of concd H_2SO_4 to the precipitate and heat on a steam bath for 5 min. Dilute to 25 ml with H_2O , centrifuge, transfer the supernate to a clean polyethylene tube, and discard the BaSO_4 precipitate. To the supernate, add an excess of concd NH_4OH to precipitate $\text{Zr}(\text{OH})_4$. Centrifuge, and discard the supernate. Repeat the BaZrF_6 precipitation and conversion to BaSO_4 . Reprecipitate $\text{Zr}(\text{OH})_4$ with concd NH_4OH . Add 6 ml of filter paper pulp slurry, filter through a 9-cm No. 40 Whatman filter paper, and transfer the paper to a porcelain crucible. Ignite to ZrO_2 at 1000°C for 15 min. Cool, weigh, and place in a NaI well tube for counting.

June 1979

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, BaZrF_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% hydrogen peroxide solution and precipitated as the hydrous oxide, $\text{Ta}_2\text{O}_5 \cdot \text{XH}_2\text{O}$, which is ignited to the anhydrous compound. The chemical yield is 60-70%.

2. Reagents

Ta carrier: 10 mg Ta/ml, prepared by dissolving the pure metal in a minimum of a mixture of concd HNO_3 and HF and diluting to the appropriate volume with H_2O .

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

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

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

HNO_3 : concd, fuming

HF: concd

H_3BO_3 : saturated aqueous solution

H_2S : gas

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

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

NH_4OH : dilute; concd

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 polyethylene 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 basic to phenolphthalein with concd NH_4OH , centrifuge, and discard the supernate. Wash the precipitate with 30 ml of dilute NH_4OH (1 ml of concd NH_4OH and 29 ml of H_2O) and 2 ml of saturated $\text{N}^+\text{I}_4\text{NO}_3$, centrifuge, and discard the wash.

Step 2. Add 10 ml of fuming HNO_3 , place on a steam bath, and permit the $\text{Ta}_2\text{O}_5 \cdot \text{XH}_2\text{O}$ to coagulate. Centrifuge, and discard the supernate. Dissolve the precipitate in 7 drops of concd HF, dilute to 10 ml with H_2O , and add 100 mg of $\text{NH}_2\text{OH} \cdot \text{HCl}$. Add 3 drops of lanthanum carrier, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean polyethylene tube. Repeat the LaF_3 scavenge twice more.

Step 3. To the supernate from the final LaF_3 scavenge, add 4 drops of Sb(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 polyethylene 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 polyethylene tube and heat on a steam bath to expel H_2S . Add 6 drops of concd HF and 2.75 ml of concd 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 BaZrF_6 coagulates. Centrifuge, transfer the supernate to a clean polyethylene tube, and repeat the BaZrF_6 scavenge. Transfer the supernate to a 1-oz polyethylene 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 about one-fourth of its volume of 1.5% H_2O_2 . Repeat the extraction three times, combining all extracts in a Teflon beaker and discarding the hexone layer.

Step 7. Add 5 ml of concd HNO_3 and boil the solution to a volume of 2-3 ml. Repeat. Add 5 ml of concd HNO_3 , boil down the solution to about 2-3 ml, and transfer the mixture to a 40-ml polyethylene centrifuge tube using concd HNO_3 . Centrifuge, and discard the supernate. Wash the precipitate twice with concd HNO_3 , each time centrifuging and discarding the supernate.

Step 8. To the precipitate, add a slurry of filter paper pulp, stir, and filter through a 9-cm No. 40 Whatman filter paper. Transfer the paper to a Coors 00 porcelain crucible and ignite at 900°C for 20 min. Permit the crucible to cool.

Step 9. Add 1-2 ml of ethanol to the Ta_2O_5 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 polyethylene squeeze bottle to transfer the oxide onto a weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and a filter chimney. Filter, wash the precipitate with ethanol, and dry at 110°C . Cool, weigh, and mount for counting.

June 1979

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^- and BiI_4^- . In each case, the thallium is then purified by $\text{La}(\text{OH})_3$ scavenges, then precipitated as Tl_2CrO_4 . Chemical yields are approximately 50%.

2. Reagents

Tl carrier: 10 mg Tl(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

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

HNO_3 : concd; 6M; 2M

NH_4OH : concd

NaI: solid

NaI reagent: 3M in NaI and 2M in HNO_3

Na_2CrO_4 : 10% aqueous solution

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 about 2 ml, 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 (3M in NaI and 2M in HNO_3) and discard the washes.

Step 2. Dissolve the TII in a minimum of 6M HNO_3 (the thallium remains in the +1 condition)

and heat over a burner to volatilize any I_2 present. Dilute the solution to about 20 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 $\text{La}(\text{OH})_3$ with an excess of concd 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 $\text{La}(\text{OH})_3$ scavenge.

Step 4. To the supernate, add 2 ml of 10% Na_2CrO_4 solution and 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 1-in. No. 42 Whatman filter paper, and mount for counting. Without the heating and washing, the small Tl_2CrO_4 crystals will 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. With the flask on a hot plate, add 5 ml of 6M HNO_3 , then add 5 ml of the concd acid in small portions to continue the dissolution process. Evaporate the solution to 2-3 ml and transfer to a 40-ml glass centrifuge tube with 20 ml of 2M HNO_3 . 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 washes. The washing removes adhering BiI_3 and I_2 from the TII.

Step 2. Repeat Steps 2, 3, and 4 of Procedure A.

June 1979

TUNGSTEN III

B. P. Bayhurst and R. J. Prestwood

1. Introduction

In this procedure, the alkaloid cinchonine ($C_{19}H_{22}N_2O$) is used to precipitate tungsten from a medium 3M in HCl. After dissolution of the precipitate in 10M NaOH, $La(OH)_3$ scavenges are carried out and the tungsten is then precipitated as the 8-hydroxyquinolate in the presence of EDTA. The precipitate is wet ashed, the WO_3 formed is dissolved in 10M NaOH, and $La(OH)_3$ scavenges are repeated. Niobium is further removed by extraction with cupferron into chloroform. PdS is precipitated from the aqueous layer to remove molybdenum. The hydrous oxide, $WO_3 \cdot XH_2O$, is then precipitated by concd HNO_3 and ignited to the anhydrous form for weighing and counting. The chemical yield is 60-70%.

2. Reagents

W carrier: 10 mg W/ml, added as $Na_2WO_4 \cdot 2H_2O$ in H_2O ; standardized

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

Pd carrier: 10 mg Pd/ml, added as $PdCl_2$ in 1M HCl

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

HCl: concd

HNO_3 : concd

H_2SO_4 : concd

Tartaric acid: 50% aqueous solution

$HC_2H_3O_2$: concd

H_2S : gas

NaOH: 10M

EDTA solution: 0.2M solution of disodium ethylenediamine tetraacetate

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

Cinchonine wash solution: 25 ml of cinchonine solution plus 30 ml of concd HCl, diluted to 1 l with H_2O

8-Hydroxyquinoline reagent: 5% solution in 2M $HC_2H_3O_2$

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

Ethanol: absolute

$CHCl_3$

3. Preparation and Standardization of Carrier

Same as in original TUNGSTEN procedure.

4. Procedure

Step 1. To the sample in 3M HCl, add 4.0 ml of tungsten carrier and warm on a hot plate overnight. Boil down to about 30 ml, add 100 ml of hot H_2O , and keep at low heat on hot plate for 30 min. Add 6 ml of cinchonine solution and heat for an additional 30 min. Centrifuge portions of the solution in a 40-ml glass centrifuge tube, and discard the supernates. Wash the precipitate with 30 ml of hot cinchonine wash solution and discard the wash.

Step 2. Dissolve the precipitate in 10 drops of 10M NaOH and dilute to 10 ml with H_2O . Centrifuge off any insoluble material and transfer the supernate to a clean centrifuge tube. Add 3 drops of lanthanum carrier, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean centrifuge tube. Repeat the $La(OH)_3$ scavenge.

Step 3. To the supernate, add 5 ml of 0.2M EDTA solution, adjust the pH to between 5.0 and 5.6 with concd $HC_2H_3O_2$, and heat on a steam bath for 5 min. Add 5 ml of 8-hydroxyquinoline 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 concd HNO_3 and transfer the solution to a 125-ml Erlenmeyer flask. Add 4 ml of concd 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 $WO_3 \cdot XH_2O$ precipitate in 10 drops of 10M NaOH and dilute to 15 ml with

H₂O. 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 La(OH)₃ scavenge twice more.

Step 6. Repeat Steps 3, 4, and 5.

Step 7. Transfer the supernate to a 60-ml separatory funnel and add 10 drops of tartaric acid solution and 10 drops of concd HCl. Add 10 ml of CHCl₃ and shake vigorously for about 1 min. Add 5 ml of 6% cupferron reagent, shake for 1 min, and discard the CHCl₃ (lower) layer. To the aqueous layer, add 10 ml of CHCl₃ and 3 ml of cupferron reagent, shake for 1 min, and discard the CHCl₃ layer. Wash the aqueous layer with 5 ml of CHCl₃ 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 concd H₂SO₄, 5 drops of palladium

carrier, and 1 drop of molybdenum carrier, and saturate the solution with H₂S. Heat for a few minutes, centrifuge, transfer supernate to a clean centrifuge tube, and discard the precipitate.

Step 9. Add 5 drops of palladium carrier and saturate with H₂S on a steam bath. Centrifuge, and filter the precipitate onto a 9-cm No. 541 Whatman filter paper. Collect the filtrate in a clean centrifuge tube.

Step 10. To the filtrate, add 10 ml of concd HNO₃, then heat on a steam bath to coagulate the WO₃·XH₂O formed. Centrifuge, discard the supernate, and slurry the precipitate with 6 ml of filter paper pulp and 4 ml of concd HCl. Filter through a Millipore filter (AAWP, 0.8-μ) and ignite for 15 min at 800°C. Weigh and mount the WO₃.

June 1979

ZIRCONIUM II

R. J. Prestwood, B. P. Bayhurst,
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 soil. The various steps in the analysis are given below in Sec. 4.A. Zirconium is first extracted from a solution 6M in HCl into HDEHP [bis-(2-ethylhexyl)phosphoric 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 about 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

Zr carrier: ≈ 20 mg ZrO₂/ml, added as ZrOCl₂·8H₂O in H₂O; standardized

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

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

Sc carrier: 10 mg Sc/ml, added as ScCl₃ in 1M HCl
HNO₃: concd

HCl: concd; 6M

H₂SO₄: concd

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

NH₄OH: concd

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

NH₄H₂PO₄: 1.5M aqueous solution

HDEHP solution: 0.5M solution of bis-(2-ethylhexyl)phosphoric acid in *n*-heptane; source, Stauffer Chemical Company, Chicago Heights, Illinois; reported purity >94%

BaCl₂: 1M 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 ℓ with 0.1M HCl. Pipet 5.0 ml of the carrier solution into an ignited and tared Coors 0 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 Soil

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

Step 2. Transfer the heptane layer to a 4-oz. polyethylene bottle fitted with a tight cap and add 20 ml of a solution that is 4M in HNO₃ and 2.5M in HF. Add 2 drops of methyl red indicator solution to help distinguish the aqueous from the organic layer. Place on a mechanical shaker and shake for 5-10 min. The zirconium is now in the aqueous layer as fluorocomplex. Use a syringe attached to a polyethylene pipet to transfer the aqueous layer to a 40-ml polyethylene 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 polyethylene centrifuge tube. Repeat the LaF₃ scavenge four more times and after each scavenge transfer the supernate to a clean polyethylene tube.

Step 4. Place the sample on a steam bath, add 1 ml of 1M BaCl₂, and heat for a few minutes. Centrifuge, and discard the supernate. To the BaZrF₆ precipitate, add 1-2 ml of concd H₂SO₄, stir, and place on a steam bath for a few minutes. Dilute to 20 ml with H₂O and allow to stand until BaSO₄ 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 and neutralize with concd NH₄OH, adding 4-5 drops in excess. Place on a steam bath for 2 min, centrifuge, and discard the supernate.

Step 6. Dissolve the Zr(OH)₄ precipitate in 10 drops of concd HCl and dilute to 20 ml with H₂O. (At this point there may be a small amount of BaSO₄ present, which is removed by centrifugation after the Zr(OH)₄ has been dissolved completely.) To the solution containing the zirconium, add an excess of concd NH₄OH, centrifuge, and discard the supernate. The Zr(OH)₄ precipitate may be used for milking experiments or may be converted to ZrO₂ for counting as described below.

Step 7. Dissolve the Zr(OH)₄ in concd HCl, add 5 ml of filter paper pulp slurry, make ammoniacal with concd NH₄OH, and filter onto a 9-cm No. 40 Whatman filter paper. Transfer to a Coors 00 crucible and ignite at 900°C for 5-10 min. With a polished stirring rod or the ultrasonic technique, powder the ZrO₂ and, using absolute ethanol, transfer to a tared filter circle. Dry at 110°C, weigh as ZrO₂, 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 about 4M in either HNO₃ or HCl. For each 50 ml of sample solution add 2 ml of 1.5M NH₄H₂PO₄ solution. Heat until the Zr₃(PO₄)₄ coagulates, centrifuge portions of the solution in a 40-ml polyethylene tube, and discard the supernate. (This is an excellent decontamination step, especially for the removal of macroquantities

of iron, aluminum, barium, calcium, and magnesium.)

Step 2. Add 4 ml of NH₄HF₂ to dissolve the Zr₃(PO₄)₄. Add 2 drops each of lanthanum and yttrium carriers, stir vigorously, dilute to 15 ml with H₂O, and neutralize to a methyl red end point with concd NH₄OH. Centrifuge, and transfer the supernate to a clean polyethylene centrifuge tube. Discard the LaF₃-YF₃ precipitate.

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

Step 4. Add 1 ml of scandium carrier, 6-8 ml of concd HCl, and heat on a steam bath until ScF₃ coagulates. Centrifuge, transfer the supernate to a clean polyethylene tube, and discard the precipitate.

Step 5. Add 1.5 ml of 1M BaCl₂, place on a steam bath until BaZrF₆ coagulates, centrifuge, and discard the supernate.

Step 6. Add 2 ml of concd H₂SO₄ to the BaZrF₆ precipitate, stir, and place on a steam bath for a few minutes. Dilute to 20 ml with H₂O and let stand until BaSO₄ precipitates. Centrifuge, transfer the supernate to a clean polyethylene tube, and discard the precipitate.

Step 7. Add 2 drops each of lanthanum and yttrium carriers and an excess of concd NH₄OH. Centrifuge, and discard the supernate.

Step 8. Repeat Steps 2 (no lanthanum and yttrium carriers), 3, 4, and 5.

Step 9. Repeat Step 6, but transfer the supernate to a clean 40-ml glass centrifuge tube. Add concd NH₄OH to precipitate Zr(OH)₄, centrifuge, and discard the supernate.

Step 10. Dissolve the Zr(OH)₄ in concd HCl, centrifuge out any BaSO₄, and reprecipitate Zr(OH)₄ with concd NH₄OH. The Zr(OH)₄ may be used for milking experiments or may be converted to ZrO₂ for counting as described in Sec. 4.A, Step 7.

June 1979

**PROCEDURES FOR QUALITY CONTROL IN COUNTING
RADIOACTIVE NUCLIDES**

PROCEDURES FOR QUALITY CONTROL IN COUNTING RADIOACTIVE NUCLIDES

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These procedures are designed to control the quality of the data obtained in α - and β -counting and in γ - and α -spectroscopy. They ensure that the various detectors behave consistently from day to day.

α -Counting

Uncovered ^{239}Pu standards (plutonium electroplated on platinum disks) and background are counted daily. If abnormal fluctuations in the count rate of the standard are observed (Note), a "plateau" is run, or other special diagnostic procedures are applied. The plateau, which is determined once a week, is a plot of counting rate vs voltage applied to the central wire anode of the gas detector. From this measurement one can determine whether overall gain (gas and electronic) has changed. The voltage is increased in 100-V steps and a 5-min count is taken at each step. Changes in the shape of the curve are looked for. If the plot shows abnormalities (experience permits the ready recognition of abnormalities), proper maintenance steps are taken.

Once a month, a special ^{239}Pu standard is counted on every α -counter. The decay rate of this standard is known absolutely and if the counters are operating normally, they must give the correct counting rate. Any counter that does not give the correct count is repaired.

Note

In our laboratory, we use a mode of operation that accepts standard deviation limits of ± 1.5 as normal statistical variation. If the fluctuations in count rate exceed these limits, a second count is taken, and normal limits for this determination are ± 3.0 standard deviations.

β -Counting

Daily counts of ^{234}Pa (U_3O_8 source) standard and background are taken. Except that no monthly absolute standard count is made, what applies to α -counting applies here.

γ -Spectroscopy

Multichannel analyzers with two types of detectors, NaI and Ge(Li), are used for γ -spectroscopy.

NaI Detectors. To determine whether the analyzers are operating consistently, ^{137}Cs standards and background are counted daily. The electronic gain (energy span) of the system is adjusted to place the photopeak of the standard in a specific channel. If, on any day, the electronic gain settings for the standard are different from those of the previous day, the system is examined to determine the reason for the anomalous behavior.

Each day, total counts under the photopeak of the standard are determined. If the system is operating consistently, the number of counts should be approximately the same from day to day. The same statistical considerations are applied as for α - and β -counting.

Ge(Li) Detectors. Standard and background counts are made daily. For these detectors, the standard is a mixture of ^{57}Co , ^{60}Co , and ^{137}Cs isotopes. The electronic gain of the system is adjusted and checked in the same manner as for NaI detectors.

Two options are available for the absolute calibration of the detectors for intensities vs energies of γ rays. One option uses a source of mixed radionuclides obtained from the National Bureau of Standards. This source provides absolutely known γ -ray intensities for calibration purposes. The second option uses an intensity calibrated ^{152}Eu standard (also supplied by the National Bureau of Standards). Use of the ^{152}Eu standard is preferable because the many γ rays of the single nuclide all

decay with the same long half-life. In contrast, the γ rays of some of the nuclides in the mixed standard have short half-lives and new standards must be obtained yearly.

Deviations in the positions, intensities, and full width at half-maximum (energy resolution) are monitored for abnormal fluctuations.

α -Spectroscopy

Two types of spectrometers with multichannel analyzers are used for α -spectroscopy: Frisch grid

and Silicon diode. Background counts and the α -spectrum of a mixed ^{238}Pu and ^{239}Pu standard are taken daily. The important quality control parameters in α -spectroscopy are (1) the full width at half-maximum of the α -particle full energy peak, (2) the ratio of the full energy peak integrals of the ^{239}Pu to ^{238}Pu , and (3) the absolute intensity of the ^{239}Pu integral. These parameters are monitored daily for abnormal statistical fluctuations. Abnormal behavior indicates that maintenance is necessary.

June 1979