LA-1721, 2nd Ed. (Rev.)
CHEMISTRY-GENERAL
TID-4500, 13th Ed., Rev.

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT REVISED: January 1958
REPORT DISTRIBUTED: August 18, 1958
Change 1 distributed: March 11, 1960
Change 2 distributed: April 11, 1962

COLLECTED RADIOCHEMICAL PROCEDURES*

(Radiochemistry Group J-11)

Work done by:

D. P. Ames
J. W. Barnes
B. P. Bayhurst
N. A. Bonner
W. H. Burgus
G. A. Cowan
B. E. Cushing
W. R. Daniels
P. B. Elkin
G. P. Ford
J. S. Gilmore
D. C. Hoffman
E. J. Lang
M. A. Melnick
C. O. Minkkinen
H. A. Potratz
R. J. Prestwood
J. E. Sattizahn
T. T. Shull
H. L. Smith
C. W. Stanley
G. F. Wagner
B. Warren
K. Wolfsberg

Report compiled by:

Jacob Kleinberg

*This report supersedes LA-1566; LA-1567; LA-1721, 1st Ed.; and LA-1722.

Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

---

CONTENTS

(Elements are arranged in order of increasing atomic number)

CONTENTS (cont'd.)

CESIUM II

B. E. Cushing

1. Introduction

The procedure outlined below is based on the method of analysis described by Yamagata and Yamagata, Analyst, 85, 282 (1960). Cesium is first precipitated as the silicotungstate. Dissolution of this precipitate is followed by a ferric hydroxide scavenge, and then the cesium is precipitated as the dipicrylaminate. This salt is dissolved in 4-methyl-2-pentanone and the cesium extracted by means of 2M hydrochloric acid. Cesium is finally precipitated as the perchlorate, in which form it is weighed and counted. The chemical yield approximates 70% and eight analyses can be performed in about 8 hours.

2. Reagents

Cs carrier: 10 mg Cs/ml [added as CsCl in H_2O] - standardized

Fe carrier: 10 mg Fe/ml [added as $Fe(NO_3)_3 \cdot 9H_2O$ in very dilute HNO_3]

$HClO_4$: 3M

$HClO_4$: conc.

HCl: 2M

HCl: 6M

HCl: conc.

HNO_3: conc.

NaOH: pellets

Silicotungstic acid: 1 g/ml H_2O

Sodium dipicrylaminate solution: Stir 25 gm of dipicrylamine* with 500 ml of H_2O and add 6M NaOH until solution is complete. Allow the solution to stand for several hours and filter.

Ethanol: absolute

4-methyl-2-pentanone

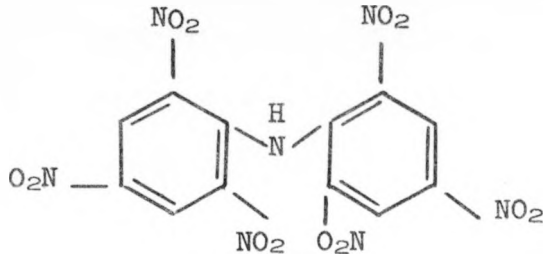
Thymol blue indicator solution: Mix 100 mg of thymol blue with 2 ml of 0.1M NaOH and dilute to 100 ml with H_2O.

3. Preparation and Standardization of Carrier

Make up an aqueous solution containing 12.7 gm of CsCl per liter. Pipet 5 ml of the solution into a 125-ml Erlenmeyer flask and add 1 ml of conc. HNO_3 and 5 ml of conc. $HClO_4$. Boil until dense white fumes appear, cool to room temperature, and add 15 ml of absolute ethanol. Cool for 15 min in an ice bath. Filter on a weighed sintered glass Gooch crucible (fine porosity) and wash three times with 3-ml portions of absolute ethanol. Dry at 110° for 15 min, cool, and weigh as $CsClO_4$.

Four standardizations gave results agreeing within 0.5%.

*Dipicrylamine:



4. Procedure

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

Step 2. Add 2 ml of H_2O to the precipitate, heat to boiling, and then add 3 pellets of NaOH to dissolve the precipitate.

Step 3. Pour the alkaline solution into 20 ml of hot 3M $HClO_4$ in a 125-ml Erlenmeyer flask. Boil over a burner until the volume is reduced to about 10 ml. Transfer to a 40-ml centrifuge tube and again heat to boiling. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate which consists of silica and tungsten(VI) oxide.

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

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

Step 6. Filter through a fine sintered glass crucible. Wash the precipitate with 10 ml of ice cold water and dry in an oven at 110°.

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

Step 8. To the aqueous extracts add 1 ml of conc. HNO_3 and evaporate the solution to approximately 10 ml. Add 5 ml of conc. $HClO_4$ and boil until dense white fumes are evolved.

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

Step 10. Slurry the precipitate in 5 ml of absolute ethanol and filter onto a weighed No. 42 Whatman filter paper circle (1"), using a ground-off Hirsch funnel and filter chimney. Use absolute ethanol to complete the transfer of the $CsClO_4$ precipitate. Wash the precipitate several times with 5-ml portions of the alcohol. Dry at 110° for 15 min, cool for 10 min, weigh and mount. Count immediately.

ANTIMONY*

D. C. Hoffman and J. W. Barnes

1. Introduction

In this procedure for the determination of antimony in fission product solutions the antimony is first converted to the +5 state. Decontamination from the bulk of the molybdenum activity present is then effected by MoS_3 precipitation in the presence of fluoride ion which strongly complexes Sb(V), thus keeping it in solution. After reduction of antimony to the tripositive state, separation from tin is effected by precipitation of Sb_2S_3 in the presence of tin carrier and fluoride ion, the latter this time keeping the tin in solution as a fluoro complex. Tellurium, which precipitates along with antimony, is removed by precipitation with hydrogen sulfide from concentrated hydrochloric acid solution, the antimony remaining in solution. The antimony is then adsorbed on a Dowex 1-X10 anion exchange column from 0.9M hydrochloric acid solution. The last traces of molybdenum are removed with a wash of the acid. The antimony is eluted from the column by means of a 20% ammoniacal tartrate solution and is again precipitated as a sulfide. The sulfide is dissolved in concentrated hydrochloric acid and converted to the metal by reduction with Cr(II) chloride. In this form it is weighed and counted. The chemical yield is about 50%, and six analyses can be performed in about 8 hours.

*Revised, February 1962

2. Reagents

Sb carrier: 10 mg Sb/ml (added as $SbCl_3$ in 6M HCl) - standardized

Mo carrier: 10 mg Mo/ml (added as Na_2MoO_4 in H_2O)

Sn carrier: 10 mg Sn/ml (added as $SnCl_2 \cdot 2H_2O$ in 6M HCl)

Te^{4+} carrier: 10 mg Te/ml (added as Na_2TeO_3 in 12M HCl)

Te^{6+} carrier: 10 mg Te/ml (added as $Na_2H_4TeO_6$ in 3M HCl)

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

HI: conc.

HF: conc.

H_2SO_4: conc.

H_2S: gas

Br_2-H_2O: saturated solution

NH_4OH: conc.

$CrCl_2$ solution (Oxsorbent)

$NaKC_4H_4O_6 \cdot 4H_2O$: 20% aqueous solution

Aerosol solution: 1% in H_2O

Methanol: absolute

Dowex 1-X10 anion resin, 100-200 mesh (obtained in purified form from Bio-Rad Laboratories, Richmond, Calif.)

3. Preparation and Standardization of Carrier

Dissolve 18.7 g of $SbCl_3$ in 6M HCl and make the solution up to a volume of 1 liter with the acid.

Pipet 5 ml of the above carrier solution into a weighed filter

beaker. (This beaker has a 15-ml, fine porosity, sintered glass crucible sealed into the side near the top so that the operations which follow - reduction, filtration, drying, and weighing - may be carried out in this one vessel.) Add 5-10 ml of $CrCl_2$ solution (Oxsorbent). After conversion to Sb metal is complete, filter and wash the precipitate with small portions of H_2O and absolute methanol. Dry the filter beaker containing the Sb at 100° for 1 hour. Cool and weigh.

4. Procedure

Step 1. To a 40-ml short taper centrifuge tube add 2 ml of Sb carrier, a few drops of Mo carrier, the sample, and 2 ml of Br_2-H_2O. Boil off the Br_2 and make the solution ~ 1.5M in HCl. Add 1 ml each of conc. HF and conc. H_2SO_4 per 25 ml of solution. Bring to boiling, saturate with H_2S to precipitate MoS_3, add some filter paper pulp, centrifuge, and pour the supernate through a filter into a 90-ml centrifuge tube. Wash the filter with 2-3 ml of 1M HCl and permit the washings to drain into the same centrifuge tube.

Step 2. To the solution add 1 ml Sn carrier, 2 drops of Mo carrier, 2 ml of conc. HI, boil for about 2 min, and add 5 ml of H_2O. Saturate with H_2S to precipitate Sb_2S_3, add a few drops of aerosol solution and centrifuge. Discard the supernate, wash the precipitate with 1M HCl and discard the washings.

Step 3. Dissolve the precipitate in 4 ml of conc. HCl, boil off H_2S and remove any undissolved MoS_3 precipitate by filtering the solution through No. 41 Whatman paper into a clean 40-ml short taper centrifuge

tube. To the filtrate add 4 drops of Sn carrier, 4 drops of Te^{4+} carrier, 2 drops of Te^{6+} carrier, and 1 ml each of conc. HI and conc. HF. Boil for about 2 min (until the original vigorous reaction subsides). Dilute to 25 ml with 1M HCl, add a few drops of aerosol solution, and saturate with H_2S to precipitate Sb_2S_3. Centrifuge and wash the precipitate as in the previous step.

Step 4. Repeat Step 3, but use no Sn or Te carrier.

Step 5. Dissolve the precipitate in 4 ml of conc. HCl, boil off the H_2S, add 2 ml of Te^{4+} carrier and boil for 1-2 min. Add 2 ml more of conc. HCl, bring to boiling, saturate with H_2S and filter on a 15-ml medium fritted glass funnel into a 40-ml short taper centrifuge tube. Wash the original tube with 2 ml of conc. HCl and filter intc the original filtrate. Discard the precipitate. Boil the combined filtrate, add 2 ml of Te^{4+} carrier, boil for 1-2 min, saturate with H_2S and filter into a 40-ml short taper centrifuge tube, discarding the precipitate.

Step 6. Boil off the H_2S, evaporate the solution to about half of its original volume (it will now be ~ 6M in HCl), and dilute with H_2O to make the solution 0.9M in HCl. (Add 6 ml of H_2O for every 1 ml of solution. Measure volumes accurately and do the dilution carefully. The 0.9M value is rather critical, since the distribution coefficient for Mo rises steeply both above and below 0.9M HCl concentration.) (Note 1).

Step 7. Prepare a Dowex 1-X10 anion resin (100-200 mesh) column (1.1 cm x 5.5 cm) with a glass wool plug both above and below the resin

bed. Pre-wash the column with about 10 ml of 0.9M HCl. Place the solution from Step 6 on the column and permit it to flow through. Discard the eluate. Wash the column with 250 ml of 0.9M HCl, discarding the washings. Elute the Sb with 20 ml of 20% $NaKC_4H_4O_6$ which has been made basic with 12 drops (~ 1 ml) of conc. NH_4OH. Collect the eluate in a 40-ml short taper centrifuge tube.

Step 8. Add conc. HCl (about 2 ml) until a precipitate just forms. Dissolve the precipitate by adding conc. HCl dropwise, and then add 2 additional ml of the acid. Saturate with H_2S, centrifuge, and discard the supernate.

Step 9. Dissolve the precipitate in 5-10 ml of conc. HCl and boil off the H_2S. Make the solution 3-5M in HCl and filter through a 60-ml fine sintered glass crucible into a 40-ml short taper centrifuge tube.

Step 10. Add sufficient $CrCl_2$ solution (Oxsorbent) to completely precipitate Sb as the metal. Start filtering through a weighed No. 40 Whatman filter circle, 7/8" diameter, within 1 min. or less, using a ground-off Hirsch funnel and a chimney. Wash the metal with 5-ml portions of H_2O and absolute methanol. Dry at 100° for 15 min. Cool, weigh, and mount (Note 2).

Notes

1. As an alternative to Step 6, after the H_2S is boiled off, the solution may be evaporated nearly to dryness on a steam bath, but the material must not be left on the steam bath dry or at elevated temperatures or the Sb may volatilize. Then add a few drops of H_2O until a

white precipitate forms, dilute to 10 ml with 0.9M HCl, and proceed with Step 7.

2. The Sb is ordinarily not counted until four days after the column step (Step 7), to allow 9.3h Te^{127} to grow into equilibrium with 93h Sb^{127}.

TIN II

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

1. Introduction

This procedure is much less tedious to carry out than the previous one described in LA-1721. The latter, however, does give satisfactory decontamination.

The chemistry is performed about two days after irradiation; this time interval is necessary to allow 2h Sn^{127} to decay to 93h Sb^{127}. When performed after the two-day waiting period, the procedure gives excellent decontamination from fission products.

The sample is first treated with bromine water to convert all the tin to the +4 condition and to promote complete exchange between fission-product tin and Sn(IV) carrier. The oxidation is followed by precipitation of SnS_2 from acid solution and then the tin is dissolved and adsorbed on an anion exchange column from 0.9M hydrochloric acid solution; molybdenum, tellurium, and antimony pass through the column. The tin is eluted from the column with 1.8M perchloric acid and again precipitated as the sulfide. The sulfide is dissolved, the tin complexed by means of hydrofluoric acid, and two acid sulfide scavenges performed. Following destruction of fluoride ion with boric acid, the tin is again precipitated as the sulfide, dissolved, adsorbed on an anion exchange column, and eluted. After a final SnS_2 precipitation, the tin is dissolved and

reduced to the metal by means of chromous chloride. It is weighed and counted in this form.

The chemical yield is about 70% and four samples can be analyzed in 6-7 hours.

2. Reagents

Sn carrier: 10 mg Sn/ml [added as $SnCl_4 \cdot 5H_2O$ in 3M HCl] - standardized

Te^{4+} carrier: 10 mg Te/ml [added as Na_2TeO_3 in 3M HCl]

Te^{6+} carrier: 10 mg Te/ml [added as Na_2TeO_4 in 3M HCl]

Mo carrier: 10 mg Mo/ml [added as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 6M HCl]

Sb carrier: 10 mg Sb/ml [added as $SbCl_3$ in 6M HCl]

La carrier: 10 mg La/ml [added as aqueous $La(NO_3)_3 \cdot 6H_2O$]

HCl: 0.9M

HCl: conc.

HF: conc.

$HClO_4$: 1.8M

H_3BO_3: saturated aqueous solution

H_2S: gas

Br_2-H_2O: saturated solution

$CrCl_2$ solution (Oxsorbent) - cold

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

Aerosol: 0.1% in H_2O

Ethanol: absolute

Rubber cement: 6% in benzene

3. Preparation and Standardization of Carrier

Dissolve about 15 gm of $SnCl_4 \cdot 5H_2O$ in 500 ml of 3M HCl. Pipet 2.0 ml of the carrier solution into a 40-ml centrifuge tube and precipitate the tin as the metal by means of cold $CrCl_2$ (Oxsorbent) solution. Filter the tin onto a No. 42 Whatman 1" filter circle. Wash the metal with H_2O and then with absolute ethanol. Dry in an oven at 110° for 10 min, cool for 20 min, and weigh. Four standardizations are carried out.

4. Procedure

Step 1. To 2.0 ml of the Sn carrier solution in a 40-ml centrifuge tube, add the sample and 0.5 ml of Br_2-H_2O. Heat until the Br_2 is gone and then dilute with H_2O until the solution is 1M in HCl. Place in an ice bath and saturate with H_2S. Centrifuge, discard the supernate, and wash the precipitate with 0.9M HCl, discarding the washings.

Step 2. Dissolve the precipitate in 1 ml of conc. HCl with heat and boil for 3 min to remove H_2S. If the volume is less than 1 ml, make up to this volume with conc. HCl. Add 1 drop each of the following carriers: Te^{6+}, Te^{4+}, Sb, and Mo. Then add 0.5 ml of Br_2-H_2O and heat until the Br_2 is gone.

Step 3. Dilute the sample to 12 ml with H_2O. (The solution is now approximately 1M in HCl.) Pour the solution onto a column of Bio Rad AG-1,X4, 100-200 mesh, anion resin, 5 cm x 9.5 mm, which has been treated with 10 ml of 0.9M HCl. After the solution has been permitted to pass through the resin column, wash the column with four 20-ml portions of

0.9M HCl. Discard the eluate, including the washings.

Step 4. Elute the tin with 25 ml of 1.8M $HClO_4$ and collect the eluate in a 40-ml centrifuge tube. Add 4 drops of Mo carrier and saturate with H_2S. Add 4 drops of aerosol and centrifuge. Discard the supernate, wash the precipitate with 0.9M HCl, and discard the washings.

Step 5. Dissolve the precipitate in 2 ml of conc. HCl (any MoS_3 present will not dissolve) and boil for 3 min to remove H_2S. Add 1 drop each of the following carriers: Te^{6+}, Te^{4+}, and Sb. Add 0.5 ml each of Br_2-H_2O and conc. HF. Dilute the sample to 6 ml with H_2O and boil. Saturate the hot solution with H_2S, adding 2 drops of La carrier at the completion of saturation. Add 3-4 drops of aerosol and centrifuge.

Step 6. Transfer the supernate to a clean 40-ml centrifuge tube by means of a transfer pipet and add 1 drop each of Te^{6+}, Te^{4+}, and Mo carriers. Also add 0.5 ml of Br_2-H_2O and boil. Again saturate the hot solution with H_2S, adding 2 drops of La carrier at the completion of saturation. Add 3-4 drops of aerosol, centrifuge, and transfer the supernate to a clean 40-ml centrifuge tube as above.

Step 7. Adjust the volume of the supernate to 15 ml by the addition of H_2O. Add 10 ml of saturated H_3BO_3 solution and cool in an ice bath. Bubble in H_2S. Centrifuge, discard the supernate, and wash the precipitate with 0.9M HCl.

Step 8. Dissolve the precipitate in 1 ml of conc. HCl and boil for 3 min to expel H_2S. Add 1 drop each of Te^{6+}, Te^{4+}, and Sb carriers and 0.5 ml of Br_2-H_2O. Heat until all the Br_2 has been expelled. If a

precipitate is still present (MoS_3), centrifuge, and pipet the supernate into a clean centrifuge tube.

Step 9. Repeat Steps 3 and 4.

Step 10. Dissolve the precipitate in 2 ml of conc. HCl with heat and boil the solution for 3 min to remove H_2S. Dilute the solution to about 8 ml with H_2O, cool, and add an equal volume of cold $CrCl_2$ solution. To avoid coagulation of the tin, filter immediately onto a previously washed, dried, and weighed No. 42 Whatman 1" filter circle, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate first with 0.9M HCl, then with H_2O, and finally with absolute ethanol.

Step 11. Dry the precipitate in an oven at 110° for 5 to 10 min. Cool and weigh. Secure the precipitate with 3 drops of 6% rubber cement in benzene. When the precipitate is again dry, mount it on an Al sample plate using double sided Scotch tape. Cover the sample with a square of Mylar and count (Note 1).

Notes

1. Analysis of either or both 27.0h Sn^{121} and 9.62d Sn^{125} can be carried out. Small amounts of ~136d Sn^{123} and of 2.6y Sb^{125} will also be observed. If Sn^{121} is to be determined, a least squares analysis of the data is performed on an IBM 704 computer. If only Sn^{125} is to be determined, β-counting is begun about 12 days after bombardment, when the contribution of Sn^{121} is small, and a correction is applied for the

amount of Sn^{123} in the sample. The quantity of the later isotope present in the sample at any time after bombardment is read from a previously constructed graph showing the contribution of this isotope to the total β count of the sample at given times after irradiation. This graph was obtained by following the β decay of several tin samples for at least a year; the data were resolved into the contributions from Sb^{125}, Sn^{125}, and Sn^{123} by a least squares analysis. With the counting techniques used, the contribution of Sn^{123} was found to be about 0.7% of the total Sn activity at t_o.

MOLYBDENUM II

(For rapid determination in the presence of large quantities of foreign material)

James S. Gilmore and H. Louise Smith

1. Introduction

The procedure described below, devised originally for the determination of Mo^{101}, has proved to be suitable for the removal of molybdenum from 120 g of uranium or 1 g of plutonium or about 20 g of iron. It also gives excellent decontamination from neptunium and fission products.

The chief decontamination step is an extraction into chloroform of the precipitate of Mo(VI) with α-benzoinoxime. This step may be omitted and decontamination effected by extraction of molybdenum from hydrochloric acid solution into hexone (see Note 1) if the sample contains less than 10 g of uranium. If the original sample has a volume greater than one liter the hexone extraction is essential as a volume reducing step.

Additional decontamination steps include adsorption of Mo(VI) from hydrochloric acid solution on an anion exchange resin and an iron hydroxide scavenge. The molybdenum is finally precipitated as the 8-hydroxyquinolate, in which form it is counted.

The chemical yield is 60-70% and duplicate determinations can be performed in about 45 minutes.

2. Reagents

Mo carrier: 10 mg Mo/ml $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ - standardized as described in the molybdenum procedure of Barnes and Lang (this volume)

Fe carrier: 10 mg Fe/ml (added as $FeCl_3\cdot 6H_2O$)

α-Benzoinoxime: 2% in ethanol

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

HCl: conc; 6M; 1M

HNO_3: conc.

$HClO_4$: conc.

H_2SO_4: conc.

$HC_2H_3O_2$: 6M

NaOH: 0.6M

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

$NH_4C_2H_3O_2$: 6M

Acetone

Ethanol: 95%

Chloroform

Methyl red indicator solution

Anion resin: Dowex 1-X10 (200 - 400 mesh; stored in 6M HCl; and prepared for use as described in the molybdenum procedure of Barnes and Lang (this volume).

3. Procedure

Step 1. The sample is made 6-7M in HCl and 1-2 ml of Mo carrier is added (Note 1). Boil the solution briefly and dilute with ice and water to 750 ml (Note 2). Transfer the solution to a 1 liter pear-shaped separatory funnel and precipitate Mo with 25 ml of α-benzoinoxime reagent.

Step 2. Add 50 ml of chloroform and shake vigorously. Permit the phases to separate and the precipitate to move from the aqueous to the chloroform phase (Note 3). Transfer the chloroform phase to a 250 ml pear-shaped separatory funnel. Extract the aqueous phase with 10 ml of α-benzoinoxime and 30 ml of chloroform and combine the chloroform layer with that separated previously. Discard the aqueous phase.

Step 3. Wash the chloroform layer with a mixture of 80 ml of 1M HCl and 20 ml of ethanol and discard the washings. Transfer the chloroform layer to a 125 ml separatory funnel. Add 25 ml of 0.6M NaOH and shake vigorously to remove the Mo. Discard the chloroform and transfer the aqueous layer to a 250 ml Vycor or quartz Erlenmeyer flask.

Step 4. Boil the solution briefly to expel any chloroform present. Add 10 ml of conc HNO_3 and boil the solution to half its original volume. Add 4 ml of conc. $HClO_4$ and 2 ml of conc. H_2SO_4 and boil carefully until the exothermic reaction subsides. Then boil until strong fumes of SO_3 are evolved. (This step destroys organic material.)

Step 5. Dilute the solution with 20 ml of 6M HCl and place on a Dowex 1-X10 (200 - 400 mesh) resin column (4 ml bed volume). Wash the

resin successively with 10 ml of 6M HCl, 15 ml of 0.1M HCl-HF, and 10 ml of 3M NH_4OH.

Step 6. Elute the Mo from the column with 15 ml of 6M $NH_4C_2H_3O_2$ solution. To the eluate add 3 ml of conc NH_4OH and 4 drops of Fe carrier. Boil and filter through 11 cm., 41-H Whatman filter paper, using a 2 60° funnel. Discard the precipitate (Note 4).

Step 7. To the filtrate add methyl red indicator solution, acidify with 6M $HC_2H_3O_2$, then add 2 ml in excess, boil, and add 2 ml of 8-hydroxyquinoline reagent (Note 5). Filter onto a 1" Whatman No. 42 filter circle, using a ground-off Hirsch funnel and filter chimney. Discard the filtrate.

Step 8. Dry the Mo oxinate for 30 sec. at 140°, weigh, mount, and β-count.

Notes

1. A hexone (4-methyl-2-pentanone) extraction may be performed at this point instead of or in addition to the precipitation and extraction of Mo as the α-benzoinoximate. The hexone extraction is advisable if the sample contains less that 10 g of U and is essential as a volume reducing step if the sample has a volume greater than 1 liter.

The solution, which is 6-7M in HCl, is extracted with an equal volume of hexone* to remove Mo. The hexone layer is washed with an equal volume of 6M HCl,** and is then shaken with 20-50% of its volume of H_2O in order to back-extract the Mo. If the original sample contained more than 100 mg of Fe, one now proceeds with the precipitation of Mo by means of α-benzoinoxime; otherwise, one may go directly to Step 5.***

2. Precipitation of Mo with α-benzoinoxime is more nearly complete if the solution is cold.

3. At least 15 minutes must have elapsed since end of irradiation before any Mo chemistry is performed, in order to avoid possible separation of Nb^{99} and Mo^{99} before the Mo has grown in.

4. The $Fe(OH)_3$ scavenge removes Nb, which otherwise contaminates the final sample.

5. The oxine precipitation constitutes the last Tc separation from the Mo. Therefore, the time of the addition of the 8-hydroxyquinoline is accurately observed and recorded.

---

*Hexone which has been pre-equilibrated with 6M HCl.

**6M HCl which has been pre-equilibrated with hexone.

***or, if no Fe is present at this point, the H_2O back-extract may be diluted with an equal volume of conc. HCl and the solution put directly on a Dowex-1, 40 ml reservoir, anion column. Then proceed with the regular chemistry.

ZIRCONIUM-95 and ZIRCONIUM-97*

This procedure is a modification by C. W. Stanley, G. P. Ford, and E. J. Lang of one described by D. N. Hume, CN-1312 (May 15, 1945). Second modification.

1. Introduction

In the procedure described below exchange between carrier and Zr^{95} and Zr^{97} is effected by formation of the fluorozirconate complex $ZrF_6^{=}$. Rare-earth and alkaline-earth activities are removed by lanthanum fluoride scavenging, and then zirconium is separated by three barium fluorozirconate precipitations. Zirconium is finally precipitated with mandelic acid from hydrochloric acid medium and ignited to the oxide, ZrO_2, in which form it is weighed and counted. The chemical yield is about 75% and a set of eight analyses can be performed in about 7 hours.

The procedure may be used either to assay for Zr^{95} or Zr^{97} separately or to determine them together, depending only on counting and analysis of data. To assay for Zr^{95} the chemistry is not begun until the 17h Zr^{97} had decayed. On completion of the chemical procedure, the ZrO_2 is counted on the top shelf of a β-proportional counter before too much Nb^{95} has grown in. To analyze for Zr^{97}, the ZrO_2 is counted through a 112-mg Al/cm^2 absorber.

To determine both Zr^{95} and Zr^{97} in the sample, the ZrO_2 is counted on the top shelf of the β-proportional counter for sufficient time to resolve the decay curve, which has 17h (Zr^{95}), 35d (Nb^{95}), and 65d (Zr^{95}) components. The decay curve may be analyzed by least squares.

*Revised, February 1962.

2. Reagents

Zr carrier: 10 mg Zr/ml [added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1M HNO_3] - standardized

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

Nb hold-back carrier: (solution of potassium niobate, H.P., 10 g per 100 ml of solution. Source of the niobate - Fansteel Metallurgical Corporation, North Chicago, Ill.)

HCl: 1M; conc.

HNO_3: 1M; conc.

H_2SO_4: conc.

HF: conc.

H_3BO_3: saturated aqueous solution

NH_4OH: conc.

$NH_2OH \cdot HCl$: solid

$Ba(NO_3)_2$: 50 mg Ba/ml

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

Mandelic acid: 16% aqueous solution

Aerosol: 1% aqueous solution

Ethanol: 95%

3. Equipment

Ice bath

Centrifuge

Fisher burner

Block for holding centrifuge tubes

Forceps

Porcelain crucibles: Coors 0 or 00 and Coors 1 or 2

Ground-off Hirsch funnels: Coors 0000

Stainless steel filter chimneys (i.d. 3/4")

Filter flasks

No. 42 Whatman filter circles: 1" diameter, tared

No. 42 Whatman filter paper: 11 cm

100-ml beakers

2", 60° funnels

Pipets: assorted sizes

50-ml Lusteroid test tubes

40-ml conical centrifuge tubes: Pyrex 8320

Stirring rods

4. Preparation and Standardization of Carrier

Dissolve 30.0 g of $ZrO(NO_3)_2 \cdot 2H_2O$ in H_2O and add sufficient conc. HNO_3 to make the solution 1M in HNO_3. Filter and make the filtrate up to 1 liter with 1M HNO_3.

Pipet 10.0 ml of the solution into a 100-ml beaker, make the solution 2M in HCl, and cool in an ice bath. Add a slight excess of 6% cupferron solution and filter. Wash the precipitate with 1M HCl containing a little cupferron. (Keep all solutions and the cupferron derivative of Zr cold.) Transfer the precipitate to a porcelain crucible (Coors 1 or 2)

and ignite for 1 hr at 600 to 800°. Cool and weigh as ZrO_2.

5. Procedure

Step 1. Place the same in a 50 ml Lusteroid tube and add 4 ml of Zr carrier. Adjust to 4-5M in HNO_3 and to a volume of about 12 ml. (Note 1). Add solid $NH_2OH \cdot HCl$ so that the solution is 2-3% in NH_2OH (Note 2). Add 3 drops of potassium niobate carrier and make the solution 5M in HF. Heat for 10 min. on a steam bath.

Step 2. Add 10 drops of La carrier and centrifuge for a short time. Add another 10 drops of La carrier on top of the previous precipitate and centrifuge thoroughly. Decant the supernate into another Lusteroid tube and discard the precipitate.

Step 3. Repeat Step 2 twice.

Step 4. After a total of six LaF_3 scavengings, add 1 ml of $Ba(NO_3)_2$ solution per 5 ml of the supernate. Let stand for 1 min and centrifuge. Discard the supernate.

Step 5. To the precipitate add 4 ml of saturated H_3BO_3 (Note 3) and slurry. Add 2 ml of conc. HNO_3 and slurry again. Add 10 to 12 ml of H_2O and mix well. If the precipitate does not dissolve completely, centrifuge and decant the supernate into another Lusteroid tube. (This step is made easier by heating the H_3BO_3, the HNO_3, and the H_2O on a steam bath prior to their use.)

Step 6. Precipitate $BaZrF_6$ by the solution of 2 ml of $Ba(NO_3)_2$ solution and 2 ml of conc. HF. Centrifuge and dissolve as before (Step 5).

Step 7. Precipitate $BaZrF_6$ as before (Step 6) and dissolve the precipitate in 4 ml of saturated H_3BO_3, 4 ml of conc. HCl, and 10 ml of H_2O. Add 3 drops of conc. H_2SO_4 diluted with 5 ml of H_2O and let stand for 15 min. Add a drop or two of aerosol solution and centrifuge. Transfer the supernate to a 40-ml glass centrifuge tube and discard the $BaSO_4$ precipitate.

Step 8. To the supernate add conc. NH_4OH until the solution is basic. Centrifuge down the $Zr(OH)_4$ and discard the supernate. Dissolve the precipitate in 2 ml of conc. HCl, 4 ml of saturated H_3BO_3, and 10 ml of H_2O. Centrifuge and, if a precipitate is formed, transfer the supernate to a 40-ml centrifuge tube, discarding the precipitate. Centrifuge and dissolve the precipitate in 15 ml of 8M HCl. Heat to boiling, add 10 ml of 16% mandelic acid and again bring to a boil. Wait 2-3 min, centrifuge, and discard the supernate. Dissolve the zirconium mandelate in 20 ml of H_2O and 8 drops of conc. NH_4OH. (The dissolution of the precipitate takes 2-3 min and may be hastened by the addition of another drop or two of NH_4OH.) Add 3 ml of conc. HCl, heat to boiling, and add 10 ml of 16% mandelic acid. Again bring to a boil, wait 2-3 min, centrifuge and discard the supernate.

Step 9. Slurry the precipitate with 10 ml of ethanol and filter onto a No. 42 Whatman filter circle (1"), using a ground-off Hirsch funnel and stainless steel filter chimney. Powder the ZrO_2 with the fire polished end of a stirring rod. Add 2 drops of ehtanol, slurry, and grind again. Add 10 ml of ethanol, stir, and filter onto a previously

washed, dried, and tared No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Wash the ZrO_2 and chimney with 5 ml of ethanol. Dry at 110° for 10 to 15 min, cool, weigh and mount, and count (Note 4).

Notes

1. With this volume of solution, the chemical yield is good since the loss of Zr with the LaF_3 scavengings is small.

2. NH_4OH reduces Np(VI) and Pu(VI) so that these will be carried on the LaF_3 and thus not interfere in the Zr separation. NH_4OH may decompose on the addition of HF, causing the solution to effervesce.

3. H_3BO_3 removes F^- ion by conversion to BF_4^- and thus aids in the dissolution of $BaZrF_6$ by HNO_3.

4. The samples are mounted on Al plates with two-sided Scotch tape and covered with Mylar film. Four drops of rubber cement solution (6 ml of rubber cement dissolved in 100 ml of benzene) are used to keep the ZrO_2 in place.

LANTHANIDE PROCEDURE

Kurt Wolfsberg

1. Introduction

After the radiochemical purification of the lanthanides (rare-earths) as a group, the separation of individual lanthanides is accomplished on a cation column of low cross linkage and fine particle size at room temperature by eluting with α-hydroxyisobutyric acid. The separation of a number of lanthanides — Y (which behaves as a higher lanthanide), Eu, Sm, Pm, Nd, Pr, Ce, and La — is best achieved in reasonable length of time by changing the pH of the eluant continuously.

A chemical yield determination of the mounted oxide samples may be performed after counting is completed, by dissolving the samples and titrating with EDTA.

2. Reagents

$HClO_4$: conc.

HCl: conc.

HNO_3: conc.

H_3BO_3: saturated

$H_2C_2O_4$: saturated

$H_2C_2O_4$: 0.5%

HF: conc.

H_3PO_4: conc.

H_2SO_4: conc.

H_2O_2: 30%

Ethanol: 95%

Na_2CrO_4: 1.5M

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

Te carrier: ~ 10 mg Te/ml [added as Na_2TeO_3 in H_2O]

Ba carrier: ~ 10 mg Ba/ml [added as $Ba(NO_3)_2$ in H_2O]

0.5M α-hydroxyisobutyric acid solutions adjusted to pH 3.40, pH 4.20 and other pH values for specific applications

Dowex AG-50W X4, 200-325 mesh wet (minus 400 mesh dry), ammonium form

Dowex AG-50W X4, 200-400 mesh dry, ammonium form (optional)

Dowex AG-1 X8, 50-100 mesh

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Y carriers: 5 mg of oxide/ml, standardized, 99.9% pure

Pm^{145} tracer: (produced by $Sm^{144}(n,\gamma)Sm^{145}$; $Sm^{145} \longrightarrow Pm^{145}$), standardized

0.01M EDTA: 3.743 g disodium (ethylene dinitrilo) tetraacetate (direct from bottle) per liter

0.01M La^{+++} in 1M HCl: prepared from La_2O_3

NH_4Cl: ~ 25% w/v in H_2O

pH 10 buffer: 61.5 g of NH_4Cl dissolved in 400 ml of NH_4OH

Arsenazo indicator [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid trisodium salt]: 0.05% in H_2O

Phenolphthalein: ~ 1% in 50% ethanol.

3. Preparation and Standardization of Carriers

Dissolve 5 grams of the desired lanthanide oxide in ~ 50 ml 6M HCl. Heat or add a few drops of conc. HNO_3 if dissolution is difficult. Filter and dilute to 1 liter, adjusting the HCl concentration to 2 or 3M. Any pure soluble cerous salt may be used for cerium carrier.

Pipet three 10-ml portions of the carrier into 250-ml beakers. Evaporate the solutions almost to dryness under a heat lamp. Add ~ 40 ml of water and bring the solution to almost boiling on a hot plate. Then add ~ 25 ml of saturated oxalic acid dropwise while stirring the solution. Digest the precipitate hot for 15 minutes and then let the mixture stand overnight at room temperature. Filter the oxalate on No. 42 Whatman filter paper, washing with 0.5% oxalic acid. Ignite the oxalate for 1 hour at 950° in previously tared crucibles. Cool and weigh. The three weights should agree within 0.5%. Two milliliters of carrier should correspond to not more than 11 mg of oxide to avoid the spreading of one lanthanide element into the next during elution.

Pipet three 2-ml portions of the carrier into 125-ml Erlenmeyer flasks. Titrate with EDTA in the manner described in Section 10. The titrations should agree within 0.5%.

4. Standardization of Pm^{145}

The solution should contain 800-1200 counts per minute of Pm^{145} per ml. Pipet 5 ml of the solution and ~ 20 mg of standardized Nd carrier into each of 4 centrifuge tubes. Dilute to ~ 20 ml, heat on a steam bath,

and add ~ 6 ml of conc. NH_4OH. Centrifuge. Dissolve the precipitate in 1 ml of conc. HCl, dilute to 20 ml, heat on a steam bath, and add 10 ml of saturated $H_2C_2O_4$. Digest the precipitate, centrifuge, filter, ignite to the oxide, and mount as in Step 10 of Section 11. Count the samples on a sodium iodide scintillation counter for several days. The chemical yield of Nd, which corresponds to that of Pm, may be determined in three of the samples by EDTA titration (Section 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

Dissolve 208 grams of α-hydroxyisobutyric acid in water and dilute to 4 liters. If the solution is cloudy, filter. Add conc. NH_4OH to obtain solutions of the desired pH.

Different commercial batches of the reagent may give rise to different elution curves for a particular concentration and pH. This is not as serious a problem when performing elutions by continuously changing pH as when performing elutions at a single pH. However, it is advisable to determine whether a new batch of α-hydroxyisobutyric acid gives the desired elution curves. If it does not, the pH values or concentrations of the solutions should be adjusted accordingly.

6. Treatment of Resin

Bio-Rad Laboratories will prepare cation resin according to the following specifications: Dowex AG-50W X4 "minus 400 mesh"; actual range — minus 200 mesh wet (U.S. Std.) on the large end down to 0.27 cm/sec settling rate (nominal 62 to 23 microns). The resin is washed with 6M HCl, 1M NH_4CNS, 6M HCl, 1M NH_4OH, and H_2O. Dowex AG-1 resins as supplied by Bio-Rad need no further purification.

7. Preparation of Cation Exchange Columns

Select a 27-in length of 8 mm I.D. pyrex tubing. Draw one end out to a drip tip (I.D., 0.8 to 1.2 mm) and make a slight constriction 1/4-in. 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. Then add the cation resin slurry from the polyethylene wash bottle, releasing the water. The settling rate of the resin may be increased by using air pressure. Resin should be added to a height of about 25 inches. Care should be taken that no portion of the resin goes dry. Columns prepared in this manner may be stored by sealing both ends with small pieces of knotted tubing or dropper bulbs.

8. Preparation of Anion Columns

A 15 ml centrifuge tube is blown out at the bottom and a 6 inch length of 6 mm I.D. glass tubing is attached. The end of the glass tubing is drawn to a 1 mm I.D. drip tip. The glass tubing part of the column is loaded with anion resin in the same manner that the cation resins were loaded. These columns may also be stored as long as the resin is kept wet.

Prior to use two 5 ml portions of conc. HCl are passed through the column.

9. Gradient Elution Equipment

A schematic diagram of the gradient elution equipment is shown in Fig. 1. Several columns may be operated from one setup by delivering the eluant from the low pH flask through "Y" connecting tubes. 500-ml flasks are used for 1 or 2 columns; 1000-ml flasks for 3 or 4 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 continuously being replaced by high pH solution by gravitational leveling. Thus the pH of the eluant changes continuously from that of the low pH solution at the beginning of elution to that of the high pH solution at the end of elution.

10. EDTA Titrations (Note 1)

Dilute the sample to ~ 30 ml in a 125-ml Erlenmeyer flask and add an excess of 0.01M EDTA from a 10-ml buret (~0.6 to 0.7 ml for each milligram of rare earth oxide and ~ 0.9 ml for each milligram of yttrium oxide). Add ~ 4 ml of 25% NH_4Cl and a drop of phenolphthalein. Then add pH 10 buffer until the solution just 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^{+++} 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 on the addition of ~ 1/2 drop. More EDTA may be

added and another back titration performed.

The relative strengths of the EDTA and La^{+++} solution titrants are obtained by starting the back titration from a solution of ~ 6 ml La^{+++} solution and an excess of EDTA. The volume of La used in any titration is then multiplied by the EDTA/La^{+++} solution ratio, and 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 (Section 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 which has been ignited at 950°. (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. To a 125-ml Erlenmeyer flask add 10 mg (no more than 11 mg) of each of the lanthanides to be determined and the active solution. It is not necessary to add carriers of lanthanides whose yields are not to be determined. If Pm is to be determined also add ~ 5,000 counts per minute of Pm^{145}. Add 3 ml of conc. $HClO_4$ and boil the solution down to

thick fumes of $HClO_4$ over a flame. Continue boiling for 1 min. After the sample has cooled, add 15 ml of H_2O and 4 ml of conc. HNO_3 (Note 2). Transfer the solution to a centrifuge tube. Add 10 drops of Zr carrier, heat on a steam bath, and add 5 drops of conc. H_3PO_4. Digest the precipitate for 1 or 2 min and centrifuge.

Step 2. Pour the supernate into a polyethylene or polypropylene centrifuge tube, heat the solution on a steam bath, add ~ 2 ml of conc. HF, digest the precipitate for 1 to 2 min, and centrifuge. Wash the precipitate with 30 ml of H_2O containing a few drops of conc. HF, heating on a steam bath for about 1 minute.

Step 3. Add 2 ml of saturated H_3BO_3 and slurry. Add 2 ml of conc. HNO_3 and slurry again. Add 30 ml of H_2O, 2 ml of 1.5M Na_2CrO_4, and 2 drops of Zr carrier. Heat the solution on a steam bath. Reprecipitate and wash the lanthanide fluorides as in Step 2.

Step 4. Dissolve the precipitate in H_3BO_3 and HNO_3 as in Step 3 and add 15 ml of H_2O. Transfer the solution into a glass centrifuge tube. Add 10 drops of Ba carrier, heat the solution on a steam bath, and add 5 drops of conc. H_2SO_4. Digest the $BaSO_4$ for 10 min on the steam bath, and centrifuge. (The anion exchange columns may be prepared and equilibrated with conc. HCl while the $BaSO_4$ is aging.)

Step 5. Pour the supernate into a centrifuge tube containing 6 to 8 ml of conc. NH_4OH. Heat for 2 min on a steam bath and centrifuge. Wash the precipitate with 30 ml of H_2O containing a few drops of conc. NH_4OH, heating for about 1 min.

Step 6. Dissolve the hydroxides in 4 ml of conc. HCl and add 1 or 2 drops of Zr and Te carriers. Heat the samples for only 30 sec on steam bath (to cause the Te to exchange, but not to reduce the HCl concentration). Pass the solution through a prepared anion column. Collect the eluant in a 125-ml Erlenmeyer flask. Rinse the column with 4 ml of conc. HCl.

Step 7. Boil out the excess HCl by heating the flask over a flame and reduce the volume to 4 or 5 ml. Add 15 ml of H_2O and transfer the solution to a long tapered centrifuge tube containing 6-8 ml of conc. NH_4OH. Digest and wash the precipitate as in Step 5.

Step 8. Dissolve the lanthanide hydroxides in 2 to 4 drops of conc. HNO_3, dilute the solution to 30 ml, add ~ 1 ml of 200-400 mesh cation resin, and stir for a few min. (Note 3.) Centrifuge for 5 min and discard the supernate. Slurry the resin in ~ 1 ml H_2O and transfer to the top of a previously prepared cation exchange column with a transfer pipet. Allow the resin to settle and remove the water. Add 2 or 3 ml of H_2O to the top of the resin; after the resin has settled, remove the water.

Step 9. Connect the column to a delivery tube from the gradient elution equipment. For the analysis of Y, Eu, Sm, Pm, Pr, Ce, and La, the initial pH of the eluant (0.5M α-hydroxyisobutyric acid) is 3.40 and the pH is changed at an average rate of ~ 0.025 pH units per hour. The rate of elution for one column is one drop every 17-19 sec or ~ 9 ml per hr. For the operation of one column, this condition is met by starting with 144 ml of 0.5M α-hydroxyisobutyric acid, pH 3.40, in the first flask

and with 144 ml of eluant, pH 4.20, in the second flask. If several columns are operated from one set of flasks, the volumes of eluants are increased proportionally. A small additional volume of low pH solution is added to the first flask to compensate for the difference of volumes between the delivery tubing and the stirring bar. The rate of elution is controlled by the air pressure applied to the reservoirs.

Collect the eluant in fractions of 15 min in tubes in an automatic fraction collector. Add a few drops of saturated oxalic acid to precipitate and locate the individual lanthanides. Pm is located by measuring the activity in the tubes between Sm and Nd. (Notes 4 and 5.)

Step 10. Combine the individual lanthanide fraction in centrifuge tubes. To the Pm fraction add 2 ml of Nd 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 ~ 5 ml of H_2O, and filter on No. 42 Whatman paper using a ground-off Hirsch funnel and filter chimney assembly (any convenient size). Ignite the oxalates in a 00 crucible for approximately 1 hr at 950°. After the crucibles have cooled, add 2 drops of ethanol to each sample and grind up the oxides with the fire polished ends of a stirring rod. Suspend each sample in several milliliters of ethanol and filter onto a circle of No. 42 paper using a 4/0 ground-off Hirsch funnel and an 11 mm I.D. glass chimney. Dry the sample for 15 min at 110° and mount it on an aluminum plate, covering with Scotch polyester film tape (No. 850 type 2PTA). (Note 6.)

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 prior to the mounting operation. The papers and samples should be cooled for 20 min before weighing.

Step 11. After counting of a sample is completed, yield determination by EDTA titration may be performed. Remove the sample, filter paper, and tape cover from the counting plate by cutting just 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 conc. HCl. Bring to just boiling and then 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 Section 10.

CeO_2 does not dissolve with the HCl treatment described above. After the sample sandwich is placed in the flask add ~ 2 ml of conc. H_2SO_4 and heat the mixture to SO_3 fumes over a flame. Then cautiously add a mixture of 2 parts of conc. 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 ~ 1/4 ml. Dilute to 30 ml, add a small spatula full of ascorbic acid, and proceed with the EDTA titration as described in Section 10.

Notes

1. The following references may be consulted for general familiarization with 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 in:

> 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 Ce is to be determined, steps must be performed to promote exchange between radiocerium and carrier. Consult Steps 1 and 2 of the cerium procedure.

3. 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.

4. Under the conditions in Step 9, the lanthanides elute in the following manner:

Element	Time that element starts eluting off column
Y	3.1 hr.
Gd	6.5
Eu	8.2
Sm	10.5
Pm	13.2
Nd	16.5

Note 4 (Cont'd.)

Element	Time that element starts eluting off column
Pr	19.5
Ce	22.5
La	28.0

Those lanthanides which are present in 6 to 9 mg quantities have elution widths of less than 2 hrs. Carrier-free lanthanides elute more sharply. Eu, therefore, is not contaminated with Gd, which is present carrier-free. Decontamination factors for a particular lanthanide from other lanthanides vary from 3×10^{-5} to 2×10^{-6}. In a Eu^{156} sample from fresh thermal neutron fission of U^{235}, ~ 0.5% of the activity will be due to Y^{91}. If better decontamination is required, this lanthanide should be recycled by itself through a second cation column.

5. For special applications, it may be more convenient to elute with an eluant of one pH. For example, if only Nd is to be purified, conditions may be chosen so that Nd is separated from the other lanthanides in a reasonable length of time. Nd elutes between 10 and 12.5 hrs. after the start of column operation with 0.5M α-hydroxyisobutyric acid, pH 3.73. Pm has completely eluted after 7.5 hrs. and Pr does not start to elute until after 14 hrs.

Five-tenths molar α-hydroxyisobutyric acid, pH 3.30, may be used to separate 6-9 mg quantities of Tb and Gd from carrier free Y. Most of the Y elutes between 3.5 and 4.5 hrs. after the start of column operation; Tb between 6.1 and 8.3 hrs.; Gd between 11.5 and 14.3 hrs.; and Eu between

17 and 24 hrs. The Y activity in the Tb and Eu samples is reduced by factors of ~ 6×10^{-5} and ~ 3×10^{-6}, respectively. In most analyses of Tb and Gd from low energy fission it will be necessary to recycle these lanthanides a second time to obtain adequate decontamination from Y.

6. The thickness of Scotch polyester film tape (No. 850 type 2PTA) is quite uniform along the length of a roll and among most of the rolls produced from the same batch, the variation being about 1.5%. However, there may be a larger variation between batches. The tape of two batches examined had thicknesses of 4.9 and 6.3 mg cm^{-2}. This variation does not pose a serious problem since a large number of rolls of tape can be obtained from a single batch.

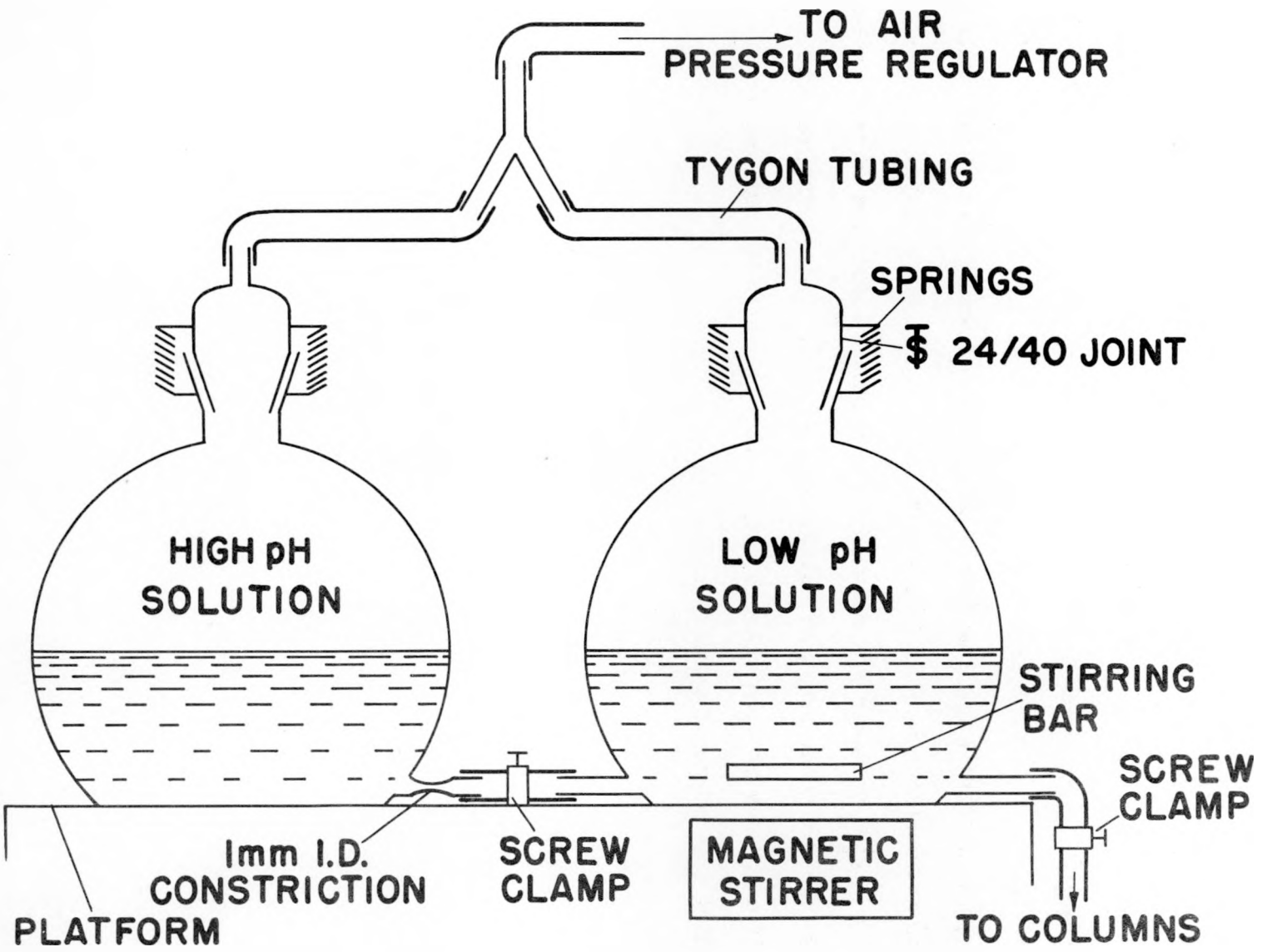


Figure 1

CERIUM-144

J. W. Barnes

1. Introduction

The procedure described below has been successfully employed for the analysis of cerium-144. The major steps include: (a) an oxidation-reduction cycle in the presence of cerium carrier to insure exchange; (b) two by-product extractions from nitric acid solution with dibutyl-phosphate (DBP) in carbon tetrachloride to remove contaminants such as zirconium, neptunium, thorium, plutonium, and uranium; (c) a cerium(III) fluoride preceipitation; (d) the extraction of cerium(IV) into hexone; and (e) the final conversion of cerium to the dioxide. The chemical yield is 50-60%, and eight samples can be analyzed in 6-8 hours.

2. Reagents

Ce carrier: 12 mg Ce/ml [added as $(NH_4)_2Ce(NO_3)_6$ in 3M HNO_3] - standardized

HNO_3: conc. 9M

HF: conc.

H_3BO_3: saturated aqueous solution

NH_4OH: conc.

$NaBrO_3$: 2M

$(NH_4)_2C_2O_4$: saturated aqueous solution

H_2O_2: 30%

Dibutylphosphate (DBP): 5% in carbon tetrachloride

(The DBP employed was obtained from the Victor Chemical Works, Chicago Heights, Ill.)

Hexone (4-methyl-2-pentanone)

Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 47.8 g of $(NH_4)_2Ce(NO_3)_6$ in 190 ml of conc HNO_3 and dilute to 1 liter.

Pipet 5 ml of the cerium carrier solution into a 100-ml beaker and dilute to about 20 ml with H_2O. Warm on a steam bath and add about 50 ml of saturated $(NH_4)_2C_2O_4$ solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter through a filter funnel, using a No. 42 Whatman filter paper (11 cm). Ignite in a porcelain crucible at 800°C for 30 min, cool, and weigh as CeO_2.

Four standardizations, with results agreeing within 0.5%, are carried out.

4. Procedure

Step 1. To 2 ml of Ce carrier in a 40-ml conical centrifuge tube, add the sample, then 3-5 drops of 2M $NaBrO_3$ and heat on a steam bath for 10 min. Dilute to 30 ml and add sufficient conc NH_4OH to precipitate $CeO_2 \cdot XH_2O$. Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of conc HNO_3 and add 3-5 drops of 30% H_2O_2 and 7-8 ml of H_2O.

Step 2. Transfer the solution to a 60-ml pear-shaped separatory funnel and shake with about 25 ml of 5% DBP in carbon tetrachloride solution. Permit the layers to separate and drain off the organic (lower) layer. If the original sample contains uranium or plutonium, transfer the organic layer to the appropriate waste bottle. If these elements are absent, discard the organic layer.

Step 3. Repeat the extraction with another 25 ml portion of the 5% DBP, again appropriately disposing of the organic layer.

Step 4. Transfer the aqueous layer into a 40-ml conical centrifuge tube. Dilute to about 20 ml with H_2O, add 3-4 ml of conc HF, and stir well to permit the precipitate to coagulate. Centrifuge and discard the supernate. Wash the precipitate with about 20 ml of H_2O and discard the washings.

Step 5. Stir the precipitate with 1 ml each of conc H_3BO_3 and conc NHO_3, heating if necessary to obtain complete solution. Dilute to 20-30 ml with H_2O and add an excess of conc NH_4OH. Centrifuge and discard the supernate.

Step 6. Pretreat 50 ml of hexone with a mixture of 50 ml of 9M HNO_3 and 2 ml of 2M $NaBrO_3$ by shaking for about 1 min. and discarding the aqueous layer. Dissolve the precipitate from Step 5 in 10 ml of 9M HNO_3 and add 2 ml of 2M $NaBrO_3$. Transfer to a 125-ml pear-shaped separatory funnel, add 50 ml of hexone and shake for about half a minute. Discard the aqueous layer. Wash the organic layer twice with 5 ml of 9M HNO_3 containing 2-3 drops of 2M $NaBrO_3$ and discard the washings. Back extract the cerium by shaking the hexone solution with 5 ml of H_2O containing a few drops of 30% H_2O_2. Discard the hexone layer.

Step 7. Add conc NH_4OH to the aqueous layer until an orange precipitate just persists. Add conc HNO_3 dropwise until the precipitate dissolves, then add 10-15 ml of saturated $(NH_4)_2C_2O_4$. Stir briefly, cool, centrifuge, and discard the supernate. Transfer the precipitate by means of a stream of ethanol onto a No. 42 Whatman filter circle, 1" diameter, using a Hirsch funnel. Transfer the precipitate to a porcelain crucible and ignite at 800° for 30 min. Cool, weigh as CeO_2, mount and β-count through a 217 mg/cm^2 Al absorber. (Note 1).

Notes

1. The procedure probably can be used for Ce^{143}, although it has not been thoroughly checked out for this isotope.

TOTAL URANIUM II

B. Warren

1. Introduction

This procedure is an adaptation of a procedure developed by the Analytical Chemistry Group of the Chemistry-Metallurgy Division of the Los Alamos Scientific Laboratory. It is appropriate for samples containing x - x milligrams of uranium.

Uranium(VI) is reduced to a mixture of uranium(III) and uranium(IV) by means of zinc amalgam in a Jones reductor. All the uranium is then converted to the +4 state by atmospheric oxidation and the uranium(IV) is determined by titration with standard ceric sulfate in the presence of ferroin as indicator. The running of appropriate blanks is essential. The chief interferences in the determination are iron, molybdenum, tungsten, vanadium, and nitrate ion. Four samples can be analyzed in about 5 hours.

2. Reagents

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

H_2SO_4: conc.

Ferric ammonium sulfate: approximately 0.1M

Ceric sulfate: Standardized. Make up an aqueous solution approximately 0.01M and standardize against pure uranium in the following manner. Weigh out to the nearest tenth of a mg about 1 gm of pure U and dissolve the metal in conc. HCl, adding a few drops of conc. HNO_3 if necessary. Make the solution up to exactly 100 ml by the addition of 2.5M HNO_3. Analyze aliquots of the U solution as described under Procedure. The solution should be standardized once a month while it is in use.

Jones reductor: For preparation, see any good book on quantitiative analysis.

Ferroin indicator: 0.025M (in H_2O)

3. Procedure

Step 1. Place the weighed or pipetted sample in a 250-ml beaker. If the sample is in metallic form, bring it into solution with conc. HCl and 30% H_2O_2 and proceed to Step 2. If the sample is an oxide, dissolve it in a minimum of conc. $HClO_4$, add 100 ml of 5% H_2SO_4, and proceed to Step 3. If the sample is in liquid form, start with Step 2.

Step 2. Add 5 ml of conc. H_2SO_4, cover the beaker with a Speedyvap, and take the solution to dryness to remove nitrate and organic matter. Repeat the process three additional times, washing down the Speedyvap and the walls of the beaker each time. If more than trace quantities of nitrate or organic matter are present, a few drops of conc. $HClO_4$ are added prior to the second and third evaporation. After the final

evaporation add 100 ml of 5% H_2SO_4.

Step 3. Activate a Jones reductor by passing through it 100 ml of 5% H_2SO_4, discarding the effluent. Pass the solution containing the sample through the reductor and collect it in a 500-ml Erlenmeyer flask. Pass three 50-ml portions of 5% H_2SO_4 through the reductor, in each case collecting the effluent in the Erlenmeyer flask noted above.

Step 4. Aerate the solution in the flask for about 5 min with a stream of air from a glass gas dispersion tube. The bubbles must be active enough to stir the solution. Withdraw the aerating tube and rinse it off, collecting the rinsings in the Erlenmeyer flask.

Step 5. Add 3 drops of the ferroin indicator and titrate with standard ceric sulfate until the orange color just begins to fade. At this point add 3 ml of 0.1M ferric ammonium sulfate solution to restore the orange color and proceed cautiously with the addition of ceric sulfate until the color of the solution changes to blue-green. This is the endpoint of the titration.

Step 6. Run two blanks and average their titration values.

Step 7. Subtract the average blank titration from the volume of ceric sulfate found in Step 5. Calculate the amount of U in the sample by one of the following formulas:

$$\% \text{ U in weighed sample} = \frac{\text{ml } Ce(SO_4)_2 \times N \times F \times 100}{\text{gm of sample}}$$

$$\text{Grams of total U in liquid sample} = \text{ml } Ce(SO_4)_2 \times N \times F \times \frac{\text{total volume of sample}}{\text{aliquot volume of sample}}$$

The factor F in these calculations is the milliequivalent weight of the U, with suitable corrections for the isotopic composition:

For depleted U use	0.11900 for F
For normal U use	0.11904
For 93% U^{235} use	0.11760
For 98% U^{233} use	0.11650

CURIUM-242

J. W. Barnes

1. Introduction

In this procedure curium is sufficiently decontaminated from other activities so that a pulse analysis on the final product gives the ratio of the unknown quantity of Cm^{242} present to the known quantity of added Cm^{244} tracer. The procedure has the advantage over one which utilizes an HCl-cation column in that an equally effective separation of curium from rare earth activities can be obtained with much less time and effort.

In the analysis, the first major step is the adsorption of some of the impurities on an anion column from concentrated hydrochloric acid. The curium is then adsorbed on an anion column as a thiocyanate complex from 5M ammonium thiocyanate at pH 1.5. This step gives effective decontamination from alkali and alkaline earth metal activities. The rare earths are poorly adsorbed, and any fixed on the column are eluted by washing with ammonium thiocyanate solutions. The curium is finally removed from the column by elution with a more dilute ammonium thiocyanate solution and is collected on a platinum disk. After drying and ignition at red heat, the sample is pulse analyzed.

2. Reagents

Y carrier: 10 mg Y/ml [added as $Y(NO_3)_3 \cdot 6H_2O$ in H_2O]

Cm^{244} standard solution: 100-1000 c/m/ml.

$HClO_4$: conc.

HCl: conc; 3M

HNO_3: conc.

NH_4OH: 3M

NH_4CNS: 5M; 1M (in a 3:1 ethanol to H_2O mixture)

Solution "A": a mixture containing 2-3 drops of conc. HNO_3 to 15 ml of conc. HCl

Ethanol: 95%

Hydrion paper: pH range 1.2 - 2.4

Dowex anion resin D1-X8, 100-200 mesh (obtained in purified form from Bio-Rad Laboratories, Richmond, Calif.)

Dowex anion resin D1-X2, 200-400 mesh (for source see above)

3. Procedure

Step 1. To the Cm^{244} tracer (Note 1) in a 50-ml Erlenmeyer flask, add an aliquot of the sample, 3 drops of Y carrier, and 0.5-0.7 ml of conc $HClO_4$. Boil to dryness and allow to cool.

Step 2. Prepare a column 6 mm by 7-8 cm of Dowex anion resin D1-X8, 100-200 mesh, and pretreat with 3-5 ml of Solution "A". Dissolve the dry residue from Step 1 in 1-2 ml of Solution "A" (do not heat, even though all the solid does not dissolve) and pass the resulting solution (or mixture) through the resin column. Rinse the Erlenmeyer

flask with 1 ml of Solution "A" and pass the rinsings through the column. Collect the effluent and the wash in a 50-ml Erlenmeyer flask, add 0.5 ml of conc $HClO_4$, and fume to dryness. Cool.

Step 3. Prepare a column 3.5 mm by 7-8 cm of Dowex anion resin D1-X2, 200-400 mesh, and wash the column with 2 ml of 5M NH_4CNS. Add 2 ml of 5M NH_4CNS to the dry residue in the Erlenmeyer flask and swirl to obtain solution. With the use of Hydrion paper (pH range 1.2 -2.4) and 3M NH_4OH and 3M HCl adjust the pH to about 1.5. Add the solution to the anion column and push it through at the rate of 1 drop every 7-15 seconds. Rinse the top of the column with 2 ml of 5M NH_4CNS which has been adjusted to pH 1.5 with 3M HCl and push this solution through at the rate given above. Make up a 1M NH_4CNS solution in a 3:1 ethanol to H_2O mixture and adjust the pH to 1.5 with 3M HCl. Wash the column with 3 ml of this solution and collect the washings in a clean 40-ml conical centrifuge tube. (This wash is kept as insurance, in case Cm happens to be eluted at this stage.) Dilute the 1M NH_4CNS solution with an equal volume of H_2O and add 1 drop of conc HCl for each 4 ml of the resulting solution. Pass 1 ml of the final solution through the column and collect the eluate in a clean 40-ml conical centrifuge tube.

Step 4. Transfer this eluate, which contains the Cm activity, to a Pt disk (1-3/4" diameter) on a brass ring which is located on a hot plate. Turn up the heat, gently at first, and evaporate the liquid on the Pt disk to dryness. When the disk is dry, adjust the hot plate to

its maximum heat and volatilize the NH_4CNS. Finally, heat the disk to redness in a Fisher Burner flame. Place the disk in the pulse analyzer and count (Note 2).

Notes

1. The quantity of Cm^{244} tracer employed is 3-5 times that of the estimated Cm^{242} content of the aliquot.

2. If the pulse analysis curve is unsatisfactory because of too much β-γ activity, the material on the Pt disk must be further purified. This is accomplished in the following manner. Warm the disk under a heat lamp with several small portions (each approximately 0.5 ml) of Solution "A". Pass the resulting solution through a Dowex D1-X8 column as in Step 2. Complete Step 2 and the rest of the procedure.

If experience with gamma readings on the final eluate from Step 3 indicates that further purification is necessary, do not dry the eluate. To the eluate add sufficient solid NH_4CNS to make the solution 4-5M in the salt. Pour the solution onto a clean Dowex D1-X2 column as in Step 3 and repeat this step.