4.5.5 Generic Procedures

*EPA APPROVED[*]

G-01

ELECTRODEPOSITION OF THE ACTINIDES: MITCHELL METHOD

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This method describes the preparation of separated actinide fractions for α-spectrometry measurement (Mitchell, 1960). It is applicable to any of the actinides that can be dissolved in HCl solution. The actinide fractions would be either the final elution from an ion exchange separation or the final strip from a solvent extraction separation.

SPECIAL APPARATUS

1. Electrodeposition apparatus - see Specification 7.15.
2. Electrolytic cells - see Specification 7.16.
3. Platinum - iridium stirrer - see Specification 7.15.
4. Virgin platinum discs - 17.6 mm x 0.006 mm; mirrored finish on one side.
5. Ring and discs - Specification 7.2.
6. Mylar film - see Specification 7.3.

---

[*] *Environmental Protection Agency - Guidelines Establishing Test Procedures for the Analysis of Pollutants, Under the Clean Water Act; National Primary Water Regulations and National Secondary Drinking Water Regulations; Methods Update, tentatively slated for approval, 66FR3466-3497, January 16, 2001.*

SPECIAL REAGENTS

Methyl red indicator solution 0.1% in ethanol - Fisher Chemical Co.

ELECTRODEPOSITION

1. Add 5 mL of concentrated HNO_3 to the separated actinide fraction. Evaporate the solution to dryness but do not bake.

2. Dissolve the residue in 2 mL of HCl and evaporate to near dryness. Repeat the HCl and evaporate to near dryness. Repeat the HCl addition and evaporation twice more.

3. Add 1 mL of HCl and heat the solution gently. Transfer the solution to an electrodeposition cell.

4. Rinse and police the beaker with two successive 1-mL portions of water. Add the rinsing to the cell.

5. Add one drop of methyl red indicator solution to the cell and swirl the solution to mix.

6. While swirling the solution in the cell, add 7.5$\underline{N}$ NH_4OH until the pink color just disappears.

7. Adjust the solution to a persistent pink color by dropwise additions of 2$\underline{N}$ HCl with swirling to mix. Add two drops of 2$\underline{N}$ HCl in excess.

8. Dilute the solution in the cell to 5 mL with water.

9. With the platinum anode in the chuck of the stirring motor, lower the anode to about 1 cm above the platinum disc in the electrodeposition cell. Turn on the stirring motor and adjust the speed to prevent splattering.

10. Turn on the current and adjust the flow to 1.2 A. Electrodeposit with the rotating anode for 1 h. (**Note**: At EML the electrodeposition cell is supported on a lucite

pedestal which is immersed in an ice water bath to minimize evaporation of the sample solution.)

11. Add 1 mL of NH_4OH to the cell to quench the electrolyte.

12. Turn off the stirring motor. Raise the stirring motor and anode assembly, and turn off the power supply. Pour off and discard the electrolyte solution. Rinse the cell with water and discard the rinse.

13. Disassemble the cell and rinse the disc with ethyl alcohol solution. Touch the edge of the disc with a tissue to absorb the excess alcohol.

14. Place the disc on a 200 to 250°C hot plate to dry.

15. Submit the sample for alpha spectrometry measurement.

INTERFERENCES

Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc. In particular, ^{210}Pb (5.30 MeV) deposited on the disc would interfere with the yield determination of ^{232}U (5.32 MeV) or ^{243}Am (5.28 MeV) tracers used in the determination of isotopic U and ^{241}Am, respectively.

Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic materials will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α-spectrometry measurement.

Samples containing more than 20 μg of U are unsuitable for measurement by α spectrometry due to the thickness of the deposit.

REFERENCE

Mitchell, R. F.
"Electrodeposition of Actinide Elements at Tracer Concentrations"
Anal. Chem., 32, 326-328 (1960)

G-02

ELECTRODEPOSITION OF THE ACTINIDES: TALVITIE METHOD

Contact Person(s) : Isabel M. Fisenne and Pamela M. Perry

APPLICATION

This method describes the preparation of separated actinide fractions α-spectrometry measurement (Talvitie, 1972). It is applicable to any of the actinides that can be dissolved in dilute ammonium sulfate solution. Examples of applicable actinide fractions would be the final elution from an ion exchange separation or the final strip from a solvent extraction separation.

SPECIAL APPARATUS

1. Electrodeposition apparatus - see Specification 7.15.

2. Electrolytic cells - see Specification 7.16.

3. Platinum - iridium stirrer - see Specification 7.15.

4. Virgin platinum discs - 17.6 mm x 0.006 mm; mirrored finish on one side.

SPECIAL REAGENTS

Thymol blue indicator, sodium salt solution (0.04%) - dissolve 0.04 g of the salt in 100 mL of H_2O.

ELECTRODEPOSITION

1. Add 2 mL of 0.36M $NaHSO_4$ to the separated actinide fraction. Add 5 mL of concentrated HNO_3, swirl to mix, and evaporate the solution to dryness but do not bake.

2. Dissolve the residue in 5 mL of electrolyte solution and warm the solution.

3. Transfer the sample solution to the electrodeposition cell. Rinse the beaker with 5 to 10 mL of electrolyte solution and add the rinsing to the electrodeposition cell.

4. Add three to four drops of thymol blue indicator to the sample and adjust the pH with 1.8M H_2SO_4 or concentrated NH_4OH, or both, until a salmon pink color persists.

5. With the platinum anode in the chuck of the stirring motor, lower the anode to about 1 cm above the stainless steel disc in the electrodeposition cell. Turn on the stirring motor and adjust the speed to prevent spattering.

6. Turn on the current and adjust the flow to 1.2 A. Electrodeposit with the rotating anode for 1 hour. (**Note**: At EML the electrodeposition cell is supported on a lucite pedestal which is immersed in an ice water bath to minimize evaporation of the sample solution.)

7. After 1 h, add 1 mL of NH_4OH to the cell to quench the electrolyte.

8. Turn off the stirring motor. Raise the stirring motor and anode assembly and turn off the power supply. Pour off and discard the electrolyte solution. Rinse the cell with three successive portions of 0.15M HN_4OH. Discard the rinsings.

9. Disassemble the cell and rinse the disc with ethyl alcohol. Touch the edge of the disc with a tissue to absorb the excess alcohol.

10. Place the disc on a 200 to 250°C hot plate to dry.

11. Submit the sample for α-spectrometry measurement.

INTERFERENCES

1. Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc. In particular, ^{210}Pb (5.30 MeV) deposited on the disc would interfere with the yield determination of ^{232}U (5.32 MeV) or ^{243}Am (5.28 MeV) tracers used in the determination of isotopic U and ^{241}Am, respectively.

2. Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic material will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α-spectrometry measurement.

3. Samples containing more than 20 μg of U are unsuitable for measurement by α spectrometry due to the thickness of the deposit.

REFERENCE

Talvitie, N. A.
"Electrodeposition of Actinides for Alpha Spectrometric Determination"
Anal. Chem., 44, 280-283 (1972)

G-03

MICROPRECIPITATION SOURCE PREPARATION FOR ALPHA SPECTROMETRY

Contact Person(s) : Isabel M. Fisenne

APPLICATION

Microprecipitates of Th, U, Pu, Am, and Cm, suitable for α-spectrometry measurements, are prepared by coprecipitation with Nd as the F^-. [Adapted from Sill and Williams (1981) and Hindman (1983).]

SPECIAL APPARATUS

1. Ultrasonic bath.
2. Millipore 47 mm diameter Pyrex glass filtration chimney, fitted glass support and metal clamp.
3. Millipore 47 mm diameter filters, 0.45 µm pore size.
4. Gelman 25 mm diameter polysulfone filtration chimney, stem support and stainless steel screen.
5. Gelman 25 mm Metricel filter, 0.1 µm pore size.
6. Eppendorf 100 µL pipette or equivalent.
7. 100 µL disposable pipette tips.
8. 10 mL plastic pipette.

9. 10 mL plastic culture tubes.
10. Pipetting bulb.
11. 50 mL plastic graduated cylinder.
12. 10 mL plastic graduated cylinder.
13. 20 L plastic carboy with spigot.
14. 2 L vacuum filtration flask.
15. 250 mL vacuum filtration flask.

Special Precautions - Due to the use of HF in the preparation of the reagents and in the precipitation procedure, rubber gloves must be worn and plasticware must be used as noted above.

SPECIAL REAGENTS

1. Filtered deionized water - filter 20 L of deionized water through 0.45 µm pore size Millipore filters. Store the filtered water in a 20-L capacity plastic carboy with a spigot (see **Note 1**).

2. 1N HCl - add 83 mL of concentrated HCl to 917 mL of filtered deionized water and store in a plastic bottle.

3. Neodymium carrier solution, 1000 µg mL^{-1} (Spex Industries, Wayne, NJ), or equivalent (see **Note 2**).

4. Neodymium carrier solution, 0.5 mg mL^{-1}. Dilute 10 mL of the 1000 µg mL^{-1} Nd carrier solution to 20 mL with filtered deionized water.

5. 48% HF.

6. Neodymium fluoride substrate solution - 10 µg mL^{-1} - pipette 5 mL of Nd carrier (1000 µg mL^{-1}) into a 500-mL plastic bottle. Add 460 mL of 1N HCl to the plastic bottle. Cap the bottle and shake to mix. Measure 40 mL of 48% HF in a plastic graduated cylinder. Uncap the bottle and add the HF. Recap the bottle and shake to mix thoroughly.

7. 0.58 N HF - pour 980 mL of filtered deionized water into a 1 L pastic bottle. Measure 20 mL of 48% HF in a plastic graduated cylinder. Uncap the bottle and add the HF. Recap the bottle tightly and shake to mix.

8. Ethyl alcohol, 100%.

9. Ethyl alcohol, 80% - mix 800 mL of 100% ethyl alcohol and 200 mL of filtered deionized water. Store in a 1 L plastic bottle.

10. Titanium trichloride, 20% solution (see **Note 3**).

Notes:

1. Deionized water may contain a sufficient quantity of solid material to adversely effect the resolution of the final filtered sample.

2. Neodymium is preferred as a carrier for the determination of thorium. Cerium compounds tend to contain variable and measurable quantities of thorium.

3. Titanium trichloride is an extremely powerful reducing agent, which should be used in a well-ventilated hood.

PRECIPITATION OF Th, Pu, Am, AND Cm

1. The separated Th, Pu, Am or Cm solution for precipitation should be in a 1-2 mL volume of 1N HCI or 1N HNO_3 solution. (The conditions for the precipitation of U are noted separately.)

2. Transfer the solution to a 10-mL plastic culture tube. Wash the original sample vessel twice with 1-mL washes of the same concentration acid as the sample. Transfer the washings to the culture tube. Mix by gently shaking the tube.

3. Add 100 µL of the 0.5 mg mL^{-1} Nd carrier solution to the tube with an Eppendorf pipette. Gently shake the tube to mix the solution.

4. Add 10 drops (0.5 mL) of 48% HF to the tube and mix well by gentle shaking.

5. Place the tube in a cold-water ice bath for at least 30 min.

6. Insert the polysulfone filter stem in the 250-mL vacuum flask. Place the stainless steel screen on top of the fitted plastic filter stem.

7. Place a 25-mm Metricel filter on the stainless steel screen. **Caution** - place the less glossy side of the Metricel filter face up. The filters are usually shipped in the box in this manner, but the analyst should check each filter visually.

8. Wet the filter with 100% ethyl alcohol. Center the filter on the stainless steel screen support and apply a vacuum.

9. Lock the filter chimney firmly in place on the filter stem. Open the system to full vacuum.

10. Wash the filter with 100% ethyl alcohol, followed by a filtered deionized water wash.

11. Draw 5000 µL (5 mL) of Nd substrate solution into a plastic pipette.

12. Add 5 mL of the Nd substrate solution down the side of the filter chimney. Apply a vacuum to the filter for at least 15 sec.

13. Repeat Steps 11 and 12 with an additional 5000 µL of the substrate solution.

14. Place the sample to be filtered in a 150 mL beaker containing 25 mL of H_2O. Set the beaker in an ultrasonic unit containing about a 2.54 cm depth of H_2O.

15. Ultrasonicate the sample tube for about 1 min to suspend the NdF_3 precipitate.

16. Pour the sample down the side of the filter chimney and apply a vacuum.

17. Add about 2 mL of 0.58N HF to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.

18. Repeat Step 17.

19. Add about 2 mL of filtered deionized water to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.

20. Repeat Step 19.

21. Add about 2 mL of 80% ethyl alcohol to the tube and ultrasonicate briefly. Pour the wash down the side of the filter chimney.

22. Repeat Step 21.

23. Wash any drops remaining on the sides of the chimney down toward the filter with 80% ethyl alcohol. **Caution** - Directing of a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for α-spectrometry resolution.

24. Without turning off the vacuum, remove the filter chimney.

25. Reduce or turn off the vacuum to remove the filter. Discard the filtrate. (**Caution** - If the filtrate is to be retained, it should be placed in a plastic container to avoid dissolution of the glass vessel by dilute HF.)

26. Place the filter directly on a suitable mounting disc. Secure with a mounting ring.

27. Place the mounted sample under a heat lamp (sample to lamp distance should be about 10 cm) for 10 min prior to α-spectrometry measurement.

PRECIPITATION OF U

1. The U bearing solution must be in HCl solution.

2. Transfer 1-2 mL of the U bearing solution (1N HCl) to a 10-mL plastic culture tube. Wash the original sample vessel twice with 1-mL portions of 1N HCl. Transfer the washings to the culture tube. Mix by gently shaking the tube.

3. Add 100 µL of the 0.5 mg mL^{-1} Nd carrier with an Eppendorf pipette. Gently shake the tube to mix the solution.

4. Add four drops of 20% Ti trichloride to the tube and gently shake the tube. A strong permanent violet color should appear. If the color fails to appear, add a few more drops of Ti trichloride.

5. Continue the precipitation from Step 4, Precipitation of Th, Pu, Am, and Cm.

REFERENCES

Hindman, F. D.
"Neodymium Fluoride Mounting for Alpha Spectrometric Determination of Uranium, Plutonium, and Americium"
Anal. Chem., 55, 2460-2461 (1983)

Sill, C. W. and R. L. Williams
"Preparation of Actinides for Alpha Spectrometry Without Electrodeposition"
Anal. Chem., 53, 421-415 (1981)

G-04

PREPARATION OF MICROPRECIPITATION SOURCES FOR REANALYSIS

Contact Person(s): Michele L. DeGennaro

APPLICATION

This procedure is applicable for the reanalysis of microprecipitation sources on Metricel filters (see Procedure G-03).

A 25 mm Metricel filter is removed from the sample mount and dry ashed in a temperature programmed oven that is held at a final temperature of 475°C for 6 h. The residue is redissolved in preparation for additional treatment.

SPECIAL APPARATUS

1. Temperature programmed oven.
2. Sample mounts.

SPECIAL REAGENTS

Analytical grade concentrated nitric acid.

SAMPLE PREPARATION

1. Remove the 25 mm Metricel filter from the mount using a pair of tweezers and place it in a small Pyrex beaker.

2. Place the beaker in a programmable oven.

3. Program the oven to ramp at 1.5°C min^{-1} to a final temperature of 475°C. Hold that temperature for 6 h.

4. Allow the sample to cool to room temperature before treating it any further.

5. Treat the residue with several additions of concentrated nitric acid (~5-10 mL), evaporating each addition (1-2 mL).

6. Redissolve the residue in the appropriate solution (based on the nuclide of interest).

7. The sample is now ready for further treatment or analysis (based on the nuclide of interest).