AMERICIUM, PLUTONIUM, AND URANIUM IN WATER

1. SCOPE

1.1. This is a method for the separation of americium, plutonium and uranium from up to 1L of water. After completing this method, source preparation for measurement of americium, plutonium and uranium by alpha spectrometry is performed by electrolytic deposition onto stainless steel planchets (Eichrom Method SPA02) or by rare earth fluoride micro precipitation onto polypropylene filters (Eichrom Method SPA01).

1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. SUMMARY OF METHOD

2.1. Americium, plutonium and uranium are separated by Eichrom UTEVA and TRU resins prior to measurement by alpha spectrometry. A calcium phosphate precipitation can be used to concentrate actinides from water samples. Tracers are used to monitor chemical recoveries and correct results to improve precision and accuracy.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of actinides in water samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

4. INTERFERENCES

4.1. Nuclides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu, ^{237}Np and ^{234}U, or ^{232}U and ^{210}Po must be chemically separated to enable measurement. This method separates these isotopes effectively.

4.2. Very high levels of phosphate in the sample may cause reduced recoveries of actinides during calcium phosphate precipitation and column separations. Adjusting the amount of phosphate added to co-precipitate the actinides may be necessary in these cases.

4.3. The sample preparation procedure outlined in this method will adequately recover actinides from freshly collected, well preserved, homogenous water samples. Older, poorly preserved samples or samples with significant organic or solid matter may require more aggressive treatment to recover actinides which have precipitated or adsorbed to the walls of the storage container or solid matter. Rinsing the empty storage container with warm HNO_3, adjusting the HNO_3 concentration of the sample to 1M HNO_3 and boiling, and/or wet-ashing the calcium phosphate precipitate may be required for older, poorly preserved samples.

4.4. This method may also be applied using TEVA-TRU separation chemistry as described in Eichrom Application Note AN-1413.

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Beakers, glass
- Centrifuge tubes, 50mL and 250mL
- Centrifuge, with rotor and carriers for 50mL and 250mL tubes
- Column rack, Eichrom Part: AC-103
- Extension funnels, 25 mL, Eichrom Part: AC-120
- Fume hood
- Hotplate
- Stir rods, glass
- Vortex mixer

6. REAGENTS

Note: Analytical grade or ACS grade reagents are recommended. Evaluation of key reagents, such as aluminum nitrate and ammonium hydrogen phosphate, for contribution to method background levels from naturally occurring radioactive materials is recommended.

Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$
Ammonium hydrogen phosphate, $(NH_4)_2HPO_4$
Ammonium hydroxide(57% NH_4OH or 28% NH_3), concentrated NH_4OH
Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4.H_2O$

Ammonium thiocyanate, NH_4SCN
Appropriate tracers or standards (U-232, Am-243, Pu-242 or Pu-236)
Ascorbic acid powder, $C_6H_8O_6$
Calcium nitrate, $CaNO_3$
Deionized water, All reagents are prepared with deionized water
Ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$
Hydrochloric acid (37%), concentrated HCl
Hydrofluoric acid (49%), concentrated HF
Hydrogen peroxide (30%), concentrated H_2O_2
Isopropyl alcohol, C_3H_7OH
Nitric acid (70%), concentrated HNO_3
Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$
Phenolphthalein pH indicator
Sodium nitrite, $NaNO_2$
Sulfamic acid, H_3NSO_3
TRU® resin, 2mL prepacked column, 100-150□m, Eichrom Part TR-C50-A
UTEVA® resin, 2mL prepacked column, 100-150μm, Eichrom Part UT-C50-A

6.1. *Ammonium bioxalate (0.1M)* - Dissolve 6.31g of oxalic acid dihydrate and 7.11g of ammonium oxalate monohydrate in 900mL of water. Dilute to 1L with water.

6.2. *Ammonium hydrogen phosphate (3.2 M)* - Dissolve 104g of $(NH_4)_2HPO_4$ in 200mL of water, heat gently to dissolve. Dilute to 250mL with water.

6.3. *Ammonium thiocyanate indicator (1M)* - Dissolve 7.6g of ammonium thiocyanate in 90mL of water. Dilute to 100mL with water.

6.4. *Ascorbic acid (1M)* - Dissolve 17.6g of ascorbic acid in 90mL of water. Dilute to 100mL with water. **Prepare fresh weekly.**

6.5. *Calcium nitrate (1.25M)* - Dissolve 51g of $Ca(NO_3)_2$ in 100mL of water. Dilute to 250mL with water.

6.6. *Hydrochloric acid (1M)* - Add 83mL of concentrated HCl to 900mL of water. Dilute to 1L with water.

6.7. *Hydrochloric acid (4M)* - Add 333mL of concentrated HCl to 500mL of water. Dilute to 1L with water.

6.8. *Hydrochloric acid (4M) - hydrofluoric acid (0.1M)*- Add 333mL of concentrated HCl and 3.6mL of concentrated HF to 500mL of water. Dilute to 1L with water.

6.9. Hydrochloric acid (5M) - oxalic acid (0.05M) solution - Dissolve 6.3g oxalic acid dihydrate in 400mL water. Add 417 mL concentrated HCl. Dilute to 1L with water.

6.10. Hydrochloric acid (9M) - Add 750mL of concentrated HCl to 100mL of water. Dilute to 1L with water.

6.11. Nitric acid (2M) - sodium nitrite (0.1M) solution- Add 31mL of concentrated HNO_3 to 200 mL of water. Dissolve 1.72g of sodium nitrite in the solution. Dilute to 250mL with water. Prepare fresh daily.

6.12. Nitric acid solution (8M) - Add 500mL of concentrated HNO3 to 400mL of water. Dilute to 1L with water.

6.13. Nitric acid solution (3M) - Add 188mL of concentrated HNO3 to 700mL of water. Dilute to 1L with water.

6.14. Nitric acid (3M) - Aluminum nitrate (1M) solution - Dissolve 375g of $Al(NO_3)_3 \cdot 9H2O$ in 500mL of water. Add 188mL of concentrated HNO3. Dilute to 1L with water.

6.15. Ferric Nitrate Solution (5 mg/mL Fe) in 0.1M HNO3 - To a 500mL volumetric flask, add 18g Fe(NO3)3·9H2O, 400mL of water and 3.12mL of concentrated HNO3. Swirl to dissolve. Dilute to 500mL with water.

6.16. Sulfamic acid (1.5M) - In a 500mL volumetric flask, add 73g of sulfamic acid to 400mL of water. Swirl to dissolve. Dilute to 500mL with water.

6.17. Phenolphthalein solution - dissolve 1g phenolphthalein in 100 mL 95% isopropyl alcohol and dilute with 100 mL of water.

7. PROCEDURE

7.1. Water Sample Preparation:

7.1.1. Aliquot 500 to 1000mL of the sample (or enough to meet required detection limit) into an appropriate size beaker. If

samples larger than 1L are analyzed, evaporate the sample to approximately 1L.

7.1.2. Add 5mL concentrated HNO_3.

Note: If using self-cleaning ^{232}U tracer (Eichrom TP01), vortex mix and centrifuge standard to ensure that ^{228}Th and its daughters are effectively removed from ^{232}U by the $BaSO_4$ precipitate.

7.1.3. Add appropriate tracers per lab protocol.

7.1.4. Calcium phosphate precipitation:

7.1.4.1. Add 0.5 mL of 1.25M $Ca(NO_3)_2$ to each beaker.

7.1.4.2. Place each beaker on a hot plate.

7.1.4.3. Cover each beaker with a watch glass.

7.1.4.4. Heat at medium setting for 30-60 minutes.

7.1.4.5. Remove the watch glass and turn the heat down.

7.1.4.6. Add 2-3 drops of phenolphthalein indicator and 1mL of 3.2M $(NH_4)_2HPO_4$ solution.

7.1.4.7. While stirring, slowly add enough concentrated NH_4OH to reach the phenolphthalein end point (pH~9) and form a calcium phosphate precipitate. Allow the sample to heat for another 20-30 minutes.

7.1.4.8. Remove samples from the hot plate, cool to room temperature, and allow precipitate to settle until solution can be decanted (30 minutes to 2 hours) or centrifuge.

7.1.4.9. Decant supernate and discard to waste.

7.1.4.10. Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.

7.1.4.11. Decant supernate and discard to waste.

7.1.4.12. Wash the precipitate with an amount of water approximately twice the volume of the precipitate. Mix well on a vortex mixer. Centrifuge for 5-10 minutes. Discard the supernate.

7.1.4.13. If an ammonia odor persists, repeat water wash of precipitate.

7.1.4.14. Dissolve precipitate in 5mL concentrated nitric acid. Transfer solution to a 100mL beaker. Rinse centrifuge tube with 2-3 mL of concentrated nitric acid and transfer to beaker. Evaporate the solution to dryness.

7.2. Actinide Separations using Eichrom Resins:

7.2.1. Dissolve each precipitate with 10mL of 3M HNO_3- 1M $Al(NO_3)_3$.

Note: An additional 5-10mL may be necessary if the volume of precipitate is large.

Note: Make sure that all reagents and the load solution have cooled to room temperature. Warm solutions can cause reactions that will affect oxidation adjustments performed in the following steps.

7.2.2. Add 1mL of 1.5 M sulfamic acid and 0.5mL of 5mgFe/mL to each solution. Swirl to mix.

Note: If the additional 5-10 mL was used to dissolve the sample in step 7.2.1., add a proportionally larger volume of sulfamic acid and Fe solution.

7.2.3. Add 1 drop of 1M ammonium thiocyanate indicator to each sample and mix.

Note: The color of the solution turns deep red, due to the presence of iron in Fe (III).

7.2.4. Add 1mL of 1M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes.

Note: The red color should disappear which indicates reduction of Fe(III) to Fe(II). If the red color still persists then additional ascorbic acid solution should be added drop-wise with mixing until the red color disappears. Once the red color disappears, add an additional 0.5mL of 1M ascorbic acid.

Note: If particles are observed suspended in the solution, centrifuge the sample. The supernatant will be transferred to the column in step 7.2.5.5. The precipitate will be discarded.

7.2.5. U separation from Pu, Am using UTEVA Resin

7.2.5.1. For each sample solution, place a UTEVA Resin column in the column rack.

7.2.5.2. Place a beaker below each column, remove the bottom plug and caps from each column, push top frit down to the top of the resin bed, and allow to drain. Attach column reservoirs to each column.

7.2.5.3. Add 5mL of 3M HNO_3 into each column to precondition the resin. Allow solution to drain.

7.2.5.4. Place a clean, labeled 50 mL beaker below each column.

7.2.5.5. Transfer each solution from step 7.2.4. into the appropriate UTEVA Resin column reservoir. Allow solution to drain through column.

7.2.5.6. Add 5mL of 3M HNO_3 to rinse to each sample beaker. Transfer each beaker rinse into the appropriate UTEVA Resin column reservoir. Allow solution to drain through column.

7.2.5.7. Add 5mL of 3M HNO_3 into each column and collect in the same beaker as in 7.2.5.6.

7.2.5.8. Set aside the solutions collected in steps 7.2.5.5, 7.2.5.6, and 7.2.5.7 for Am and Pu separations on TRU.

7.2.5.9. Place a new beaker below each UTEVA resin column. Add 15mL of 8M HNO_3 to each UTEVA column. Allow solution to drain.

Note: This rinse will remove Po isotopes, including ^{210}Po, which can interfere with the measurement of ^{232}U by alpha spectrometry.

7.2.5.10. Add 5mL of 9M HCl into each column and allow to drain.

Note: This rinse converts the resin to the chloride system. Some Th may be removed here.

7.2.5.11. Add 20mL of 5M HCl- 0.05 M oxalic acid into each column and allow solution to drain.

Note: This rinse removes neptunium and thorium from the column and any residual ferrous ion that might interfere with electrodeposition.

7.2.5.12. Place a clean, labeled beaker below each column.

7.2.5.13. Add 15mL of 1M HCl into each column to strip the uranium. Allow solution to drain.

7.2.5.14. Set U samples aside for alpha source preparation.

7.2.6. Pu, Am Separation Using TRU Resin:

7.2.6.1. For each sample dissolved, place a TRU Resin column in the column rack.

7.2.6.2. Place a beaker below each TRU column, remove the bottom plug from each column, push the top frit down to the top of the resin bed, and allow each column to drain.

7.2.6.3. Add 5mL of 3M HNO_3 into each column to precondition the resin. Allow the solution to drain.

7.2.6.4. Transfer solution from step 7.2.5.8. into the appropriate TRU Resin reservoir. Allow the load solution drain though the columns.

7.2.6.5. Add 5mL of 3M HNO_3 into the sample beaker and transfer this rinse to the appropriate TRU column reservoir. Allow solution to drain through the columns.

7.2.6.6. Add 5mL of 2M HNO_3- 0.1M $NaNO_2$ into each TRU column. Allow solution to drain through the columns.

Note: Sodium nitrite is used to oxidize Pu(III) to Pu(IV) to enable the Pu/Am separation.

7.2.6.7. Discard the load and rinse solutions to waste.

7.2.6.8. Ensure that clean, labeled beakers are below each column.

7.2.6.9. Make sure that all of the 2M HNO_3-0.1M $NaNO_2$ is removed from the column reservoir. If necessary, invert each column and rinse the reservoir (but not the column) with a small volume of water.

7.2.6.10. Add 15mL of 4M HCl to elute americium. Allow solution to drain through columns.

7.2.6.11. Set Am/Cm samples aside for alpha source preparation.

7.2.6.12. Place a new beaker below each TRU resin column. Rinse the columns with 25mL of 4M HCl- 0.1 MHF. Discard eluate.

Note: 4M HCl- 0.1 MHF is used to selectively remove any residual Th that may be present on the TRU column.

7.2.6.13. Place clean, labeled beakers or centrifuge tubes below each TRU resin column.

7.2.6.14. Add 10mL of 0.1M ammonium bioxalate to elute plutonium from each column.

7.2.6.15. Set Pu samples aside for alpha source preparation.

7.3. Prepare samples for measurement of actinides by alpha spectrometry using electrodeposition (Eichrom SPA02) or rare earth fluoride micro precipitation (Eichrom SPA01).

8. CALCULATIONS

Calculate the actinide activity as follows:

Calculate tracer yield:

$$\text{Yield} = \frac{(C_s - B_s)}{E_s \times A_s}$$

where:

C_s = measured actinide tracer, cpm
B_s = background, cpm
E_s = counting efficiency for tracer
A_s = tracer activity, dpm

Note: If any tracer may be present in the sample, a spiked and unspiked sample must be analyzed to determine chemical yield, where:

$$\text{Yield} = \frac{(\text{spiked sample tracer cpm - unspiked sample tracer cpm})}{\text{E} \times \text{actinide spike activity dpm}}$$

Percent yield = Yield x 100

Calculate actinide isotope activity:

$$\text{Sample dpm / g or dpm / L} = \frac{S - B}{E \times V \times Y}$$

where:

S =sample activity, cpm
B =background, cpm
E =counting efficiency = measured cpm/dpm of isotopic standard V = sample weight, g or volume, L
Y =yield

Conversion of dpm/g to pCi/g: pCi/g = (dpm/g)/2.22

9. PRECISION AND BIAS

9.1. *Precision*- A relative standard deviation of 4.2% at the 25 dpm level has been reported for uranium. A relative standard deviation of 3.2% at the 60 dpm level has been reported for plutonium.

9.2. *Bias*- Mean chemical recoveries of 95% for americium, 93% for plutonium and 86% for uranium have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

9.3. The data is based on the calcium phosphate precipitation option.

10. REFERENCES

1) Horwitz, E.P., et al. "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," Analytica Chimica Acta. 281 (1993), 361-372.

2) Horwitz, E.P., et al. "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," Analytica Chimica Acta. 266 (1992), 25-37.

3) Maxwell, S.L., "Rapid Column Extraction Methods for Actinides and Sr-89/90 in Water Samples," Journal of Radioanalytical and Nuclear Chemistry, 267(3), 537-543 (2006).

4) ASTM Method D3972-09, "Standard Test Method for Isotopic Uranium in Water by Radiochemistry."

5) ASTM Method D7282-06, "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements."

6) ASTM Method D3648-14, "Standard Practices for the Measurement of Radioactivity."

7) Eichrom Application Note AN-1413, "Rapid Determination of Actinides in Emergency Water Samples."

1) Aliquot up to 1000mL of water into glass beaker.
2) Add 5mL conc. HNO_3.
3) Add yield tracers and 0.5mL of $Ca(NO_3)_2$ to each sample.
4) Cover with watch glass and heat at medium setting for 30-60 minutes.
5) Turn down heat. Add 1mL of 3.2M $(NH_4)_2HPO_4$ and 2-3 drops of phenolphthalein indicator.
6) While stirring sample, slowly add conc. NH_4OH until pH 9.
7) After 30 minutes, cool samples to room temperature. Allow precipitate to settle or centrifuge.
8) Decant supernate and discard as waste.
9) Transfer precipitate to centrifuge tube with DI water.
10) Centrifuge ~10minutes at 2000rpm. Decant supernate.
11) Add 10mL DI water to precipitate. Mix well. Centrifuge. Decant supernate.
12) Dissolve precipitate with 5mL conc. HNO_3. Tranfer to 100mL beaker.
13) Rinse centrifuge tube with 2-3mL conc. HNO_3. Transfer rinse to same 100mL beaker.
14) Evaporate samples to dryness.
15) Dissolve residue in 10-20mL 3M HNO_3-1M $Al(NO_3)_3$.
16) Add 1mL 1.5M Sulfamic Acid, 0.5 mL Fe, and 1mL 1M Ascorbic Acid.
Water Sample in glass beaker. Acidify pH 2.
Calcium Posphate ppt.
Digest residue in glass beaker with conc. HNO_3
Sample in 3M HNO_3 1M $Al(NO_3)_3$
17) Precondition UTEVA column with 5mL 3M HNO_3.
18) Load sample on to column. Allow liquid to drain to waste. U is retained. Am and Pu pass through.
19) Rinse sample tube with 5mL 3M HNO_3. Add rinse to UTEVA column.
20) Rinse UTEVA column with 5mL 3M HNO_3. Allow liquid to drain.
21) Set aside beaker with eluate from 19-21 for Am-Pu separation on TRU. Place fresh beaker below UTEVA column.
22) Rinse UTEVA column with 15mL 8M HNO_3.
23) Rinse UTEVA column with 5mL 9M HCl.
24) Rinse UTEVA column with 20mL 5M HCl-0.05M oxalic acid. Discard to Waste.
25) Place clean centrifuge tube or glass beaker below column. Strip Uranium with 15mL 1M HCl.
2mL UTEVA
(17) (22) (23) (24)
Waste
(18) (19) (20)
Am-Pu Separation on TRU
(25)
U sample to source preparation
26) Precondition TRU column with 5mL 3M HNO_3.
27) Load solution from (19)-(21) on TRU column.
28) Rinse sample beaker with 5mL 3M HNO_3. Add to TRU.
29) Rinse TRU with 5mL 2M HNO_3-0.1M $NaNO_2$.
30) Add clean beaker. Strip Am with 15mL 4M HCl.
31) Add clean beaker. Rinse TRU with 25mL 4M HCl-0.1M HF.
32) Add clean beaker. Strip Pu with 10mL 0.1M ammonium bioxalate.
2mL TRU
(26) (27) (28) (29) (31)
Waste
(30)
Am sample to source preparation
(32)
Pu sample to source preparation