AMERICIUM, PLUTONIUM AND URANIUM IN URINE

1. SCOPE

1.1. This is a method for the separation of americium, plutonium and uranium in urine. 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 urine samples. Tracers are used to monitor chemical recoveries to improve precision and accuracy.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of actinides in urine 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 ^{210}Po and ^{232}U must be chemically separated to enable accurate 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. TEVA-TRU resin separation chemistry may also be applied for the measurement of actinides in urine samples, as described in Eichrom Application Note 1412.

4.4. The sample preparation procedure outlined in this method will adequately recover actinides from freshly collected, well preserved, homogenous urine 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.

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.

1-Octanol, $C_8H_{17}OH$
Aluminum nitrate nonahydrate, $Al(NO_3)_3.9H_2O$
Ammonium hydrogen phosphate, $(NH_4)_2HPO_4$

Ammonium hydroxide(57% NH_4OH or 28% NH_3), concentrated NH_4OH
Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4 \cdot H_2O$
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
Nitric acid (70%), concentrated HNO_3
Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$
Sodium nitrite, $NaNO_2$
Sulfamic acid, H_3NSO_3
TRU® resin, 2mL prepacked column, 100-150µm, Eichrom Part TR-C50-A
UTEVA® resin, 2mL prepacked column, 100-150µm, Eichrom Part UT- C50-A

6.1. *Ammonium bioxalate (0.1M)* - Dissolve 6.3g of oxalic acid and 7.1g of ammonium oxalate in 900mL of water. Dilute to 1L with water.

6.2. *Ammonium hydrogen phosphate (3.2M)* - Dissolve 208g of $(NH_4)_2HPO_4$ in 400mL of water. Heat gently to dissolve. Dilute to 500mL 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. *Calcium nitrate (1.25M)* - Dissolve 102g of $Ca(NO_3)_2$ in 400mL of water. Dilute to 500mL with water.

6.5. *Hydrochloric acid (1M)* - Add 83mL of concentrated HCl to 800mL of water. Dilute to 1L with water

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

6.7. *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.

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

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

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

6.11. *Nitric acid solution (3M)* - Add 188mL of concentrated HNO_3 to 700mL of water. Dilute to 1L with water.

6.12. *Nitric acid (8M)* - add 500mL of concentrated HNO_3 to 45 mL of water. Dilute to 1L with water.

6.13. *Nitric acid (3M) - aluminum nitrate (1.0M) solution*- Dissolve 375g of $Al(NO_3)_3 \cdot 9H_2O$ in 500mL of water. Add 188mL of concentrated HNO_3. Dilute to 1L with of deionized water.

6.14. *Ferric Nitrate Solution (5 mg/mL Fe) in 0.1M HNO_3* - To a 500mL volumetric flask, add 18g $Fe(NO_3)_3 \cdot 9H_2O$, 400mL water and 3.1mL concentrated HNO_3. Swirl to dissolve. Dilute to 500mL with water.

6.15. *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.

7. PROCEDURE

7.1. Urine Sample Preparation:

7.1.1. Aliquot up to 1200mL of the filtered sample (or enough to meet required detection limit) into an appropriate size beaker.

Note: If using self-cleaning ^{232}U tracer (Eichrom Method 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.

7.1.2. Add appropriate tracers per lab protocol.

7.1.3. Place each beaker on a hot plate.

7.1.4. Add 2-3 drops of 1-octanol and 1mL of 1.25M $Ca(NO_3)_2$ to each sample.

7.1.5. Add 25mL of concentrated HNO_3 to each sample with stirring.

7.1.6. Cover each beaker with a watch glass.

7.1.7. Heat samples at medium setting for at least 30-60 minutes.

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

7.1.9. Add 2.5mL of 3.2M $(NH_4)_2HPO_4$ solution to each sample with stirring.

7.1.10. Slowly add concentrated NH_4OH, while stirring, to reach a pH of 9. Calcium phosphate will precipitate carrying the actinides with it. Heat samples for 30 minutes.

7.1.11. Remove samples from hot plate, cool samples to room temperature, and allow the precipitate to settle until solution can be decanted (at least 2 hours, preferably overnight). Alternatively, samples can be centrifuged to more rapidly separate the precipitate and supernate solution.

7.1.12. Decant supernate and discard to waste.

7.1.13. Transfer the precipitate to a centrifuge tube with deionized water and centrifuge the precipitate for approximately 10 minutes at 2000 rpm. Save the beaker in which the precipitation was performed.

7.1.14. Decant the supernate from the centrifuge tube and discard to waste.

7.1.15. Add 10mL of water to the centrifuge tube. Mix well and centrifuge.

7.1.16. Decant supernate from the centrifuge tube and discard to waste.

7.1.17. Add 5mL of concentrated HNO_3 to the precipitation beaker, rinsing the sides to dissolve any residual precipitate.

7.1.18. Add the HNO_3 from the beaker rinse to the centrifuge tube containing the corresponding precipitate. Carefully swirl to dissolve the precipitate.

7.1.19. Transfer the solution to a 200mL beaker. Rinse the centrifuge tube with two additional 5mL aliquots of concentrated HNO_3 and transfer to the 200mL beaker.

7.1.20. Add 1mL of 30% H_2O_2. Evaporate the solutions to dryness. While the sample is hot, carefully add 2-3 drops of 30% H_2O_2 to each sample to oxidize the remaining organics in the sample.

7.1.21. Allow the samples to cool slightly, add 5mL of 30% H_2O_2 and 5mL conc. HNO_3. Evaporate to dryness.

7.1.22. Repeat step 7.1.21 until the precipitate is white or near white.

7.2. Actinide Separations using Eichrom resins:

7.2.1. Re-dissolve calcium phosphate precipitate:

7.2.1.1. Dissolve each precipitate with 20mL of 3M HNO_3-1M $Al(NO_3)_3$.

Note: Make sure all reagent solutions and the sample solutions have cooled to room temperature. Warm solutions can cause reactions which can affect the oxidation state adjustments performed in subsequent steps.

7.2.1.2. Add 1mL of 1.5M sulfamic acid and 0.5 mL of $Fe(NO_3)_3$ (5mg/mL Fe) solution to each sample. Swirl to mix.

7.2.1.3. 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 Fe (III).

7.2.1.4. Add 1 mL 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 persists, then additional ascorbic acid solution should be added drop-wise with mixing. When the red color disappears, add an additional 0.5mL of 1M ascorbic acid to ensure complete reduction throughout the separation method.

Note: If particles are observed suspended in the solution, centrifuge the sample. The supernate will be transferred to the column in step 7.2.2.5. The precipitate will be discarded.

7.2.2. U separation from Pu, Am using UTEVA Resin

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

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

7.2.2.3. Add 5mL of 3M HNO_3 into each column to precondition resin. Allow the solution to drain. Discard eluate as waste.

7.2.2.4. Place a clean, labeled 50mL beaker or centrifuge tube below each column.

7.2.2.5. Transfer each solution from step 7.2.1.4 into the appropriate UTEVA Resin column. Allow the solution to drain through the column.

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

7.2.2.7. Add 5mL of 3M HNO_3 into each column reservoir. Allow solution to drain through the UTEVA column.

7.2.2.8. Set aside the solutions collected in steps 7.2.2.5, 7.2.2.6, and 7.2.2.7 for Am and Pu separations using TRU resin.

7.2.2.9. Place new set of beakers/tubes below each column.

7.2.2.10. Add 15mL of 8M HNO_3 rinse to each UTEVA column reservoir. Allow solution to drain through the UTEVA column. Discard this rinse as waste.

Note: This rinse will remove and residual ^{210}Po which can interfere with determination of ^{232}U by alpha spectrometry.

7.2.2.11. Add 5mL of 9M HCl into each column reservoir. Allow the solution to drain. Discard this rinse as waste.

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

7.2.2.12. Add 20mL of 5M HCl- 0.05M oxalic acid into each column. Allow the solution to drain. Discard this rinse as waste.

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

7.2.2.13. Place a clean, labeled beaker or centrifuge tube below each column.

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

7.2.2.15. Set U samples aside for alpha source preparation.

7.2.3. Pu, Am Separation Using TRU Resin:

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

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

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

7.2.3.4. Transfer each solution from step 7.2.2.8 into the appropriate TRU Resin column reservoir.

7.2.3.5. Allow the load solution to drain through column.

7.2.3.6. Add 5mL of 3M HNO_3 to rinse the sample beaker. Transfer this rinse to the appropriate TRU column reservoir. Allow the rinse to drain through the column.

7.2.3.7. Add 5mL of 2M HNO_3- 0.1M $NaNO_2$ into each column reservoir.

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

7.2.3.8. Allow the rinse solution to drain through each column.

7.2.3.9. Discard the load and rinse solutions to waste.

7.2.3.10. Place clean, labeled beakers or centrifuge tubes below each column.

7.2.3.11. Ensure all residual 2M HNO_3-0.1M $NaNO_2$ has been removed from the reservoir of each column. This can be

done by inverting each column and rinsing with a small volume of deionized water.

7.2.3.12. Add 15mL of 4M HCl to each column reservoir. Collect the eluate, containing americium (and curium), in the beaker or centrifuge tube.

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

7.2.3.14. Place fresh beakers below each column.

7.2.3.15. Rinse the columns with 25mL of 4M HCl- 0.1M HF. Discard eluate as waste.

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

7.2.3.16. Ensure that clean, labeled beakers or centrifuge tubes are below each column.

7.2.3.17. Add 10mL of 0.1M ammonium bioxalate to elute plutonium from each column. Collect the eluate in the beakers or centrifuge tubes.

7.2.3.18. Set Pu samples aside for alpha source preparation.

7.3. Prepare samples for actinide measurement by alpha spectrometry using electrodeposition (Eichrom method SP02) or rare earth fluoride micro precipitation (Eichrom method SP01).

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:

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

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. PERFORMANCE DATA

9.1. Mean tracer recoveries for a combination of 20+ real and synthetic urine samples were as follows: 74% for Am-241, 95% for Pu-242 and 84% for U-232.

10. REFERENCES

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

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

3) Maxwell, S.L., et al. "Rapid Analysis of Urine and Water Samples," Journal of Radioanalytical and Nuclear Chemistry, 275(3), 447-502 (2008).

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

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

6) Eichrom Application Note AN-1412, "Rapid Determination of Actinides in emergency urine samples".

1) Aliquot up to 1200mL of urine into glass beaker.
2) Add yield tracers.
3) Add 2-3 drops 1-octanol and 1mL of 1.25M $Ca(NO_3)_2$.
4) Add 25mL of conc. HNO_3.
5) Cover with watch glass and heat at medium setting for 30-60 at least min.
6) Turn down heat. Add 2.5mL of 3.2M $(NH_4)_2HPO_4$.
7) While stirring sample, slowly add conc. NH_4OH to pH 9.
8) After 30 minutes, cool to room temperature. Allow precipitate to settle or centrifuge.
9) Decant supernate and discard as waste.
10) Transfer precipitate to centrifuge tube with DI water.
11) Centrifuge ~10minutes at 2000rpm. Decant supernate.
12) Add 10mL DI water to precipitate. Mix well. Centrifuge. Decant supernate.
13) Rinse precipitation beaker with 5mL conc. HNO_3. Transfer to precipitate in centrifuge tube. Dissolve precipitate and transfer to 200mL beaker.
14) Rinse centrifuge tube with 2x 5mL conc. HNO_3. Transfer to same 200mL beaker.
15) Digest precipitate with HNO_3/H_2O_2 until white residue obained.
16) Dissolve reside in 20mL 3M HNO_3-1M $Al(NO_3)_3$.
17) Add 1mL 1.5M Sulfamic Acid, 0.5 mL Fe, and 1mL 1M Ascorbic Acid.
Urine Sample in glass beaker. HNO_3 digest.
Calcium Posphate ppt.
Digest residue in glass beaker with conc. HNO_3/H_2O_2
Sample in 3M HNO_3 1M $Al(NO_3)_3$
2mL UTEVA
18) Precondition UTEVA column with 5mL 3M HNO_3.
19) Load sample on to column. Allow liquid to drain to waste. U is retained. Am and Pu pass through.
20) Rinse sample tube with 5mL 3M HNO_3. Add rinse to UTEVA column.
21) Rinse UTEVA column with 5mL 3M HNO_3. Allow liquid to drain.
22) Set aside beaker with eluate from 19-21 for Am-Pu separation on TRU. Place fresh beaker below UTEVA column.
23) Rinse UTEVA column with 15mL 8M HNO_3.
24) Rinse UTEVA column with 5mL 9M HCl.
25) Rinse UTEVA column with 20mL 5M HCl-0.05M oxalic acid. Dlscard to Waste.
26) Place clean centrifuge tube or glass beaker below column. Strip Uranium with 15mL 1M HCl.
(18) (23) (24) (25) Waste
(19) (20) (21) Am-Pu Separation on TRU
(26) U sample to source preparation
2mL TRU
27) Precondition TRU column with 5mL 3M HNO_3.
28) Load solution from (19)-(21) on TRU column.
29) Rinse sample beaker with 5mL 3M HNO_3. Add to TRU.
30) Rinse TRU with 5mL 2M HNO_3-0.1M $NaNO_2$.
31) Add clean beaker. Strip Am with 15mL 4M HCl.
32) Add clean beaker. Rinse TRU with 25mL 4M HCl-0.1M HF.
33) Add clean beaker. Strip Pu with 10mL 0.1M ammonium bioxalate.
(27) (28) (29) (30) (32) Waste
(31) Am sample to source preparation
(33) Pu sample to source preparation