THORIUM AND NEPTUNIUM IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

1.1. This is a method for the separation of neptunium and thorium from water samples. After completing this method, source preparation for measurement of thorium and neptunium 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. Thorium and neptunium are separated by Eichrom TEVA resin prior to measurement by alpha spectrometry. A calcium phosphate precipitation is 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. Actinides 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 lead to reduced recovery 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.

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Beakers, glass
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge tubes, 50mL and 250mL
- Centrifuge, with rotor and carriers for 50mL and 250mL tubes
- Fume hood
- Hotplate
- Stir rods, glass
- Vacuum box system- Eichrom Part: AR-12-BOX or AR-24-BOX
- Vacuum box white inner support tube-PE, Eichrom Part: AR-1000-TUBE-PE
- Vacuum box yellow outer tips, Eichrom Part: AR-1000-OT
- Vacuum pump, 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Optional item for collection of load and rinse fractions:
  - Vacuum box inner liner, Eichrom Part: AR-12-LINER or AR-24-LINER

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 (Th-229, Am-243/Np-239)
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
Isopropanol, C_3H_7OH
Nitric acid (70%), concentrated HNO_3
Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$
Sulfamic acid, H_3NSO_3
TEVA® resin, 2mL prepacked cartridge, 50-100μm, Eichrom Part TE-R50-S

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 (3.2M) - Dissolve 104g of (NH4)2HPO4 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 (9M) - Add 750mL of concentrated HCl to 100mL of water. Dilute to 1L with water.

6.7. Nitric acid solution (3M) - Add 188mL of concentrated HNO3 to 800mL of water. Dilute to 1L with water.

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

6.9. Phenolphthalein indicator - Dissolve 1g of phenolphthalein in 50mL of isopropyl alcohol and add 50mL of water.

6.10. 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 of water and 3.1mL of concentrated HNO_3. Swirl to dissolve. Dilute to 500mL with water.

6.11. 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.

6.12. Nitric acid (2.5M) - Sulfamic Acid (0.1M) - Ascorbic Acid (0.1M) - Fe Solution – To 250mL of water, add 78mL of concentrated HNO_3, 33mL 1.5M sulfamic acid and 15mL ferric nitrate solution (5mg/mL Fe). Swirl to mix. Add 50mL 1M ascorbic acid solution. Dilute to 500mL with water. **Prepare fresh daily.**

7. PROCEDURE

7.1. Water Sample Preparation:

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

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

7.1.3. Add 5mL concentrated HNO_3 acid.

7.1.4. Add appropriate tracers per lab protocol.

7.1.5. Calcium phosphate precipitation:

7.1.5.1. Add 0.5mL of 1.25M $Ca(NO_3)_2$ to each sample.

7.1.5.2. Place each beaker on a hotplate. Cover each beaker with a watch glass. Heat at medium setting for 30-60 minutes.

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

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

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

7.1.5.6. 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.

7.1.5.7. Decant supernate and discard to waste.

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

7.1.5.9. Decant supernate and discard to waste.

7.1.5.10. 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.

7.1.5.11. If an ammonia odor persists repeat 7.1.5.10.

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

7.2. Np, Th separation from using TEVA Resin

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.

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

Note: If the additional 5-10mL was used to dissolve the sample in step 7.2.1.1, add a proportionately larger amount of sulfamic acid and iron solution.

7.2.1.2. 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).

7.2.1.3. 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 persists then additional ascorbic acid solution should be added drop-wise with mixing until the red color disappears. Following disappearance of the red color, add an additional 0.5mL of 1M ascorbic acid.

Note: If particles are observed suspended in the solution, centrifuge the sample. The supernate will be transferred to the column in step 7.2.8. The residue will be discarded.

7.2.2. Place the inner tube rack (supplied with vacuum box system) into the vacuum box with the centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, a vacuum box inner liner may be used.

7.2.3. Place yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit a white inner support tube into each yellow tip.

7.2.4. For each sample solution, fit a TEVA cartridge on to the inner support tube.

7.2.5. Add syringe barrels (funnels/reservoirs) to the top end of each TEVA cartridge.

Note: The unused openings on the vacuum box should be sealed. Vacuum manifold plugs can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape.

7.2.6. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

7.2.7. Add 5mL of 3M HNO_3 into TEVA cartridge reservoir to condition the resin. Adjust vacuum to achieve a flow rate of 1-2mL/min. Allow solution to completely pass through each TEVA cartridge.

7.2.8. Transfer each dissolved sample into the appropriate TEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.

7.2.9. Add 5mL of 2.5M HNO_3 - 0.1M Sulfamic Acid - 0.1M Ascorbic Acid- Fe Solution to rinse to each sample tube. Transfer each rinse solution into the appropriate TEVA cartridge reservoir.

Allow solution to pass completely through each cartridge at 1-2mL/min.

7.2.10. Add 10mL of 2.5M HNO_3 - 0.1M Sulfamic Acid - 0.1M Ascorbic Acid- Fe Solution to each TEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.

7.2.11. Disengage vacuum. Empty centrifuge tubes to waste or place fresh centrifuge tubes below each TEVA cartridge. Place a clean reservoir above each TEVA cartridge.

7.2.12. Add 20mL of 3M HNO_3 to each TEVA cartridge reservoir. Engage vacuum. Allow solution to completely pass through each TEVA cartridge at 1-2mL/min. Disengage vacuum. Discard eluate as waste.

Note: Plutonium, uranium and americium are removed with the load solution and rinses.

7.2.13. Place a clean, labeled 50mL centrifuge tube below each column. Replacing yellow outer tips and inner support tubes at this point will help ensure clean Th fractions in the following steps.

7.2.14. Add 15mL of 9M HCl into each TEVA cartridge reservoir to elute Th. Engage vacuum. Allow solution to completely pass through each TEVA cartridge at 1-2mL/min. Disengage vacuum.

7.2.15. Set Th samples aside for alpha source preparation.

7.2.16. Place a clean, labeled 50 mL centrifuge tube below each TEVA cartridge. Replacing yellow outer tips and inner support tubes at this point will help ensure clean Np fractions in the following steps.

7.2.17. Add 10 mL of 0.1M ammonium bioxalate into TEVA cartridge reservoir to strip the neptunium. Engage vacuum. Allow solution to completely pass through each TEVA cartridge at 1-2mL/min.

7.3. Prepare samples for the 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:

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

Percent yield = Yield x 100

Calculate actinide isotope activity:

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

where:

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

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

9. PRECISION AND BIAS

9.1. *Precision* - A relative standard deviation of 3.5% for Th in the range of 1 pCi/L to 20 pCi/L has been reported. A relative standard deviation of 6.3% for Np in the same range has been reported.

9.2. *Bias* - A mean recovery of 102% ± 3.5% for Th and 102% ± 6% for Np have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

10. REFERENCES

1) Horwitz, E P, et al. "Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions." Analytica Chimica Acta, 310, 63-78 (1995).

2) 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).

3) ASTM Method C1475-05, “Standard Method for Determination of Neptunium-237 in Soil.”

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

5) ASTM Method D3648-14, “Standard Practices for the Measurement of Radioactivity.”

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, 0.5mL 5mg/mL Fe, and 1 mL 1M Ascorbic Acid. Mix.
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 TEVA cartridge with 5mL 3M HNO_3.
18) Load sample on to TEVA. Allow liquid to drain to waste. Np and Th are retained.
19) Rinse sample tube with 5mL 2.5M HNO_3 - 0.1M Sulfamic Acid - 0.1M Ascorbic Acid - Fe solution. Add rinse to TEVA. Allow liquid to drain to waste.
20) Rinse TEVA with 10mL 2.5M HNO_3 - 0.1M Sulfamic Acid - 0.1M Ascorbic Acid - Fe solution. Allow liquid to drain to waste.
21) Rinse TEVA with 20mL 3M HNO_3. Allow liquid to drain to waste.
22) Strip Th with 15mL of 9M HCl.
23) Strip Np with 10mL 0.1M ammonium bioxalate.
2mL TEVA Cartridge
(17) (18) (19) (20) (21) Waste
(22) Thorium sample to source preparation
(23) Neptunium sample to source preparation