URANIUM AND THORIUM IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

1.1. This is a method for the separation of uranium and thorium from water samples. After completing this method, source preparation for measurement of uranium and thorium by alpha spectrometry is performed by electrolytic deposition onto stainless steel planchets (Eichrom Method SPA02) or by rare earth fluoride microprecipitation 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. Uranium and thorium are separated by Eichrom TEVA and UTEVA 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. Radionuclides 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 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.

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
- Vortex mixer
- Optional item for collection of load and rinse solutions:
    - Vacuum box inner liner, Eichrom Part: AR-24-LINER or AR-12-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, $(NH_4)_2C_2O_4.H_2O$
Appropriate tracers or standards (U-232, Th-229)
Ascorbic acid powder, $C_6H_8O_6$
Calcium nitrate, $CaNO_3$
Deionized water, All reagents are prepared with deionized water
Hydrochloric acid (37%), concentrated HCl
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
TEVA® resin, 2mL prepacked cartridge, 50-100□m, Eichrom Part TE-R50-S
UTEVA® resin, 2mL prepacked cartridge, 50-100μm, Eichrom Part UT-R50-S

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

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

6.3. *Hydrochloric acid (9M)* - Add 750mL of concentrated HCl to 10mL of water and dilute to 1L with water.

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

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

6.6. *Nitric acid (3M) - Aluminum nitrate (1M) solution* - Dissolve 375g of $Al(NO_3)_3.9H_2O$ in 500mL of water, add 188mL of concentrated HNO_3 and dilute to 1L with water.

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

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

7.1.3. Add 5mL concentrated HNO_3.

Note: If using self-cleaning ^{232}U tracer (Eichrom Method TP01), mix for 1-2 minutes to suspend $BaSO_4$ precipitate to remove ^{228}Th and daughters, centrifuge and then take aliquot for Uranium tracing.

7.1.4. Add appropriate tracers per lab protocol.

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

7.1.6. Place each beaker on a hot plate.

7.1.7. Cover each beaker with a watch glass.

7.1.8. Heat samples at medium setting for 30-60 minutes.

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

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

7.1.11. While stirring, slowly add enough concentrated NH_4OH with a squeeze bottle to reach the phenolphthalein end point and form a calcium phosphate precipitate. Allow the sample to heat for another 20-30 minutes.

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

7.1.13. Decant supernate and discard to waste.

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

7.1.15. Decant supernate and discard to waste.

7.1.16. 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.

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

7.1.18. Dissolve precipitate in 5mL of 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 solution to dryness.

7.2. Actinide Separations using Eichrom Resins:

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

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

7.2.2. Th and U separation using TEVA and UTEVA Resins

7.2.2.1. 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.

7.2.2.2. 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.

7.2.2.3. For each sample solution, fit a UTEVA cartridge on to the inner support tube. Fit a TEVA cartridge to the top end of each UTEVA cartridge.

7.2.2.4. 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.

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

7.2.2.6. Add 5mL of 3M HNO_3 into each catridge rervoir to condition the resin. Adjust vacuum to achieve a flow rate

of 1-2mL/min. Allow solution to completely drain through each cartridge.

7.2.2.7. Transfer each redissolved sample into the appropriate cartridge reservoir. Allow solution to completely drain through each cartridge at 1-2mL/min.

7.2.2.8. Add 5mL of 3M HNO_3 to rinse to each sample tube. Transfer each rinse solution into the appropriate catridge reservoir. Allow solution to completely drain through each cartridge at 1-2mL/min.

7.2.2.9. Add 15mL of 3M HNO_3 into each TEVA cartridge reservoir. Allow solution to completely drain at 1-2mL/min.

7.2.2.10. Disengage vacuum. Remove the UTEVA cartridges and set aside for uranium separation. Place a new centrifuge tube below each cartridge or empty centrifuge tubes to waste. Place TEVA cartridges on the vacuum box inner support tubes. Place a clean reservoir above each TEVA cartridge.

7.2.2.11. Add 15mL of 3M HNO_3 into each TEVA cartridge reservoir. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min. Discard eluate as waste.

Note: Residual Uranium is removed with the extended 3M HNO_3 rinse.

7.2.2.12. Disengage vacuum. Place a clean, labeled 50mL centrifuge below each TEVA cartridge. Replacing yellow outer tips and inner support tubes at this point can help to ensure a clean Th fraction in the following steps.

7.2.2.13. Add 15mL of 9M HCl into each TEVA cartridge reservoir. Engage vacuum. Elute Th at 1-2mL/min.

Note: 9M HCl will strip Th from the column. Pu^{4+} and Np^{4+} are retained on the column.

7.2.2.14. Set Th samples aside for alpha source preparation.

7.2.3. Uranium separation using UTEVA Resin

7.2.3.1. Place each UTEVA cartridge in the appropriate inner support tube on the vacuum box.

7.2.3.2. Place a 50mL centrifuge tube below each cartridge. Place a clean reservoir above each UTEVA cartridge.

7.2.3.3. Add 5mL of 3M HNO_3 into each UTEVA cartridge reservoir. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min.

7.2.3.4. Add 5mL of 9M HCl into each UTEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.

Note: This rinse converts the resin to the chloride system.

7.2.3.5. Add 20mL of 5M HCl-0.05M oxalic acid into each UTEVA cartridge reservoir. Allow solution to pass through each cartridge at 1-2mL/min. Disengage vacuum. Discard the combined eluate to this point as waste.

Note: This rinse removes any traces of plutonium, neptunium and thorium from the column.

7.2.3.6. Place a clean, labeled 50mL centrifuge tube below each UTEVA cartridge. Replacing yellow outer tips and inner support tubes at this point can help ensure a clean U fraction in the following steps.

7.2.3.7. Add 15mL of 1M HCl into each UTEVA cartridge reservoir to strip U. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min.

7.2.3.8. Set U samples aside for alpha source preparation.

Prepare samples for actinide measurement by alpha spectrometry using electrodeposition (Eichrom method SP02) or rare earth fluoride microprecipitation (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:

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

Percent yield = Yield x 100

Calculate actinide isotope activity:

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

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

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.

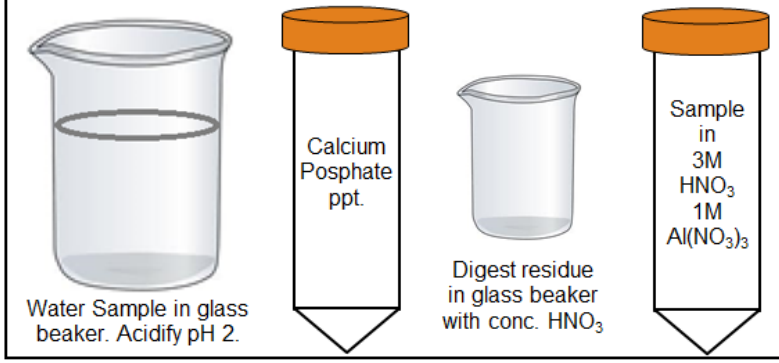
11) Add 10mL DI water to precipitate. Mix well. Centrifuge. Decant supernate.

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 $Al(NO_3)_3$.



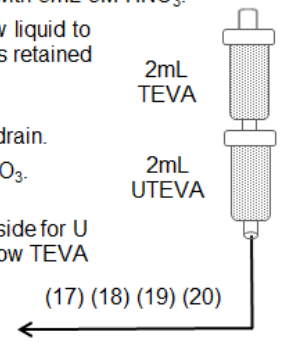
17) Precondition TEVA-UTEVA cartridges with 5mL 3M HNO_3.

18) Load sample on to TEVA-UTEVA. Allow liquid to drain to waste. Th is retained on TEVA. U is retained on UTEVA.

19) Rinse sample tube with 5mL 3M HNO_3. Add rinse to TEVA-UTEVA. Allow liquid to drain.

20) Rinse TEVA-UTEVA with 15mL 3M HNO_3. Allow liquid to drain.

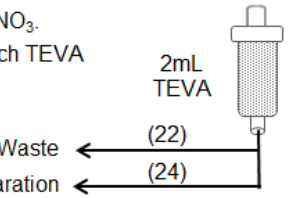
21) Separate TEVA-UTEVA. Set UTEVA aside for U separation. Place clean centrifuge tube below TEVA on vacuum box.



22) Rinse TEVA cartridge with 15mL 3M HNO_3.

23) Place a clean centrifuge tube below each TEVA Column.

24) Strip Th from TEVA with 15mL 9M HCl.



25) Rinse UTEVA with 5mL 3M HNO_3. Allow liquid to drain.

26) Rinse UTEVA with 5mL 9M HCl. Allow liquid to drain.

27) Rinse UTEVA with 20mL 5M HCl-0.05M oxalic acid. Allow liquid to drain.

28) Place clean centrifuge tube below each UTEVA cartridge.

29) Strip U with 15mL 1M HCl.