THORIUM, PLUTONIUM, AND URANIUM IN WATER

1. SCOPE

1.1. This is a method for the separation of thorium, plutonium and uranium in water. After completing this method, source preparation for measurement of thorium, 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. Thorium, plutonium and uranium 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. 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. The ^{232}U tracer should be cleaned prior to use in this method (Eichrom Method TP01) to avoid false positive measurement of ^{228}Th in the thorium fraction.

4.3. Neptunium will be in the Pu fraction if present. Since the energies of ^{242}Pu and ^{237}Np are overlapping, ^{236}Pu tracer maybe used to achieve a cleaner separation of neptunium and plutonium peaks.

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

4.5. 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.

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

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Beakers, glass
- Centrifuge
- Centrifuge 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 (Th-229, 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
TEVA® resin, 2mL prepacked column, 100-150μm, Eichrom Part TE-C50-A
Titanium (III) chloride, 10wt% $TiCl_3$ *in 20-30wt% HCl*
UTEVA® resin, 2mL prepacked column, 100-150μm, Eichrom Part UT-C50-A

6.1. *Ascorbic Acid (1M)* - Dissolve 17.6g of ascorbic acid in 75mL of water. Dilute to 100 mL with water. **Prepare Fresh Weekly.**

6.2. *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.

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

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

6.5. *Hydrochloric acid (5M) - oxalic acid (0.05M) solution* - Dissolve 6.3g oxalic acid dihydrate in 400mL water. Add 417mL concentrated HCl. Dilute to 1L 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 (0.05M) - Hydrofluoric acid (0.05M) - titanium chloride (0.02M)*- Add 3.2mL of concentrated HNO_3, 1.8mL of concentrated HF and 30.8mL of $TiCl_3$ in 800mL of water. Dilute to 1L with water

6.8. *Nitric acid (3M) - Aluminum nitrate (1M) 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 water.

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

6.10. Sodium nitrite (3M) solution - Dissolve 5.2g of NaNO2 in 20mL of water. Dilute to 25mL with water. Prepare fresh daily.

6.11. *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.

6.12. *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.

6.13. *Phenolphthalein solution* - dissolve 1g phenolphthalein in 10mL 95% isopropyl alcohol. Dilute with 100mL of water.

7. PROCEDURE

7.1. Water Sample Preparation:

7.1.1. If required, filter the sample through a 0.45 micron filter.

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

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

7.1.4. Add 5mL concentrated HNO_3.

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.

7.1.5. Add appropriate tracers per lab protocol.

7.1.6. Calcium phosphate precipitation:

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

7.1.6.2. Place each beaker on a hot plate.

7.1.6.3. Cover each beaker with a watch glass.

7.1.6.4. Heat the samples at medium setting for 30-60 minutes.

7.1.6.5. Remove the watch glass from the beaker and turn the heat down.

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

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

7.1.6.8. 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.

7.1.6.9. Decant supernate and discard to waste.

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

7.1.6.11. Decant supernate and discard to waste.

7.1.6.12. 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.

7.1.6.13. If an ammonia odor persists repeat 7.1.6.12.

7.1.6.14. Dissolve precipitates with 5mL conc. HNO_3 and transfer to a 100mL glass beaker. Rinse centrifuge tube with 2-3mL conc. HNO_3 and transfer to the same 100mL beaker. Evaporate to dryness.

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

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

Note: Pu must be present in Pu (IV) to be retained on TEVA resin. The following steps will ensure that Pu (III) and Pu (VI) is converted to Pu (IV)

7.1.6.16. Add 1mL of 1.5M sulfamic acid, 0.5mL of 5mg/mL Fe solution, and 1mL of 1M ascorbic acid to each sample. Swirl to mix and wait 5 minutes.

Note: If the additional 5-10mL was used to dissolve the sample in step 7.1.6.15, add a proportionately larger amount of sulfamic acid and ascorbic acid.

7.1.6.17. Add 1mL of 3M $NaNO_2$. Mix well and wait for 5 minutes.

Note: $NaNO_2$ is added to oxidize Pu(III) to Pu(IV).

7.1.7. Th and Pu separation from U using TEVA Resin

7.1.7.1. For each sample solution, place a TEVA Resin column (with extension funnel) in the column rack.

7.1.7.2. Place a waste tray below the columns, remove the bottom plugs from each column, push top frit down to the top of the resin bed, and allow to drain.

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

7.1.7.4. Place a clean labeled beaker or centrifuge tube below each column to collect Uranium.

7.1.7.5. Transfer each sample solution from step 7.1.6.17. into the appropriate TEVA column reservoir. Allow the solution to drain by gravity flow. Th and Pu will be retained by the resin.

7.1.7.6. Add 5mL of 3M HNO_3 to rinse to each sample tube. Transfer each rinse solution into the appropriate TEVA column reservoir. Allow solution to drain.

7.1.7.7. Add 15mL of 3M HNO_3 into each TEVA column reservoir. Allow solution to drain. Set beakers aside for uranium separation on UTEVA resin.

7.1.7.8. Place a waste tray or beakers below the TEVA columns.

7.1.7.9. Add 15mL of 3M HNO_3 to each TEVA column reservoir. Allow solution to drain. Dispose of eluate as waste.

Note: The extended 3M HNO_3 rinse removes any traces of Uranium from the TEVA column.

7.1.7.10. Ensure that clean, labeled tubes or beakers are placed below each TEVA column.

7.1.7.11. Add 15mL of 9M HCl to TEVA column reservoir to elute Th. Allow solution to drain.

7.1.7.12. Set Th samples aside for alpha source preparation.

7.1.7.13. Place clean labeled tubes below each TEVA column.

7.1.7.14. Add 25 mL of 0.05M HNO_3/0.05M HF/0.02M $TiCl_3$ to each TEVA column reservoir to strip Th. Allow solution to drain.

Note: Electrodeposition CANNOT be carried out on the Pu fraction because of $TiCl_3$ in the strip solution. If electrodeposition is desired then another suitable stripping agent may be used, such as 0.1M ammonium bioxalate.

7.1.7.15. Set Pu samples aside for alpha source preparation.

7.1.8. Separation of Uranium on UTEVA Resin

7.1.8.1. For each sample solution, place a UTEVA Resin column (with extension funnel) in the column rack.

7.1.8.2. Place a waste tray below the columns, remove the bottom plugs from each column, push the top frit down to the top of the resin bed, and allow to drain.

7.1.8.3. Add 5mL of 3M HNO_3 into each column to precondition resin and allow to drain.

7.1.8.4. Transfer each uranium fraction from step 7.1.7.7. into the appropriate UTEVA Resin column. Allow the solution to drain by gravity flow. Uranium will be retained by the resin.

7.1.8.5. Add 5mL of 3M HNO_3 to rinse to each sample tube. Transfer each rinse solution into the appropriate UTEVA Resin column. Allow solution to drain.

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

7.1.8.7. Add 5mL of 9M HCl into each UTEVA column reservoir. Allow liquid to drain.

7.1.8.8. Add 20mL of 5M HCl- 0.05M oxalic acid into each UTEVA column. Allow liquid to drain.

Note: The rinses remove any residual neptunium, thorium and americium if present on UTEVA, and any residual ferrous ion that might interfere with electrodeposition. Po-210 will have been removed by the TEVA cartridge.

7.1.8.9. Place clean, labeled beakers or tubes below each UTEVA column.

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

7.1.8.11. Set U samples aside for alpha source preparation.

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

8. CALCULATIONS

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. PERFORMANCE DATA

9.1. Chemical recoveries of tracers in various matrixes were measured on 1 liter samples.

	Spike*	DI Water	Tap Water
Th-229	97.2 ± 11%	87.2 ± 7%	102 ± 4%
Pu-242	99.7 ± 2%	90.8 ±6%	103 ± 5%
U-232	91.0 ± 6%	80.3 ± 3%	87.2 ± 7%

*Load solution spiked with tracers. No precipitation carried out.

9.2. Decontamination factors were measured for the actinide elements shown below. The decontamination factors reported were calculated by dividing the activity spiked by the activity found in the fraction. Where the activity found was below the detection limit, the value is reported as “>.”

	In Th fraction	In Pu Fraction	In U fraction
U-232	>800	13,000	NA
Pu-242	>1500	NA	20,000
Am-241	>800	21,000	>2200
Th-229	NA	>3600	>2000
Np-237	>3000	NA	4600

10. REFERENCES

1) Horwitz, E.P., et al. “Separation and Preconcentration of Actinides by Extraction Chromatography using a supported liquid anion exchanger: Application of the characterization of high-level nuclear waste solutions” Analytica Chimica Acta, 310, 63-78 (1995).

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 Method for Isotopic Uranium in Water by Radiochemistry.”

4) Maxwell, S.L., “Rapid Analysis of Emergency Urine and Water Samples,” Journal of Radioanalytical and Nuclear Chemistry, 275(3), 497-502 (2008).

5) 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.

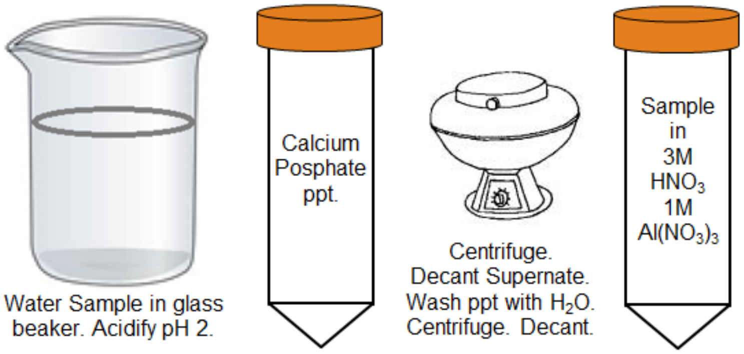
12) Dissolve precipitate in 5mL conc. HNO_3. Transfer to a 100mL beaker. Rinse centrifuge tube with 2-3mL conc. HNO_3.

13) Evaporate to dryness.

14) Dissolve residue in 10-20mL 3M HNO_3-1M $Al(NO_3)_3$.

15) Add 1mL 1.5M Sulfamic Acid, 0.5 mL Fe, and 1mL 1M Ascorbic Acid.

16) Add 1mL 3M $NaNO_2$.



17) Precondition TEVA column with 5mL 3M HNO_3.

18) Load sample onto TEVA column. Allow liquid to drain. TEVA retains Pu and Th. U is not retained.

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

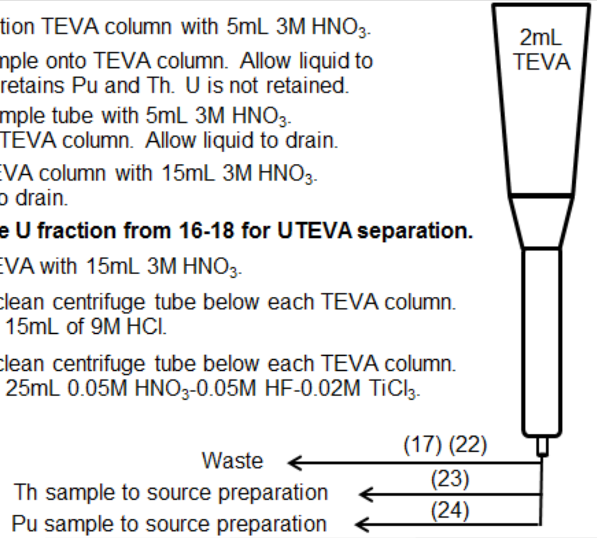
20) Rinse TEVA column with 15mL 3M HNO_3. Allow liquid to drain.

21) **Set aside U fraction from 16-18 for UTEVA separation.**

22) Rinse TEVA with 15mL 3M HNO_3.

23) Place a clean centrifuge tube below each TEVA column. Strip Th with 15mL of 9M HCl.

24) Place a clean centrifuge tube below each TEVA column. Strip Pu with 25mL 0.05M HNO_3-0.05M HF-0.02M $TiCl_3$.



25) Precondition UTEVA column with 5mL 3M HNO_3.

26) Load solution from 16-18 on UTEVA column. U is retained.

27) Rinse sample tube with 5mL 3M HNO_3. Add rinse to UTEVA column.

28) Rinse UTEVA column with 5mL of 3M HNO_3.

29) Rinse UTEVA column with 5mL of 9M HCl.

30) Rinse UTEVA column with 20mL 5M HCl-0.05M oxalic acid. Discard to Waste.

31) Place clean centrifuge tube below each cartridge. Strip Uranium with 15mL 1M HCl.