

URANIUM IN WATER

1. SCOPE

- 1.1. This is a method for the separation and measurement of uranium in water. After completing this method, source preparation for measurement of 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. Uranium is separated by Eichrom's UTEVA Resin 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 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-washing 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.

<i>Aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$</i>
<i>Ammonium hydroxide(57% NH_4OH and 28% NH_3), concentrated NH_4OH</i>
<i>Appropriate tracers or standards (U-232 self-cleaning tracer).</i>
<i>Deionized water, All reagents are prepared with deionized water</i>
<i>Hydrochloric acid (37%), concentrated HCl</i>
<i>Isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$</i>
<i>Nitric acid (70%), concentrated HNO_3</i>
<i>Oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$</i>
<i>Phenolphthalein pH Indicator</i>
<i>UTEVA® resin, 2mL prepacked column, 100-150μm, Eichrom Part UT-C50-A</i>

6.1. *Ammonium hydrogen phosphate (3.2M)* - Dissolve 104g of $(\text{NH}_4)_2\text{HPO}_4$ in 200mL of water. Heat gently to dissolve. Dilute to 250mL with water.

- 6.2. *Calcium nitrate (1.25M)* - Dissolve 51g of $\text{Ca}(\text{NO}_3)_2$ in 100mL of water and dilute to 250mL with water.
- 6.3. *Hydrochloric acid (1M)* - Add 83mL of concentrated HCl to 900mL 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. Dilute to 1L with water.
- 6.5. *Hydrochloric acid (9M)* - Add 750mL of concentrated HCl to 100mL of water. Dilute to 1L with water.
- 6.6. *Nitric acid solution (3M)* - Add 188mL of concentrated HNO_3 to 700mL of water. Dilute to 1L with water.
- 6.7. *Nitric acid solution (8M)* - Add 500mL of concentrated HNO_3 to 400mL of water. Dilute to 1L with water.
- 6.8. *Nitric acid (3M) - Aluminum nitrate (1M) solution* - Dissolve 375g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500mL of water, add 188 mL of concentrated HNO_3 . Dilute to 1L with water.
- 6.9. *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. 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 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.*

- 7.1.3. Add appropriate tracers per lab protocol.
- 7.1.4. Calcium phosphate precipitation:
- 7.1.4.1. Add 0.5mL of 1.25M $\text{Ca}(\text{NO}_3)_2$ 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 the samples at medium setting for 30-60 minutes.
- 7.1.4.5. Take the watch glass off the beaker and turn the heat down.
- 7.1.4.6. Add 2-3 drops of phenolphthalein indicator and 1mL of 3.2M $(\text{NH}_4)_2\text{HPO}_4$ solution.
- 7.1.4.7. Slowly add enough concentrated NH_4OH with stirring to reach the phenolphthalein end point (light pink color). A calcium phosphate precipitate should form. Heat the sample for another 20-30 minutes.
- 7.1.4.8. 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.
- 7.1.4.9. Decant supernate and discard to waste.
- 7.1.4.10. Transfer the precipitate to a centrifuge tube with deionized water and centrifuge 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. Dissolve precipitate in 5mL concentrated HNO_3 . Transfer solution to a 100mL beaker. Rinse centrifuge tube with 2-3mL of concentrated nitric acid and transfer to beaker. Evaporate solution to dryness.
- 7.1.4.14. Dissolve each precipitate with 10mL of 3M HNO_3 -1M $\text{Al}(\text{NO}_3)_3$.

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

7.2. U separation using UTEVA Resin

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

- 7.2.2. Place a waste tray below the columns, remove the bottom plugs from each column, push top frit down to top of resin bed, and allow to drain.
- 7.2.3. Add 5mL of 3M HNO₃ into each column to precondition resin. Allow solution to drain.

Note: Make sure all reagent solutions have cooled to room temperature before proceeding with the method.

- 7.2.4. Transfer each solution from step 7.1.4.14. into the appropriate UTEVA Resin reservoir. Allow solution to drain. Uranium will be retained by the resin.
- 7.2.5. Add 5mL of 3M HNO₃ to rinse to each sample beaker. Transfer each rinse solution into the appropriate UTEVA Resin column reservoir. Allow solution to drain.
- 7.2.6. Add 5mL of 3M HNO₃ to each column and allow to drain.
- 7.2.7. Add 15mL of 8M HNO₃ to each column reservoir. Allow solution to drain.
- 7.2.8. Add 5mL of 9M HCl into each column reservoir. Allow solution to drain.

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

- 7.2.9. Add 20mL of 5M HCl-0.05M oxalic acid into each column reservoir. Allow solution to drain. Discard the combined eluate to this point as waste.

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

- 7.2.10. If using electrodeposition to prepare sources for alpha spectrometry, place a clean, labeled beaker below each column. If using rare earth fluoride micro precipitation to prepare sources for alpha spectrometry, place a clean, labeled 50mL polypropylene centrifuge below each column.
- 7.2.11. Add 15mL of 1M HCl into each column reservoir to strip the uranium. Allow solution to drain.
- 7.2.12. Prepare sources for uranium measurement by alpha spectrometry using electrodeposition (Eichrom Method SPA02) or rare earth fluoride micro precipitation (Eichrom Method 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:

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

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. PRECISION AND BIAS

- 9.1. *Precision*- A relative standard deviation of 4.2% at the 25 dpm level has been reported for uranium.
- 9.2. *Bias*- Mean chemical recoveries of 86% for uranium 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 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."

