

# URANIUM IN WATER

(WITH VACUUM BOX SYSTEM)

## 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 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 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  $^{241}\text{Am}$  and  $^{238}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{234}\text{U}$ , or  $^{232}\text{U}$  and  $^{210}\text{Po}$  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<sub>3</sub>, adjusting the HNO<sub>3</sub> concentration of the sample to 1M HNO<sub>3</sub> 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
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge tubes, 50mL and 250mL
- Centrifuge, with rotors 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:** Vacuum Box Inner Liner - For collection of load and rinse fractions, 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 <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O
Ammonium hydroxide(57% NH <sub>4</sub> OH or 28% NH <sub>3</sub> ), concentrated NH <sub>4</sub> OH
Appropriate tracers or standards (U-232 self-cleaning tracer).
Deionized water, All reagents are prepared with deionized water
Hydrochloric acid (37%), concentrated HCl

Isopropyl alcohol, C <sub>3</sub> H <sub>7</sub> OH
Nitric acid (70%), concentrated HNO <sub>3</sub>
Oxalic acid dihydrate, H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O
Phenolphthalein pH indicator
UTEVA® resin - 2mL prepacked cartridge, 50-100µm, Eichrom Part UT-R50-S

- 6.1. *Ammonium hydrogen phosphate (3.2M)* - Dissolve 104g of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> in 200mL of water. Heat gently to dissolve. Dilute to 250mL with water.
- 6.2. *Calcium nitrate (1.25M)* - Dissolve 51g of Ca(NO<sub>3</sub>)<sub>2</sub> 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<sub>3</sub> to 700mL of water. Dilute to 1L with water.
- 6.7. *Nitric acid solution (8M)* - Add 500mL of concentrated HNO<sub>3</sub> to 400mL of water. Dilute to 1L with water.
- 6.8. *Nitric acid (3M) - Aluminum nitrate (1M) solution* - Dissolve 375g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 500mL of water, add 188 mL of concentrated HNO<sub>3</sub>. 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<sub>3</sub>.

**Note: If using self-cleaning <sup>232</sup>U tracer (Eichrom Method TP01), mix for 1-2 minutes to suspend BaSO<sub>4</sub> precipitate to remove <sup>228</sup>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 Ca(NO<sub>3</sub>)<sub>2</sub> 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 (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution.

7.1.4.7. Slowly add enough concentrated NH<sub>4</sub>OH 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 the hot plate, cool to room temperature, and allow precipitate to settle until solution can be decanted (30 minutes to 2 hours) or centrifuge.

7.1.4.9. 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<sub>3</sub>. 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<sub>3</sub>-1M Al(NO<sub>3</sub>)<sub>3</sub>.

**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. 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. 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.
- 7.2.3. For each sample solution, fit a UTEVA cartridge on to the inner support tube.
- 7.2.4. Add syringe barrels (funnels/reservoirs) to the top end of each UTEVA cartridge.
- 7.2.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

**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. Add 5mL of 3M HNO<sub>3</sub> into each cartridge reservoir to precondition the resin. Adjust vacuum to achieve a flow rate of 1-2mL/min. Allow solution to completely pass through each UTEVA cartridge.

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

- 7.2.7. Transfer each sample load solution from step 7.1.4.14. into the appropriate UTEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min. Uranium will be retained by the resin.
- 7.2.8. Add 5mL of 3M HNO<sub>3</sub> to rinse to each sample tube. Transfer each rinse solution into the appropriate UTEVA Resin cartridge

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

- 7.2.9. Add 5mL of 3M HNO<sub>3</sub> to each UTEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.
- 7.2.10. Disengage vacuum. Empty centrifuge tubes to waste or place empty centrifuge tubes below each UTEVA cartridge. Place a clean reservoir above each UTEVA cartridge.
- 7.2.11. Add 15mL of 8M HNO<sub>3</sub> to each UTEVA cartridge reservoir. Engage vacuum. Allow solution to completely drain through each cartridge at 1-2mL/min.
- 7.2.12. 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. Some Np and Th may be removed here.**

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

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

- 7.2.14. Place a clean, labeled 50mL polypropylene centrifuge below each UTEVA cartridge. Replacing yellow outer tips and inner support tubes at this point will help ensure clean U fractions in the following steps.
- 7.2.15. Add 15mL of 1M HCl into each column reservoir to strip the uranium. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min.
- 7.2.16. Prepare sources for uranium measurement by alpha spectrometry using rare earth fluoride micro precipitation (Eichrom Method SPA01) or electrodeposition (Eichrom Method SPA02).

## 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:  $\text{pCi/g} = (\text{dpm/g})/2.22$

## 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."



