

AMERICIUM IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

- 1.1. This is a method for the separation of americium from water samples. After completing this method, source preparation for measurement of americium 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. Americium is separated by Eichrom TRU resin from other actinides 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 americium 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 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 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 HNO₃, adjusting the HNO₃ concentration of the sample to 1M HNO₃ 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 rotor and carriers for 50mL and 250mL tubes
- Fume hood
- Hotplate with stirrer
- Magnetic stir bars, suitable for 1L samples
- 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 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

<i>Ammonium oxalate monohydrate, (NH₄)₂C₂O₄·H₂O</i>
<i>Appropriate tracers or standards (Am-243)</i>
<i>Ascorbic acid powder, C₆H₈O₆</i>
<i>Calcium nitrate, CaNO₃</i>
<i>Deionized water, All reagents are prepared with deionized water</i>
<i>Hydrochloric acid (37%), concentrated HCl</i>
<i>Isopropyl alcohol, C₃H₇OH</i>
<i>Nitric acid (70%), concentrated HNO₃</i>
<i>Phenolphthalein pH indicator</i>
<i>Sodium nitrite, NaNO₂</i>
<i>TRU[®] resin, 2mL prepacked cartridge, 50-100µm, Eichrom Part TR-R50-S</i>

- 6.1. *Ammonium hydrogen phosphate (3.2M)* - Dissolve 104g of (NH₄)₂HPO₄ in 200mL of water. Heat gently to dissolve. Dilute to 250mL with water.
- 6.2. *Ascorbic acid (1M)* - Dissolve 17.6g of ascorbic acid in 90mL of water and dilute to 100mL with water. **Prepare fresh weekly.**
- 6.3. *Calcium nitrate (1.25M)* - Dissolve 51 g of Ca(NO₃)₂ in 100 mL of water. Dilute to 250mL with water.
- 6.4. *Hydrochloric acid (4M)* - Add 333mL of concentrated HCl to 500mL of water. Dilute to 1L with water.
- 6.5. *Nitric acid (3M) - Aluminum nitrate (1M) solution* - Dissolve 375g of Al(NO₃)₃·9H₂O in 500mL of water. Add 188mL of concentrated HNO₃. Dilute to 1L with water.
- 6.6. *Nitric acid solution (3M)* - Add 188mL of concentrated HNO₃ to 800mL of water. Dilute to 1L with water.
- 6.7. *Nitric acid (2 M) - sodium nitrite (0.1M) solution*- Add 31mL of concentrated HNO₃ to 200mL of water. Dissolve 1.72g of sodium nitrite in the solution. Dilute to 250mL with water. **Prepare fresh daily.**
- 6.8. *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 sample (or enough to meet required detection limit) into an appropriate size beaker.
- 7.1.3. Add 5mL of concentrated HNO₃ per 1L of sample to acidify each sample.
- 7.1.4. Add appropriate tracers and/or reference standards per lab protocol.
- 7.1.5. Calcium phosphate precipitation:
 - 7.1.5.1. Add 0.5mL of 1.25M Ca(NO₃)₂ to each sample.
 - 7.1.5.2. Place each beaker on a hotplate.
 - 7.1.5.3. Cover each beaker with a watch glass.
 - 7.1.5.4. Heat at medium setting for 30-60 minutes.
 - 7.1.5.5. Remove watch glass and turn the heat down.
 - 7.1.5.6. Add 2-3 drops of phenolphthalein indicator and 1mL of 3.2M (NH₄)₂HPO₄ solution.
 - 7.1.5.7. While stirring, slowly add enough concentrated NH₄OH to reach the phenolphthalein end point (pH~9) and form a calcium phosphate precipitate. Heat samples at ~50°C for another 20-30 minutes.
 - 7.1.5.8. Remove samples from the hot plate, cool to room temperature, and allow precipitate to settle until the supernate can be decanted (30 minutes to 2 hours) or centrifuge.
 - 7.1.5.9. Decant supernate and discard to waste.
 - 7.1.5.10. Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.
 - 7.1.5.11. Decant supernate and discard to waste.

- 7.1.5.12. 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.
- 7.1.5.13. If an ammonia odor persists repeat 7.1.5.12.
- 7.1.5.14. Dissolve precipitate in 5mL concentrated HNO₃. Transfer solution to a 100mL beaker. Rinse centrifuge tube with 2-3mL of concentrated HNO₃ and transfer to beaker. Evaporate solution to dryness.
- 7.1.5.15. Dissolve each precipitate with 10mL of 3M HNO₃-1M Al(NO₃)₃.

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

- 7.1.5.16. Add approximately 1mL of 1M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes.

Note: The ascorbic acid will reduce any Fe in the sample to Fe(II), which will not be retained on TRU Resin.

Note: If particles are observed suspended in the solution, centrifuge the sample. The supernate will be transferred to the column in step 7.1.6.4. The particles will be discarded.

7.1.6. Am Separation Using TRU Resin:

- 7.1.6.1. 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.
- 7.1.6.2. 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.
- 7.1.6.3. For each sample solution, fit a TRU cartridge on to the inner support tube.
- 7.1.6.4. Add syringe barrels (funnels/reservoirs) to the top end of each TRU 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.

- 7.1.6.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.
- 7.1.6.6. Add 5mL of 3M HNO₃ into each TRU cartridge reservoir to condition resin. Adjust vacuum to achieve a flow rate of 1-2mL/min. Allow solution to completely pass through each cartridge.
- 7.1.6.7. Transfer each sample load solution from step 7.1.5.16 into the appropriate TRU Resin cartridge reservoir. Allow the solution to completely pass through each cartridge at 1-2mL/min.
- 7.1.6.8. Add 5mL of 3M HNO₃ into the sample tube and transfer the beaker rinse to the appropriate TRU cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.
- 7.1.6.9. Add 10mL of 3M HNO₃ into each TRU cartridge reservoir. Allow solution to completely pass through each TRU cartridge at 1-2mL/min. Place clean reservoirs above each TRU cartridge.
- 7.1.6.10. Add 5mL of 2M HNO₃-0.1 M NaNO₂ to each TRU cartridge reservoir. Allow solution to completely pass through each TRU cartridge at 1mL/min.

Note: Sodium nitrite is used to oxidize Pu(III) to Pu(VI) and enable the Pu/Am separation.

- 7.1.6.11. Disengage vacuum Discard the load and rinse solutions to waste.
- 7.1.6.12. Place clean, labeled centrifuge are below each column. Replacing yellow outer tips and inner support tubes at this point will help ensure clean Am fractions in the following steps.
- 7.1.6.13. Add 15mL of 4M HCl to each TRU cartridge reservoir to elute americium. Engage vacuum. Allow solution to completely drain through each TRU cartridge at 1-2mL/min.

Note: If poor resolution is observed in the measurement of americium by alpha spectrometry or significant (>100µg) amounts of rare earth metal ions are suspected in the sample, separation of Am from rare earths using Eichrom method SPA03 may be necessary.

7.1.7. Prepare samples to measure americium 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:

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

$$\text{Percent yield} = \text{Yield} \times 100$$

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

$$\text{Conversion of dpm/g to pCi/g:} \quad \text{pCi/g} = (\text{dpm/g})/2.22$$

9. PRECISION AND BIAS

- 9.1. *Precision* - This data has not yet been generated.
- 9.2. *Bias* - A mean chemical recovery of 95% has been reported for americium. Since results are corrected based on spike recovery, no significant bias exists for the method.
- 9.3. *Precision and Bias* - The data is based on the calcium phosphate precipitation option.

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) 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 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."

