AMERICIUM IN WATER

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 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. 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 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
- Centrifuge tubes, 50mL and 250mL
- Centrifuge, with rotor and carriers for 50mL and 250mL tubes
- Column rack, Eichrom Part: AC-103
- Extension Funnels, 25mL, Eichrom Part: AC-120
- Fume hood
- Hotplate with stirrer
- Magnetic stir bars, suitable for 1L samples
- 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.

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 (Am-243)
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

Isopropyl alcohol, C_3H_7OH
Nitric acid (70%), concentrated HNO_3
Phenolphthalein pH indicator
Sodium nitrite, $NaNO_2$
TRU® resin, 2mL prepacked column, 100-150□m, Eichrom Part TR-C50-A

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. *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 $Ca(NO_3)_2$ 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 $Al(NO_3)_3 \cdot 9H_2O$ in 500mL of water. Add 188mL of concentrated HNO_3. Dilute to 1L with water.

6.6. *Nitric acid solution (3M)* - Add 188mL of concentrated HNO_3 to 800mL of water. Dilute to 1L with water.

6.7. *Nitric acid (2 M)- sodium nitrite (0.1M) solution*- Add 31mL of concentrated HNO_3 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 HNO_3 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 $Ca(NO_3)_2$ 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 samples 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 $(NH_4)_2HPO_4$ solution.

7.1.5.7. While stirring, slowly add enough concentrated NH_4OH 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 hot plate, cool samples 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 HNO_3. Transfer solution to a 100mL beaker. Rinse centrifuge tube with 2-3mL of concentrated HNO_3 and transfer to beaker. Evaporate solution to dryness.

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

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

7.1.5.16. Add 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. For each sample, place a TRU Resin column in the column rack. Place a beaker below each column.

7.1.6.2. Remove the bottom plug from each column, push top frit down to the top of the resin bed, and allow each column to drain.

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

7.1.6.4. Transfer each solution from step 7.1.5.16 into the appropriate TRU Resin column.

7.1.6.5. Allow the load solution to drain through column.

7.1.6.6. Add 5mL of 3M HNO_3 into the sample beaker and transfer the beaker rinse to the appropriate column reservoir.

7.1.6.7. Allow the rinse solution to drain through each column.

7.1.6.8. Add 10mL of 3M HNO_3 into each column reservoir. Allow solution to drain through columns.

7.1.6.9. Add 5mL of 2M HNO_3-0.1 M $NaNO_2$ to each column. Allow rinse to drain through each column.

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

7.1.6.10. Discard the load and rinse solutions to waste.

7.1.6.11. Ensure that clean, labeled beakers or vials are below each column.

7.1.6.12. Make sure all traces of 2M HNO_3-0.1M $NaNO_2$ have been removed from the column reservoir. If necessary, invert column and rinse the reservoir (but not the column) with a small amount of deionized water.

7.1.6.13. Add 15mL of 4M HCl to elute americium. Allow solution to drain through all TRU columns.

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:

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

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* - 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."

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 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 $Al(NO_3)_3$.
16) Add 1mL 1M Ascorbic Acid. Mix.
Water Sample in glass beaker. Acidify pH 2.
Calcium Posphate ppt.
Digest residue in glass beaker with conc. HNO_3
Sample in 3M HNO_3 1M $Al(NO_3)_3$
17) Precondition TRU column with 5mL 3M HNO_3.
18) Load sample on to column. Allow liquid to drain to waste. Am is retained.
19) Rinse centrifuge tube with 5mL 3M HNO_3. Add rinse to column. All liquid to drain to waste.
20) Rinse column with 10mL 3M HNO_3. Allow liquid to drain to waste.
21) Rinse column with 5mL 2M HNO_3-0.1M $NaNO_2$. Allow liquid to drain to waste.
22) Add 15mL 4M HCl to strip Am. Allow solution to drain through TRU columns.
2mL TRU Column with 25mL extension funnel
(17) (18) (19) (20) (21)
Waste
(22)
Americium sample to source preparation