

Eichrom Industries provides total solutions for radiochemical separations challenges. Eichrom not only manufactures state of the art extraction chromatography and ion-exchange products, but also provides R&D and consulting services to enhance the value of these products. ORTEC has organized a number of the procedures developed by Eichrom (and its collaborating partners) for convenient access to our Customers, Sales Team, and Technical Support Specialists. For questions about radiochemical separations and alpha-spectrometry please contact:

Michael Schultz, Application Specialist, ORTEC, 801 S. Illinois Avenue, Oak Ridge, TN, 37830-0895, Phone: (865) 481-2446, Fax: (865) 483-0396, Email: michael.schultz@ortec-online.com

Thorium in Water

1. Scope

- 1.1 This procedure describes a method for separation and measurement of thorium in water.

2. Summary of Method

- 2.1 Thorium is separated by Eichrom resins prior to measurement by alpha spectrometry. A calcium phosphate precipitation technique is used to concentrate and remove 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 method 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 Actinides with unresolvable alpha energies such as Am-241 and Pu-238 or Np-237 and U-234 must be chemically separated to enable measurement. This method separates these isotopes effectively.
- 4.2 Very high levels of phosphate in the sample may cause an interference. Adjusting the amount of phosphate added to coprecipitate the actinides may be necessary in these cases.

5. Apparatus

- 5.1 *Analytical balance* - 0.0001 g sensitivity
- 5.2 *Centrifuge*
- 5.3 *Centrifuge tubes*
- 5.4 *Column rack* - Eichrom part number AC-103
- 5.5 *Column reservoirs* - 25 mL, Eichrom part number AC-120
- 5.6 *Electrodeposition cell assembly* - consisting of disposable plastic vial, cap assembly containing stainless steel for plating planchet (cathode) and Teflon cover with platinum electrode (anode).
- 5.7 *Filter apparatus* - Gelman apparatus 0.1 micron with 25 mm filters with polycarbonate base and metal screen, polysulfide funnel and 100 mL polypropylene flask.
- 5.8 *Filter* - 0.45 micron
- 5.9 *Fume hood*
- 5.10 *Hotplate*
- 5.11 *Low background alpha counter*
- 5.12 *Stirring glass rods*
- 5.13 *Plastic Millipore Petri dishes, 5-1/2 x 1 cm*
- 5.14 *Stainless steel planchets - 3/4 inch diameter*
- 5.15 *Stainless steel tweezers*

6. Reagents

- 6.1 Unless otherwise indicated, all references to water should be understood to mean deionized distilled water.
- 6.2 *Acetone*
- 6.3 *Ammonium hydrogen phosphate (3.2M)* - Dissolve 104 g of $(\text{NH}_4)_2\text{HPO}_4$ in 200 mL of water, heat gently to dissolve, and dilute to 250 mL with water.
- 6.4 *Ammonium hydroxide (5 wt %)* - Dissolve 50 g ammonium hydroxide in 950 g water.
- 6.5 *Ammonium hydroxide* - concentrated (sp gr 0.9)
- 6.6 *Ammonium oxalate plating solution (20 g/L)* - Dissolve 5 g of ammonium oxalate hydrate in 250 mL of water.

- 6.7 *Appropriate tracers or standards*
- 6.8 *Calcium nitrate (1.25M)* - Dissolve 51 g of $\text{Ca}(\text{NO}_3)_2$ in 100 mL of water and dilute to 250 mL with water.
- 6.9 *Cerium carrier* - Dissolve 0.155 g cerium (III) nitrate hexahydrate in 50 mL water and dilute to 100 mL with water.
- 6.10 *Ethanol, 80%* - Add 80 mL ethyl alcohol to 20 mL water.
- 6.11 *Ethyl alcohol, USP, 100%*
- 6.12 *Hydrochloric acid (12M)* - concentrated HCl (sp gr 1.19)
- 6.13 *Hydrochloric acid (9M)* - Add 750 mL of concentrated HCl (sp gr 1.19) to 100 mL of water and dilute to 1 L with water.
- 6.14 *Hydrofluoric acid (28M)* - concentrated hydrofluoric acid (sp gr 1.2).
- 6.15 *Nitric acid (15.7M)* - concentrated HNO_3 (sp gr 1.42)
- 6.16 *Nitric acid solution (2.5M)* - Add 159 mL of concentrated HNO_3 (sp gr 1.42) to 800 mL of water and dilute to 1 L with water.
- 6.17 *Nitric acid solution (3M) - aluminum nitrate (1.0M)* - Add 191 mL of concentrated HNO_3 (sp gr 1.42) to 700 mL of water . Dissolve 213 g anhydrous aluminum nitrate and dilute to 1 L with water.
- 6.18 *Phenolphthalein indicator* - Dissolve 1 g of phenolphthalein in 50 mL of ethyl alcohol and add 50 mL of water.
- 6.19 *Potassium hydroxide (25 wt %)* - Dissolve 250 g potassium hydroxide in 750 g water.
- 6.20 *Sodium hydrogen sulfate (5 wt %)* - Dissolve 50 g of sodium hydrogen sulfate in 950 g of water.
- 6.21 *Sodium sulfate (15 wt %)* - Dissolve 150 g of sodium sulfate in 850 g of water.
- 6.22 *TEVA Resin* - prepacked column, 100-150 μm resin or small particle size (50-100 μm) in appropriate plastic column.

7. Procedure

7.1 *Water Sample Preparation:*

- 7.1.1 If not already prefiltered, filter the sample through a 0.45 micron filter.
- 7.1.2 If samples larger than 1 L are analyzed, evaporate the sample to approximately 1 L.
- 7.1.3 Aliquot 500 to 1000 mL of the filtered sample (or enough to meet required detection limit) into an appropriate size beaker.
- 7.1.4 Acidify the sample to pH 2 with concentrated HNO_3 acid (sp gr 1.42) (0.6 mL per L of sample)

7.1.5 Add appropriate tracers and/or analyze standards per lab protocol.

7.1.6 *Evaporation option to reduce volume:*

7.1.6.1 Evaporate sample to less than 50 mL and transfer to a 100 mL beaker.

Note: For some water samples, calcium sulfate formation may occur during evaporation. If this occurs, use the calcium phosphate precipitation option, step 7.1.7.

7.1.6.2 Gently evaporate the sample to dryness and redissolve in approximately 5 mL of concentrated HNO₃ (sp gr 1.42).

7.1.6.3 Repeat step 7.1.6.2 two more times, evaporate to dryness and GOTO step 7.2.

7.1.7 *Calcium phosphate precipitation option:*

7.1.7.1 Add 0.5 mL of 1.25M Ca(NO₃)₂ to each beaker.

7.1.7.2 Place each beaker on a hotplate.

7.1.7.3 Cover each beaker with a watch glass.

7.1.7.4 Allow the samples to heat until boiling.

7.1.7.5 Once the samples boil, take the watch glass off the beaker and turn the heat down to medium.

7.1.7.6 Add 2-3 drops of phenolphthalein indicator and 200 μL of 3.2M (NH₄)₂HPO₄ solution.

7.1.7.7 Add enough concentrated NH₄OH with a squirt bottle to reach the phenolphthalein end point and form Ca₃(PO₄)₂ precipitate. NH₄OH should be added very slowly. Stir the solution with a glass rod. Allow the sample to heat for another 20-30 minutes.

7.1.7.8 If the sample volume is too large to centrifuge the entire sample, allow precipitate to settle until solution can be decanted (30 minutes to 2 hours) and GOTO step 7.1.7.10.

7.1.7.9 If the volume is small enough to centrifuge then GOTO step 7.1.7.11.

- 7.1.7.10 Decant supernatant and discard to waste.
- 7.1.7.11 Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.
- 7.1.7.12 Decant supernatant and discard to waste.
- 7.1.7.13 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 supernatant.
- 7.1.7.14 If an ammonia odor persists repeat 7.1.7.13, otherwise GOTO 7.1.7.15.
- 7.1.7.15 Dissolve precipitate in approximately 5 mL concentrated nitric acid. Transfer solution to a 100 mL beaker. Rinse centrifuge tube with 2-3 mLs of concentrated nitric acid and transfer to beaker. Evaporate solution to dryness.

7.2 *Actinide Separations using Eichrom resins:*

7.2.1 *Redissolve calcium phosphate precipitate or evaporated water sample:*

- 7.2.1.1 Dissolve each precipitate with 10 mL of 3.0M HNO_3 -1.0M $\text{Al}(\text{NO}_3)_3$.

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

7.2.2 *Th separation from using TEVA Resin*

- 7.2.2.1 For each sample dissolved, place a TEVA Resin column in the column rack.
- 7.2.2.2 Place a beaker below each column, remove the bottom plug from each column and allow to drain. Attach column reservoirs to each column.
- 7.2.2.3 Pipet 5 mL of 3M HNO_3 into each column to condition resin and allow to drain.
- 7.2.2.4 Place a clean, labeled beaker below each column.
- 7.2.2.5 Transfer each redissolved sample into the appropriate TEVA Resin column by pouring or by using a plastic transfer pipet and allow to drain.

7.2.2.6 Add 5 mL of 2.5M HNO₃ to rinse to each beaker and transfer each solution into the appropriate TEVA Resin column. Discard eluate.

Note: Uranium, americium and Np+5 are removed with the load solution and 2.5M HNO₃ rinse.

7.2.2.7 Add 30 mL of 2.5M HNO₃ into each column. Discard eluate.

7.2.2.8 Place a clean, labeled 50 mL beaker below each column.

7.2.2.9 Pipet 20 mL of 9M HCl into each column and collect eluate.

7.2.2.10 Pipet 5 mL of 6M HCl in each column and collect in the same beaker as in step 7.2.2.9.

Note: This 6M HCl rinse will strip any residual traces of Th from the column. Pu+4 and Np+4 are retained on the column.

7.3 *Sample preparation for counting;*

7.3.1 *Electrodeposition option:*

Note: Electrodeposition using a sulfate system is described below. Alternately, electrodeposition in approximately 1M ammonium chloride-0.1M oxalic acid system may be used in a fume hood.

7.3.1.1 Inscribe a 3/4 inch stainless steel planchet with sample number, radionuclide, and plating date. Wipe clean with acetone.

7.3.1.2 Assemble the planchet in the cell as the cathode and rinse the cell several times with water.

7.3.1.3 *Test cell for leaks:*

7.3.1.3.1 Wipe the outside of the assembled cell dry, add water to each cell and allow to stand for a short period of time to check for leaks.

7.3.1.3.2 If a leak is found, retighten the cap assembly and observe.

7.3.1.3.3 If the leak is still present, disassemble the cell, clean all surfaces with acetone and then water, reassemble cell and test again.

- 7.3.1.3.4 If the cell continues to leak, replace the plastic vial and cap, and test again.
- 7.3.1.4 Add 2.5 mL of 5 wt % NaHSO₄, 2 mL of water and 5 mL 15 wt % Na₂SO₄ to each evaporated actinide solution and heat each solution using a hotplate.
- 7.3.1.5 Transfer each electrolyte solution from step 7.3.1.4 to a cell using 3 rinses of 1 mL water, adding the rinses to the cell.
- 7.3.1.6 Add 1 mL of ammonium oxalate plating solution to each cell.
- 7.3.1.7 Insert the platinum anode into the solution and connect the electrodes to the current source.
- 7.3.1.8 Turn on the power, adjust current to 0.5 A and electrodeposit for 5 minutes.
- 7.3.1.9 Adjust current to 0.75 A and electrodeposit for 90 minutes.
- 7.3.1.10 Add 2 mL of 25 wt % KOH dropwise to stop the reaction, continuing deposition for 1 minute after the KOH addition.
- 7.3.1.11 Turn off power, remove electrodes and decant electrolyte to waste.
- 7.3.1.12 Wash each cell three times with 2 mL of 5 wt % NH₄OH.
- 7.3.1.13 Remove each planchet and rinse with a small volume of 5 wt % NH₄OH, then with ethanol and finally acetone.
- 7.3.1.14 Dry each planchet on a hotplate for 5 minutes at approximately 200° C and allow to cool.
- 7.3.1.15 Store each planchet in a covered, labeled Petri dish.
- 7.3.1.16 Measure planchet using alpha spectrometry.
- 7.3.2 *Cerium fluoride precipitation option:*
- 7.3.2.1 Add 0.2 mL of cerium carrier to each beaker from steps 7.2.2.10 (thorium)

- 7.3.2.2 Add 1.0 mL of concentrated HF to each beaker. Swirl to mix. Let the solutions sit for at least 30 minutes before filtering.
- 7.3.2.3 Set up a 0.1 micron 25 mm filter, glassy side down on a Gelman filter apparatus with stainless steel screen, 50 mL polysulfide funnel and 100 mL polypropylene Erlenmeyer flask.
- 7.3.2.4 Add 3-5 mLs of 80% ethanol to each filter, applying vacuum and ensuring there are no leaks along the sides. Add 2-3 mLs of water to each filter.
- 7.3.2.5 Filter the sample and rinse 50 mL centrifuge tube with 5 mL water, transferring this rinse to the filter apparatus.
- 7.3.2.6 Wash each filter with 3-5 mL of ethanol.
- 7.3.2.7 Remove filters, place in plastic Petri dishes, and dry under (UV) lamps for a few minutes.
- 7.3.2.8 Mount filters on stainless planchets, using double-sided tape or glue stick and count by alpha spectrometry.

8. Calculations

8.1 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:

$$\text{Sample dpm/L} = \frac{S - B}{E \times V \times Y}$$

where:

- S = sample activity, cpm
- B = background, cpm
- E = counting efficiency = measured cpm/dpm of isotopic standard
- V = sample volume, L
- Y = yield

Conversion of dpm/g to pCi/g:

$$\text{pCi/L} = (\text{dpm/L})/2.22$$

9. Precision and Bias

- 9.1 *Precision* - A relative standard deviation of 3.5% for Th in the range of 1 pCi/L to 20 pCi/L has been reported.
- 9.2 *Bias* - A mean recovery of 102% ± 3.5% for Th have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

REFERENCES

- (1) Horwitz, E.P., et al. "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography." Analytica Chimica Acta. 266 (1992), 25-37.

- (2) Horwitz, E.P., et al. "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography." Analytica Chimica Acta. 281 (1993), 361-372.
- (3) Kressin, Ivan K., "Electrodeposition of Plutonium and Americium for High Resolution Alpha Spectrometry." Analytical Chemistry. 49 (1977), 842-846.
- (4) Maxwell, III S.L., et al. "High Speed Separations to Measure Impurities in Plutonium-238 Oxide and Trace Radionuclides in Waste," 34th ORNL-DOE Conference on Analytical Chemistry in Energy and Technology. Gatlinburg, TN. October 5-7, 1993.
- (5) Nelson, D. "Improved Methods for the Analysis of Radioactive Elements in Bioassay and Environmental Samples," 38th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry. Santa Fe, NM. November, 1992.