

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

## **Uranium in soil (2 grams sample)**

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### **1. Scope**

- 1.1 This procedure describes a method for separation and measurement of uranium in soil samples.

### **2. Summary of Method**

Uranium is separated by Eichrom resins prior to measurement by alpha spectrometry. 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 uranium in soil samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

### **4. Interferences**

- 4.1 Actinides with un-resolvable 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.

## 5. Apparatus

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

## 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 *Ascorbic acid*
- 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 ethanol to 20 mL water.
- 6.11 *Ethanol, USP, 100%*

- 6.12 *Hydrochloric acid (0.01M)* - Add 0.8 mL of concentrated HCl (sp gr 1.19) to 900 mL of water and dilute to 1 L with water.
- 6.13 *Hydrochloric acid (12M)* - concentrated HCl (sp gr 1.19)
- 6.14 *Hydrochloric acid (5M) - oxalic acid (0.05M) solution* - Dissolve 6.3 g oxalic acid dihydrate in 400 mL water. Add 417 mL concentrated HCl (sp gr 1.19). Cool to room temperature and dilute to 1 L with water.
- 6.15 *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.
- 6.16 *Hydrofluoric acid (28M)* - concentrated hydrofluoric acid (sp gr 1.2).
- 6.17 *Nitric acid (15.7M)* - concentrated HNO<sub>3</sub> (sp gr 1.42)
- 6.18 *Nitric acid (3M) - Aluminum nitrate (1.0M) solution* - Dissolve 212 g of anhydrous aluminum nitrate in 700 mL of water, add 191 mL of concentrated HNO<sub>3</sub> (sp gr 1.42) and dilute to 1 L with 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 *Titanium (III) chloride* - > 10 wt % solution in 20-30 wt % HCl.
- 6.23 *UTEVA Resin* - prepacked column, 100-150 μ particle size resin.

## 7. Procedure

### 7.1 *Sample preparation - Solids*

- 7.1.1 Weigh 0.5 g to 2 g of sample in a 200 mL glass beaker on an analytical balance.
- 7.1.2 Dry the sample at 110 degrees C for approximately 12 hours.
- 7.1.3 Weigh the sample again to achieve dry weight. Sample must be weighed a few times to get a stable dry weight. If needed it should be dried in the oven for a few more hours.
- 7.1.4 After the sample is dried, place the sample in muffle furnace and ash overnight at 510 degrees C.
- 7.1.5 Transfer the ashed soil sample to a 125 mL Teflon beaker using 10 mL of concentrated HNO<sub>3</sub>.

- 7.1.6 Add 10 mL concentrated HNO<sub>3</sub> and 5 mL concentrated HCl to each beaker.
- 7.1.7 Place a watch glass on each beaker on a hot plate and heat near boiling for 3 hours.
- 7.1.8 Dilute each sample to approximately 50 mL with water and transfer to a 50 mL centrifuge tube.
- 7.1.9 Centrifuge and decant the supernatant to a clean labeled Teflon beaker and set aside.
- 7.1.10 Transfer residue to the original 125 mL Teflon beaker using 10 mL concentrated HNO<sub>3</sub>.
- 7.1.11 Add 10 mL concentrated HNO<sub>3</sub> and 15 mL concentrated HF to the beaker.
- 7.1.12 Place a Teflon cover on each beaker on a hot plate and heat until the residue is dissolved.
- 7.1.13 Remove the Teflon cover, and centrifuge the solution. Transfer the supernatant to beaker in step 7.1.9.
- 7.1.14 Transfer the residue to the Teflon beaker with 10 mL concentrated HNO<sub>3</sub>.
- 7.1.15 Repeat steps 7.1.11 through 7.1.13
- 7.1.15 Evaporate the combined solutions in the beaker from step 7.1.9 to near dryness.
- 7.1.16 Remove beaker from hot plate and add 5 mL conc. HNO<sub>3</sub>
- 7.1.17 Evaporate to near dryness and add 10 mL of 3M HNO<sub>3</sub>/1M Al(NO<sub>3</sub>)<sub>3</sub>. Cool the solution and then transfer to a centrifuge tube.
- 7.1.18 Rinse beaker with an additional 5 mL of 3M HNO<sub>3</sub>/1M Al(NO<sub>3</sub>)<sub>3</sub> solution. Add rinse to the centrifuge tube. Centrifuge the solution before loading on the columns.

*7.2.2 U separation from Pu, Am using UTEVA Resin*

- 7.2.2.1 For each sample solution, place a UTEVA Resin column in the column rack.
- 7.2.2.2 Place a waste tray below the columns, remove the bottom plugs from each column and allow to drain.
- 7.2.2.3 Pipette 5 mL of 3M HNO<sub>3</sub> into each column to condition resin and allow to drain.
- 7.2.2.5 Transfer each solution from step 7.1.19 into the appropriate UTEVA Resin column by pouring or by using a plastic transfer pipette and allow to drain.
- 7.2.2.6 Add 5 mL of 3M HNO<sub>3</sub> to rinse to each beaker and transfer each solution into the appropriate UTEVA Resin column and allow to drain.
- 7.2.2.7 Add 5 mL of 3M HNO<sub>3</sub> into each column and allow to drain.
- 7.2.2.9 Pipette 5 mL of 9M HCl into each column and allow to drain. Discard this rinse.
- Note: This rinse converts the resin to the chloride system. Some Np may be removed here.
- 7.2.2.10 Pipette 20 mL of 5M HCl-0.05M oxalic acid into each column and allow it to drain. Discard this.
- Note: This rinse removes plutonium, neptunium and thorium from the column.
- 7.2.2.11 Place a clean, labeled beaker below each column.
- 7.2.2.12 Pipette 15 mL of 0.01M HCl into each column to strip the uranium. Allow to drain.
- 7.2.2.13 Set beakers aside for cerium fluoride precipitation option 7.3.1 or evaporate to dryness for electrodeposition option 7.3.2.

7.3 *Sample preparation for counting:*

7.3.1 *Cerium fluoride precipitation option:*

- 7.3.1.1 Add 0.2 mL of cerium carrier to each beaker from steps 7.5.1.1.
- 7.3.1.2 Add 0.5 mL of titanium chloride for uranium fraction.
- 7.3.1.3 Add 1.0 mL of concentrated HF to each beaker. Swirl to mix. Let the solutions sit for at least 30 minutes before filtering.
- 7.3.1.4 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.
- 7.3.1.5 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.
- 7.3.1.6 Filter the sample and rinse 50 mL centrifuge tube with 5 mL water, transferring this rinse to the filter apparatus.
- 7.3.1.7 Wash each filter with 3-5 mL of ethanol.
- 7.3.1.8 Remove filters, place in plastic Petri dishes, and dry under (UV) lamps for a few minutes.
- 7.3.1.9 Mount filters on stainless planchets, using double-sided tape or glue stick and count by alpha spectrometry.

7.3.2 *Electrodeposition option:*

Note 7- Electrodeposition using a sulfate system is described below. Alternately, electrodeposition in approximately 1 M ammonium chloride-0.1 M oxalic acid system may be used in a fume hood.

- 7.3.2.1 Inscribe a 3/4 inch stainless steel planchet with sample number, radionuclide, and plating date. Wipe clean with acetone.
- 7.3.2.2 Assemble the planchet in the cell as the cathode and rinse the cell several times with water.
- 7.3.2.3 *Test cell for leaks:*

- 7.3.2.3.1 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.
- 7.3.2.3.2 If a leak is found, re-tighten the cap assembly and observe.
- 7.3.2.3.3 If the leak is still present, disassemble the cell, clean all surfaces with acetone and then water, reassemble cell and test again.
- 7.3.2.3.4 If the cell continues to leak, replace the plastic vial and cap, and test again.
- 7.3.2.4 Add 2.5 mL of 5 wt. %  $\text{NaHSO}_4$ , 2 mL of water and 5 mL 15 wt. %  $\text{Na}_2\text{SO}_4$  to each evaporated actinide solution and heat each solution using a hotplate.
- 7.3.2.5 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.
- 7.3.2.6 Add 1 mL of ammonium oxalate plating solution to each cell.
- 7.3.2.7 Insert the platinum anode into the solution and connect the electrodes to the current source.
- 7.3.2.8 Turn on the power, adjust current to 0.5 A and electrodeposit for 5 minutes.
- 7.3.2.9 Adjust current to 0.75 A and electrodeposit for 90 minutes.
- 7.3.2.10 Add 2 mL of 25 wt. % KOH drop-wise to stop the reaction, continuing deposition for 1 minute after the KOH addition.
- 7.3.2.11 Turn off power, remove electrodes and decant electrolyte to waste.
- 7.3.2.12 Wash each cell three times with 2 mL of 5 wt. %  $\text{NH}_4\text{OH}$ .
- 7.3.2.13 Remove each planchet and rinse with a small volume of 5 wt. %  $\text{NH}_4\text{OH}$ , then with ethanol and finally acetone.

- 7.3.2.14 Dry each planchet on a hot plate for 5 minutes at approximately 200°C and allow to cool.
- 7.3.2.15 Store each planchet in a covered, labeled Petri dish.
- 7.3.2.16 Measure planchet using 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 9- 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:*

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

where:

- S = sample activity, cpm
- B = background, cpm
- E = counting efficiency
- V = sample weight, g or volume, L
- Y = yield

Conversion of dpm/g to pCi/gram:

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

## 9. Precision and Bias

- 9.1 *Precision*- A relative standard deviation of \_\_\_\_ at the \_\_\_\_ dpm level has been reported.
- 9.2 *Bias*- A mean recovery of \_\_\_\_\_ has been reported. Since results are corrected based on spike recovery, no significant bias exists for the method

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