

*Se-03*

## AMERICIUM, PLUTONIUM AND URANIUM IN WATER

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### APPLICATION

This procedure describes a method for the separation and measurement of americium, plutonium and uranium in water (adapted from Eichrom Industries, Inc., Procedure ACW03, Rev. 1.5). Americium, plutonium and uranium are separated by Eichrom resins prior to measurements by alpha spectrometry. Tracers are used to monitor chemical recoveries and to correct the results to improve precision and accuracy. This is a rapid, reliable method for the measurement of actinides in water samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

### INTERFERENCES

Actinides with unresolvable alpha energies such as  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  or  $^{237}\text{Np}$  and  $^{234}\text{U}$  must be chemically separated to enable measurement. This method effectively separates these isotopes.

### SPECIAL APPARATUS

1. Column rack
2. Filter - 0.45 micron

### SPECIAL REAGENTS

1. Ammonium hydrogen oxalate (0.1M) - dissolve 6.31 g of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and 7.11 g of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in 900 mL of water, filter (Whatman No. 4 suggested) and dilute to 1 L with water.
2. Ammonium hydroxide (5 wt %) - dissolve 50 g ammonium hydroxide in 950 g of water.
3. Appropriate tracers or standards.
4. Ascorbic acid.
5. Ferrous sulfamate solution (0.6M) - add 57 g of  $\text{NH}_2\text{SO}_3\text{H}$  to 150 mL of water, heat to  $70^\circ\text{C}$ , add 7 g of iron, in small increments until dissolved, filter (Whatman No. 4 suggested), transfer to flask and dilute to 200 mL with water. Prepare fresh weekly.
6. Hydrochloric acid (0.01M HCl) - add 0.8 mL of HCl to 900 mL of water and dilute to 1 L with water.
7. Hydrochloric acid (4M HCl) - add 333 mL of HCl to 500 mL of water and dilute to 1 L with water.
8. Hydrochloric acid (5M), oxalic acid (0.05M) solution - Dissolve 6.3 g oxalic acid dihydrate in 400 mL of water. Add 417 mL HCl. Cool to room temperature and dilute to 1 L with water.
9. Hydrochloric acid (9M HCl) - add 750 mL of HCl to 100 mL of water and dilute to 1 L with water.
10. Iron powder - a fine mesh powder dissolves faster in sulfamic acid.
11. Nitric acid (2M) - sodium nitrite (0.1M solution) - add 32 mL of  $\text{HNO}_3$  to 200 mL of water, dissolve 1.72 g of sodium nitrite in the solution and dilute to 250 mL with water. Prepare fresh daily.
12. Nitric acid solution (0.5M) - add 32 mL of  $\text{HNO}_3$  to 900 mL of water and dilute to 1 L with water.

13. Nitric acid solution (2M) - add 127 mL of HNO<sub>3</sub> to 800 mL of water and dilute to 1 L with water.
14. Nitric acid solution (3M) - add 191 mL of HNO<sub>3</sub> to 700 mL of water and dilute to 1 L with water.
15. Nitric acid (3M) - Aluminum nitrate (1M) solution -dissolve 212 g of anhydrous aluminum nitrate in 700 mL of water, add 191 mL of HNO<sub>3</sub> and dilute to 1 L with water.
16. Hydrochloric acid (4M HCl) - hydrofluoric acid (0.1M) - add 333 mL of HCl and 3.6 mL HF to 500 mL of water and dilute to 1 L with water. Prepare fresh daily.
23. TRU Resin - prepacked column, 0.7 g 100-150 micron particle size resin.
24. U/TEVA Resin - prepacked column, 0.7 g 100-150 micron particle size resin.

### SAMPLE PREPARATION

1. If not already prefiltered, filter the sample through a 0.45 micron filter.
2. If samples larger than 1 L are analyzed, evaporate the sample to ~1 L.
3. Aliquot 500 to 1000 mL of the filtered sample (or enough to meet the required detection limit) into an appropriate size beaker.
4. Add 5 mL of HCl per liter of sample (0.5 mL per 100 mL) to acidify each sample.
5. Add the appropriate tracers.
6. Evaporate sample to <50 mL and transfer to a 100-mL beaker. (**Note:** For some water samples, calcium sulfate formation may occur during evaporation.) Gently evaporate the sample to dryness and redissolve in approximately 5 mL of HNO<sub>3</sub>. Evaporate to dryness and redissolve in HNO<sub>3</sub> two more times, evaporate to dryness and go to **Actinide Separation Using Eichrom's Resins.**

## SEPARATION

1. Dissolve each precipitate from Step 6, **Sample Preparation**, in 10 mL of  $3\text{M HNO}_3$ - $1.0\text{M Al(NO}_3)_3$ . (**Note:** An additional 5 mL may be necessary if the volume of precipitate is large.)
2. Add 2 mL of  $0.6\text{M}$  ferrous sulfamate to each solution. Swirl to mix. (**Note:** If the additional 5 mL was used to dissolve the sample in Step 1, add a total of 3 mL of ferrous sulfamate solution.)
3. Add 200 mg of ascorbic acid to each solution, swirling to mix. Wait for 2-3 min. (**Note:** If particles are observed to be suspended in the solution, centrifuge the sample. The supernatant will be transferred to the column in Step 5, **Uranium separation from plutonium, americium using U/TEVA resin**. The precipitates will be discarded.)

### **A. Uranium separation from plutonium, americium using U/TEVA resin**

1. For each sample solution, place a U/TEVA Resin column in the column rack.
2. Place a beaker below each column, remove the bottom plug from each column and allow to drain.
3. Pipette 5 mL of  $3\text{M HNO}_3$  into each column to condition the resin and allow to drain.
4. Place a clean, labeled 50-mL beaker below each column.
5. Transfer each solution from Step 3 into the appropriate U/TEVA Resin column by pouring or by using a plastic transfer pipette and collect the eluate.
6. Add 5 mL of  $3\text{M HNO}_3$  to rinse to each beaker and transfer each solution into the appropriate U/TEVA Resin column and collect eluate.
7. Add 5 mL of  $3\text{M HNO}_3$  into each column and collect eluate.

8. Set aside the solutions collected in Steps 5, 6 and 7 for americium and plutonium separations.
9. Pipette 4 mL of 9M HCl into each column and allow to drain. Discard this rinse. (**Note:** The rinse converts the resin to the chloride system. Some neptunium may be removed here.)
10. Pipette 20 mL of 5M HCl - 0.05M oxalic acid into each column and allow it to drain. Discard eluate. (**Note:** This rinse removes neptunium and thorium from the column. The 9M HCl and 5M HCl-0.05M oxalic acid rinses also removes any residual ferrous ion that might interfere.)
11. Place a clean, labeled beaker below each column.
12. Pipette 15 mL of 0.01M HCl into each column to strip the uranium. Allow to drain.
13. Evaporate to dryness. Treat with 5 mL of HNO<sub>3</sub> several times to remove traces of oxalic acid. Convert to HCl.
14. Set beakers aside for Procedure G-03, **Microprecipitation Source Preparation for Alpha Spectrometry**.

#### **B. Plutonium and americium separation using TRU resin**

1. Place a TRU Resin column in the column rack for each sample dissolved.
2. Remove the bottom plug from each column and allow each column to drain.
3. Pipette 5 mL of 2M HNO<sub>3</sub> into each column to condition resin and allow to drain (just prior to sample loading).
4. Transfer each solution from Step 8 of **Uranium Separation** into the appropriate TRU Resin column by pouring and/or using a plastic transfer pipette.
5. Allow the load solution to drain through the column.

6. Pipette 5 mL of 2M HNO<sub>3</sub> into the sample beaker and transfer this rinse to the appropriate column using the same plastic pipette.
7. Allow the initial rinse solution to drain through each column.
8. Pipette 5 mL of 2M HNO<sub>3</sub> - 0.1M NaNO<sub>2</sub> directly into each column, rinsing each column reservoir while adding the 2M HNO<sub>3</sub> - 0.1M NaNO<sub>2</sub>. (**Note:** Sodium nitrite is used to oxidize Pu<sup>+3</sup> to Pu<sup>+4</sup> and to enhance the plutonium/americium separation).
9. Allow the rinse solution to drain through each column.
10. Add 5 mL of 0.5M HNO<sub>3</sub> to each column and allow to drain. (**Note:** 0.5M HNO<sub>3</sub> is used to lower the nitrate concentration prior to conversion to the chloride system.)
11. Discard the load and rinse solutions.
12. Ensure that clean, labeled beakers or vials are below each column.
13. Add 3 mL of 9M HCl to each column to convert to HCl. Collect the eluate.
14. Add 20 mL of 4M HCl to elute americium. Collect the eluate in the same beaker. Evaporate to dryness. Treat with 5 mL HNO<sub>3</sub> several times until wet-ashing of the residue is complete. Convert to HCl. Set beakers aside for Procedure G-03, **Microprecipitation Source Preparation for Alpha Spectrometry.**
15. Rinse the columns with 25 mL of 4M HCl-0.1M HF. Discard eluate.
16. Ensure the clean, labeled beakers or vials are below each column. Add 10 mL of 0.1M NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> to elute plutonium from each column.
17. Evaporate to dryness. Treat with 5 mL HNO<sub>3</sub> several times until wet-ashing of the residue is complete. Convert to HCl. Set beakers aside for Procedure G-03, **Microprecipitation Source Preparation for Alpha Spectrometry.**

### PRECISION AND BIAS

1. Precision - A relative standard deviation of 4.2% at the 0.42 Bq level has been reported for uranium. A relative standard deviation of 3.2% at the 1 Bq level has been reported for plutonium.
2. Bias - Mean chemical recoveries of 95% for americium, 93% for plutonium and 86% for uranium have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

#### LOWER LIMIT OF DETECTION (LLD) NATURAL URANIUM

Counter Efficiency	(%)	30
Counter Background	(cps)	3.33 x 10 <sup>-6</sup> for <sup>238</sup> U 6.67 x 10 <sup>-6</sup> for <sup>234</sup> U
Recovery :	(%)	85
LLD (400 min)	(m Bq)	0.2 for <sup>238</sup> U 0.3 for <sup>234</sup> U
LLD (1000 min)	(m Bq)	0.1 for <sup>238</sup> U 0.2 for <sup>234</sup> U
LLD (5000 min)	(m Bq)	0.06 for <sup>238</sup> U 0.09 for <sup>234</sup> U

### PLUTONIUM

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Counter Efficiency	(%)	30
Counter Background	(cps)	$2 \times 10^{-5}$
Recovery	(%)	75
Blank	(cps)	-
LLD (400 min)	(mBq)	0.6
LLD (1000 min)	(mBq)	0.4
LLD (5000 min)	(mBq)	0.2

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### AMERICIUM

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Counter Efficiency	(%)	30
Counter Background	(cps)	$1.6 \times 10^{-5}$
Recovery	(%)	80
LLD (400 min)	(mBq)	0.5
LLD (1000 min)	(mBq)	0.3
LLD (5000 min)	(mBq)	0.1

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