Separation of Am and Pu from 50 g Soil and Sediment Samples (Diphonix-HEDPA-TRU-TEVA)

PROTOCOL:

REAGENTS

- ^{242}Pu and ^{243}Am spike
- Diphonix (100-200 mesh), TEVA (100-150 mesh), and TRU (100-150 mesh) resins
- Aluminum nitrate (2 M) - Dissolve 750 grams aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) in 800 mL water; dilute to 1 liter with water
- Ammonium hydroxide - concentrated (sp gr 0.9)
- Ammonium thiocyanate (4 M) – formic acid (0.1 M) – Dissolve 6 g NH_4SCN in water, add 0.1 mL 88% formic acid and dilute to 20 mL with water. Prepare fresh prior to use.
- Ammonium thiocyanate (1.5 M) – formic acid (0.1 M) – Dissolve 1.9 g NH_4SCN in water, add 0.1 mL 88% formic acid and dilute to 20 mL with water. Prepare fresh prior to use.
- Ammonium thiocyanate, crystal
- Ascorbic acid, crystal
- Boric acid, crystal
- Cerium carrier - Dissolve 0.155 g cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, in 50 mL water and dilute to 100 mL with water (0.5 mg Ce/mL)
- Ethanol, 80% - Add 80 mL ethanol to 20 mL water
- Formic acid, 88%
- Ferrous Ammonium Sulfate - $Fe(NH_4)_2(SO_4)_2{*}6H_2O$, crystal
- 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA, 0.5 M) – (1) purchase industrial grade BRIQUEST201 ADPA-60 AW U (65%), from Albright & Wilson, and add 159 mL to 500 mL water and dilute to 1 liter with water or (2) prepare from crystal form purchased from Fluka: add 103 grams of HEDPA to 300 mL of water and dilute to 1 liter with water.
- Hydrochloric acid (12 M) - concentrated hydrochloric acid (sp gr 1.19)
- Hydrochloric acid (9 M) - Add 750 mL of concentrated HCl (sp gr 1.19) to 200 mL of water and dilute to 1 liter with water
- Hydrochloric acid (6 M) - Add 500 mL of concentrated HCl (sp gr 1.19) to 300 mL of water and dilute to 1 liter with water
- Hydrochloric acid (4 M) - Add 334 mL of concentrated HCl (sp gr 1.19) to 600 mL of water and dilute to 1 liter with water

- Hydrochloric acid (2 M) - Add 167 mL of concentrated HCl (sp gr 1.19) to 800 mL of water and dilute to 1 liter with water
- Hydrochloric acid (2 M) - hydrofluoric acid (0.5 M) - Add 167 mL of concentrated HCl (sp gr 1.19) and 18 mL of concentrated HF (sp gr 1.2) to 800 mL of water and dilute to 1 liter with water
- Hydrogen peroxide (30%) - concentrated H_2O_2 w/o stabilizer: residue after evaporation ≤0.002% (purchase from Fisher)
- Hydrofluoric acid (28.9 M) - concentrated HF (sp gr 1.2)
- Nitric acid (15.8 M) - concentrated HNO_3 (sp gr 1.42)
- Nitric acid (8M) - Add 500 mL of concentrated HNO_3 (sp gr 1.42) to 300 mL of water and dilute to 1 liter with water
- Nitric Acid (2.5 M) - Add 159 mL of concentrated HNO_3 (sp gr 1.42) to 800 mL of water and dilute to 1 liter with water
- Sodium nitrite $NaNO_2$, crystal
- Titanium (III) chloride - 15 wt% solution in 20 - 30 wt% hydrochloric acid

PROCEDURE

I. Soil/Sediment Leaching and Loading to Diphonix

1.1. Accurately weigh approximately 50 gram soil sample.

1.2. Combust the sample for 4 hours at 550 °C in muffle furnace.

1.3. Transfer the sample into 500 mL glass beaker and add 150 mL 6 M HCl and 150 mL 8 M HNO_3;

1.4. Add appropriate amount of calibrated ^{243}Am and ^{242}Pu tracers to the sample, and place cover on the beaker;

1.5. Reflux the sample at ~ 90 °C for 4 hours on hot plate; add more 6 M HCl and 8 M HNO_3 during the leaching if necessary to keep the volume around 300 mL;

1.6. Centrifuge the samples for 10 min at 4200 rpm, and collect the acid soluble fractions (wash the residual soils 3 times with 3 M HCl; collect supernatant and discard the residue);

1.7. Adjust the volume to 1 liter with DI water;

1.8. Add 25 mg Fe as 0.5 mL $FeCl_3$ solution. Actinides are precipitated with $Fe(OH)_3$ by adding concentrated NH_4OH to the sample to reach pH~8;

1.9. Centrifuge the sample and collect $Fe(OH)_3$ precipitate (wash the ppt., discard supernatant solution);

1.10. Dissolve the $Fe(OH)_3$ precipitate by adding 35 mL of conc. HCl. Add 10 mL conc. HF (this is to fully complex Al^{3+} with F^-) and DI water to bring the volume to 500 mL to make the final concentration ~1 M HCl and ~0.5 M HF.

1.11. Add ascorbic acid to reduce Fe^{3+}. To ensure that all Fe is in reduced form add a small drop of the sample to a grain of ammonium thiocyanate (turns red in presence of Fe^{3+} clear otherwise);

1.12. If precipitate forms upon addition of HF, centrifuge the sample and load the supernatant onto Diphonix resin column (1.5 cm dia. Kontes borosilicate glass column; 13 mL wet resin vol., preconditioned with 10 mL 2 M HCl + 0.5 M HF); Redissolve the residue after centrifugation in a small volume of 2 M HCl and boric acid. Add the solution to Diphonix resin column separately, after the supernatant. Maintain the flow rate of the solution at not more than ~1 mL/min.

II. Actinide Elution from Diphonix Resin and HEDPA Oxidation

2.1. Add 60 mL of 2 M HCl - 0.5 M HF into the column to rinse column (2 M HCl is used for efficient removal of Ca^{2+} and Fe^{2+}); Discard load and rinse solutions; place a clean, labeled glass beaker (600 mL size) below the column;

2.2. Elute the actinides from the column by passing 40 mL of 0.5 M HEDPA through the column;

2.3. Add 1 mL conc. HNO_3 and 40 mL of 30% H_2O_2 to the beaker containing the eluate;

2.4. Heat the sample to ~90 °C, and add 0.17 g of ammonium ferrous sulfate;

2.5. Continue heating at 90 °C with a loose-fitting glass cover for 40 minutes (allowing the solution to evaporate slowly). 10 mL of 30% H_2O_2 is added every 10 minutes. After this time, only 5-10 mL of solution remains (total volume of H_2O_2 added is 70 mL). At this stage, remove the lid and add a final 5 mL of 30% H_2O_2 to ensure complete oxidation of HEDPA (a spontaneous thorough bubbling of the solution when the H_2O_2 is added indicates that the oxidation is complete). Use caution in adding H_2O_2 to prevent any overspill.

2.6. Evaporate sample without the lid until only about 3 mL solution remains;

2.7. Add 3.5 mL conc. HNO_3, 6.5 mL H_2O, 12 mL 2 M $Al(NO_3)_3$ to make 25 mL loading solution;

2.8. Add 0.1 g $NaNO_2$ let the solution stand approximately 30 minutes than heat the sample gently until brown fumes of NO_x are gone.

III. Actinide Separation *via* TRU Resin

3.1. Load the solution (~2.3 M HNO_3 - 1 M $Al(NO_3)_3$ - 0.06 M $NaNO_2$) onto TRU resin column (0.7 cm dia. Kontes borosilicate glass column; 6 mL wet resin vol.) preconditioned with 10 mL 2.5 M HNO_3;

3.2. Add 3 x 10 mL of 2.5 M HNO_3, rinsing through the sample beaker;

3.3. Place a clean beaker (100-mL Nalgene Teflon PFA baker with graphite bottom) labeled with the sample number and "Am" below the column;

3.4. Rinse with 5 mL 9 M HCl to convert column to chloride form, collect this fraction;

3.5. Elute Am with 30 mL of 4 M HCl pipetted into the column and allow to drain into beaker (**Further Am/Ln separation is necessary because of large sample size - see Part IV.**);

3.6. Place a clean beaker labeled with the sample number and "Pu" below the column;

3.7. Elute Pu with 2 x 15 mL 4 M HCl / 0.5 mL 20% $TiCl_3$ (should be well mixed in a beaker before transferring onto the column) pipetted into the column and allow to drain, **set beaker aside for source preparation**;

IV. Am/Ln separation

4.1 Evaporate Am fraction from TRU resin;

4.2 Oxidize any resin materials using HNO_3-H_2O_2;

4.3 Add 3 drops of 10% H_2SO_4 solution and evaporate until very small drop remains;

4.4 Dissolve the residue in ~1 drop of concentrated formic acid, evaporate again until very small drop remains, dissolve the residue again in a drop of concentrated formic acid; Heat the beaker carefully till the walls are completely dry.

4.5 Redissolve the sample in 10 mL 4 M ammonium thiocyanate - 0.1 M formic acid solution;

4.6 Load the solution into a TEVA column (2 mL wet resin vol. in Eichrom column) preconditioned with 5 mL 4 M NH_4SCN - 0.1 M formic acid;

4.7 Rinse the beaker with 5 mL 4 M NH_4SCN - 0.1 M formic acid, and pass through the column;

4.8 Rinse out Ln with an additional 10 mL 1.5 M NH_4SCN - 0.1 M formic acid, discard;

4.9 Place a clean, plastic beaker labeled with the sample number and "Am" below the column; Elute Am with 20 mL 2 M HCl into the column and allow to drain, **set beaker aside for source preparation**.

V. Source Preparation

5.1. Add 0.2 mL (100 μg) of cerium carrier to beakers containing final fractions for americium and plutonium. Swirl to mix;

5.2. Add 0.5 mL 20% $TiCl_3$ solution to plutonium fraction; Add 7 mL of concentrated HF to the beaker. Swirl to mix. Let solution sit for at least 20 minutes before proceeding;

5.3. Add 2 mL of concentrated HF to the beaker containing Am. Swirl to mix. Let solution sit for at least 20 minutes before proceeding;

5.4. Set up a 0.1 μm, 25-mm Metricel® polypropylene membrane filter on a Gelman filter apparatus with screen, funnel, and filtering flask;

5.5. $Ca(NO_3)_2$ should be added to filter flask before filtering to scavenge F^- from solution;

5.6. Add 3-5 mL of 80% ethanol to wet each filter, apply vacuum and ensure there are no leaks;

5.7. Filter samples and rinse beakers with 5 mL water, transfer rinse to filtering apparatus, repeat;

5.8. Rinse sides of filter funnel with 5 mL water and finally with 80% ethanol;

5.9. Am and Pu filters are dried for about 10 minutes in a <60 °C oven and then attached to a stainless steel disc using glue stick.

5.10. Count the sources by alpha spectrometry.