Actinide Recovery Method (Rev. 10/19/99)

Soil Digest Preparation (Pu^{+3}, Am^{+3}, Cm^{+3}, U^{+6}, Th^{+4}, Np^{+4})

1. Redissolve soil in 1.5M HCL- 1M HF, minimizing volume.

   Note: This solution redissolves evaporated leachates well.

   Fusions/Total digestions: If a total dissolution such as a fusion plus hydroxide precipitation is performed. The hydroxide precipitate can be acidified with 6M HCl, then evaporated to dryness to lower volume and better adjust final acidity. Redissolve total digest residue in a small volume of 1.5M HCl, with no HF present, to avoid any fluoride solids on initial redissolution. Fecal samples may be dissolved completely using multiple HNO_3-HF and HCL –HF digestions, evaporated and redissolved in 1M HCl containing 0.1M to 0.2M HF.

2. Adjust digest acidity to 0.5M HCL containing also 0.5M to 1M HF, minimizing volume.

   Note: The HCL can be 0.4M- 0.75 M as necessary. The total fluoride should be sufficient to complex Al^{+3}, etc.. For low residue soils such as QAP soils, use less fluoride, for example 0.5M to 0.7M. High residue soils with high dissolved solids may require 1M HF to fully complex aluminum present.

   Fusions/total digestion: HF can be added to the 1.5M HCL solution from step 1 to adjust to a final concentration of 0.5M to1M HF. If a small precipitate forms upon addition of HF, centrifuge, set aside supernate to load to column and redissolve fluoride precipitate in small volume of 0.5M HCL containing 0.1M to 0.25M boric acid, heating as necessary. These solutions will be loaded to same Diphonix column separately. Fecal samples require much less HF, 0.1M to 0.2M.

3. Add solid ascorbic acid (AA) or appropriate volume of 1.5M ascorbic acid to make the solution 0.075M - 0.15M AA.

   Note: For soils with low residue solids after leaching (QAP, etc.), use less ascorbic acid, such as 0.075M AA. A color change to a lighter green or greenish- yellow should be seen.

Diphonix Column Separation

1. Prepare 2.4-2.80 mL Diphonix resin column (Ex. 40 mm high- Environ. Express column P/N R1010) from water slurry of resin.

   Note: The amount of microwave pressure is determined by the quantity of resin used. For 625 psi vessels, do not exceed 2.8 mL of resin. Range extension option: prepare 2.8 mL Diphonix cartridge/column to use in series (microwave separately). For fecal samples, 2.4 mL of resin is adequate.

2. Condition resin column with 5 to 10 mL of 0.5M-0.5M HF. Press down the column frit after resin volume shrinks. For fecal samples, 0.5M-0.25M HF is used.

3. Load digest solution to Diphonix column and allow to drain.

   Note: For maximum recovery, do not exceed approximately 1 mL to 2mL mL/minute flow rate during column loading.

4. Rinse column with 10 to 15 mL 0.5M HCl-0.5M HF, minimizing volume.

   Note: Minimal rinse is desired to maximize recoveries. The goal is to remove key matrix interferences that could affect subsequent column recoveries. Additional clean-up will be achieved using individual actinide column methods. For fecal samples, 0.5M-0.25M HF is used.

5. Rinse column with 20 mL of water.

Actinide Removal from Resin

1. Transfer resin to microwave vessel rated to 600- 625 psi using an appropriate resin removal technique (i.e. cut column and tap out resin, rinsing out column if necessary, etc.)

   Note: New 1000 psi vessels available will extend method range proportionally, or in some cases eliminate predigest step, currently used to enable more resin and largest sample size possible.

2. Add 10 mL of concentrated nitric acid, rinsing residual resin into vessel.

   Note: Scale up acid volume appropriately if larger resin volume and higher pressure microwave vessels are used.

3. Predigest: Microwave resin at 190 degrees C for 20 minutes, with pressure control limit set at 550 psi.

   Note: A 4 to 8 minute temperature ramp to 190C is used depending on the number of samples digested.

4. After vessels have cooled sufficiently, open to atmosphere and replace rupture disk.

5. Digest vessels at 220-225 degrees C for 35 minutes, with pressure control limit set at 550 psi.

   Note: A 5 to 10 minute temperature ramp to 220C is used depending on the number of samples digested. If control limit is reached and the microwave reduces power and the temperature is decreased below 220C this is ok along as 220C was achieved through most of the digestion run.

6. After vessels have cooled, open to atmosphere, add 3.5 mL of 30 wt% hydrogen peroxide and replace rupture disk. Swirl solution briefly.

   Note: Scale up acid volume appropriately if larger resin volume and higher pressure microwave vessels are used.

7. Digest vessels to 210 degrees C for 20 minutes, with pressure control limit at 350 psi.

   Note: A 10 minute temperature ramp to 210C is used depending on the number of samples digested. Solutions will clear or only have a light color after this digestion step.

8. After vessels have cooled, transfer digest to small beaker, add 3 mL of 30 wt% hydrogen peroxide and evaporate to dryness on a hot plate.

   Note: The solution will turn a slightly darker yellow after heating with peroxide.

9. Add 5 to 10 mLs of 30 wt% hydrogen peroxide to each sample residue and wet ash to dryness. Repeat this step three more times until the color of the residue does not lighten any further.

10. Add 5mL of concentrated nitric acid and the very slowly add 3mL of 30 wt% hydrogen peroxide to each sample residue and wet ash to dryness. Repeat as needed.

11. Redissolve the evaporated sample matrix by adding about 6 mL of 5to 6M nitric acid and warming the solution slightly on a hot plate.

12. Add 6 mL of 2to 2.5M aluminum nitrate (if appropriate UTEVA-scrubbed to remove trace uranium) to dilute to 2.5M nitric acid-1M aluminum nitrate.

    Note: Valence adjustment of plutonium is more effective if the acid is lowered to 2.5M.

14. The actinides from the large soil sample are now in a load solution for further actinide separations using Eichrom columns.

Typical Sample Preparation Volumes for 10 grams Soil Leachate –QAP Soil Leach

Note: Low residue soils like QAP soils require less HF and AA. A microwave leach in 13 mLs 16M HNO_3 + 4mLs 12M HCL at 180C for 35 minutes, filter, evaporate has been found to be effective for Pu and Am on QAP soils.

1. Redissolve in 7.5 mL of 1.5M HCL- 1M HF, warming as necessary.

2. Transfer to 50 mL centrifuge tube with 10 mL of 0.1M HCL.

3. Add 0.75 mL of 10M HF. Mix well.

4. Dilute to 20 mLs with 0.1M HCL.

5. Add 275 mg ascorbic acid just prior to column work.

Note: The final concentration is about 0.5M HCl-0.7M HF-0.075M AA. 10 gram soils soils with higher residues to redissolve require a slightly larger volume of 1.5M HCl-1M HF to redissolve, 1M HF and 0.15M AA in the final load solution and a load volume closer to 40 mL to ensure enough HF is present to complex aluminum.

Typical Sample Preparation Volumes for 10 grams Soil Total Digest –QAP Fusion/Total Dissolution

Note: Low residue soils like QAP soils require less HF and AA. After fusion, hydroxide precipitation, acidification and silicon removal through evaporation(s), continue with the following steps.

1. Redissolve in 10 mL of 1.5M HCL, warming as necessary.

2. Transfer to 50 mL centrifuge tube with 10 mL of 0.1M HCL.

3. Dilute to 25 mLs with 0.1M HCL.

4. Add 1.5 mL of 10M HF. Mix well.

5. Dilute to 30 mLs with 0.1M HCL.

6. If a precipitate is present, centrifuge and remove supernate for separate column loading.

7. Add 400 mg ascorbic acid to the supernate solution just prior to column work.

8. If a precipitate occurred, redissolve precipitate in approximately 10 mL of 0.5M HCl-0.25M boric acid, warming as necessary. Add 100 to 200 mg ascorbic acid to this fraction just prior to column work.

9. Load the supernate solution to the Diphonix resin first, then the redissolved precipitate solution.