AP11

SEQUENTIAL DETERMINATION OF THE ACTINIDES IN ENVIRONMENTAL SAMPLES USING TOTAL SAMPLE DISSOLUTION AND EXTRACTION CHROMATOGRAPHY

PART A

PRINCIPLE

Solid and unfiltered aqueous samples are completely dissolved by a combination of potassium hydrogen fluoride and pyrosulfate fusions. Filtered aqueous samples are evaporated to dryness with a pyrosulfate fusion. The fusion cake is dissolved and for analyses requiring uranium only, two barium sulfate precipitations are performed and the uranium is separated using EDTA. For all other analyses, one barium sulfate precipitation is performed and all alpha emitters are coprecipitated on barium sulfate. The barium sulfate is dissolved and the actinides are separated by extraction chromatography. An optional section is presented for the separation of americium from the lanthanides. All actinides are coprecipitated on cerium fluoride and counted with an alpha spectrometer system.

REFERENCES

1. Sill, Claude W., Puphal, Kenneth, and Hindman, Forest D., *Anal. Chem.* **1974**, *46*, 1725.

2. Sill, Claude W., and Williams, Roger, L., *Anal. Chem.* **1981,** *53*, 412.

3. Sill, Claude, W., *Anal. Chem.* **1974**, *46*, 1426.

4. Sill, Claude, W.*, Anal. Chem.* **1964,** *36*, 675.

5. Bernabee, Roger P., Percival, Donald R., and Hindman, Forest D., *Anal. Chem.* **1980,** *52*, 2351.

6. Annual Book of ASTM, Standards, *11.02*, 300-303, 380-381, 407-411.

7. Sill, Claude W., and Sill, David, *Waste Management* **1989**, *9*, 219-229.

8. EML Procedures Manual, 27th Edition, **1992,** *Volume I*, 4.5-246, 247.

9. Bernabee, Roger P., *Health Physics* **1983**, *44*, 688-691.

10. Martin, Don B., and Pope, Dennis G., *Anal. Chem.* **1982**, *54*, 2552-2556.

11. Maxwell, S. L. III, and Fauth D. J., Rapid Separation Methods for Bioassay Samples, presented at the Eichrom Technologies, Inc. North American Users' Group Workshop, Westminster, CO, **2002**.

REFERENCES (continued)

12. Maxwell, S. L., personal communications, **2002**.

13. Thakker, Anil, personal communications, **2002**.

14. Eichrom Technologies, Inc., Analytical Procedure ACW03 VBS, Rev. 1.5, **2002.**

Certification Record for

PROCEDURE AP11

SEQUENTIAL DETERMINATION OF THE ACTINIDES IN ENVIRONMENTAL SAMPLES USING TOTAL SAMPLE DISSOLUTION AND EXTRACTION CHROMATOGRAPHY

CHECKPOINTS

1.	**JOB HAZARD ANALYSIS (JHA)**	**____**
2.	**MSDS/HAZARDS DISCUSSED**	**____**
3.	**FLUORIDE FUSION**	**____**
4.	**PYROSULFATE FUSION**	**____**
5.	**BARIUM SULFATE PPT**	**____**
6.	**EXTRACTION CHROMATOGRAPHY**	**____**
7.	**SAMPLE DEPOSITION**	**____**

ANALYST'S SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN: _____

See Task _____, Batch_____ for the original data.

COMMENTS: _____
_____
_____
_____

PART B

1.0 PURPOSE AND SCOPE

This is a radiochemical procedure for the determination of Americium, Curium, Plutonium, Neptunium, Thorium, and/or Uranium in environmental samples.

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP11 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Ammonium hydrogen oxalate, $NH_4HC_2O_4$, 0.1 M, dissolve 10.8 g $NH_4HC_2O_4 \cdot 1/2H_2O$ in 800 mL water. Filter solution through Supor-450 or equivalent. Dilute to 1 L with water and mix well.

Ammonium hydroxide, NH_4OH, concentrated, 14.8 M.

Ascorbic acid solution, $C_6H_8O_6$, 1.5 M, dissolve 13.2 g $C_6H_8O_6$ into 30 mL water. Filter solution through Supor-450 or equivalent. Dilute to 50 mL with water. Store the solution in an amber bottle. Put the date on the bottle. **This solution has a typical shelf life of one month. Before using, check the color of the solution. If the color has changed to a dark yellow, do not use and make a fresh solution. If the solution is colorless or light yellow, it is okay to use.**

Barium chloride solution, 0.45% (w/v): Dissolve 4.5 g $BaCl_2 \cdot 2H_2O$ in 900 mL water. Filter through Supor-450 filter or equivalent. Dilute to 1 L with water.

Buffer solution, pH 2.60: Add 35.4 mL 0.1 M HCl to 50 mL 0.1 M KHP and dilute to 100 mL with water in a volumetric flask.

Buffer solution, pH 2.80: Add 28.9 mL 0.1 M HCl to 50 mL 0.1 M KHP and dilute to 100 mL with water in a volumetric flask.

Buffer solution, pH 3.00: Add 22.3 mL 0.1 M HCl to 50 mL 0.1 M KHP and dilute to 100 mL with water in a volumetric flask.

Cerium carrier 1 mg/mL: AA quality Ce solution of 1000 :g/mL.

Diethylenetriaminepentaacetic acid, DTPA Eluent: Add 10 g of DTPA and 100 g of monochloroacetic acid to 800 mL of reagent water and 25 mL of concentrated NH_4OH. Slowly add more concentrated NH_4OH if necessary to completely dissolve. Adjust pH using either concentrated NH_4OH or concentrated HCl to 2.60-2.80 using a pH meter. Filter solution through Supor-450 or equivalent. Dilute solution to 1 L with water.

NOTE: This reagent must have the correct pH or the separation of Am from the lanthanides will be inadequate.

Ethanol, 95% or equivalent.

Ferrous ammonium sulfate, 25% (w/v): Dissolve 2.5 g $Fe(NH_4)_2SO_4$ in 10 mL water. Make fresh daily.

Fusion solution: Dissolve 50 g $NaHSO_4$ in 300 mL water. Slowly add 125 mL 18 M H_2SO_4 while stirring. Cool, and dilute to 500 mL with water.

Hydrochloric acid, HCl, concentrated, 12 M.

Hydrochloric acid, 9 M, add 375 mL 12 M HCl to 100 mL water. Dilute to 500 mL with water and mix well.

Hydrochloric acid, 8 M, add 667 mL 12 M HCl to 200 mL water. Dilute to 1 L with water and mix well.

Hydrochloric acid, 6 M, slowly add 500 mL 12 M HCl to 400 mL reagent water. Dilute to 1 L with water and mix.

Hydrochloric acid, 4 M, add 334 mL 12 M HCl to 500 mL water. Dilute to 1 L with water and mix well.

Hydrochloric acid, 1 M, add 42 mL 12 M HCl to 100 mL water. Dilute to 500 mL with water and mix well.

Hydrochloric acid, 0.5 M, add 21 mL 12 M HCl to 100 mL water. Dilute to 500 mL with water and mix well.

Hydrochloric acid, 0.1 M, add 25 mL 4 M HCl to 900 mL reagent water. Dilute to 1 L with water and mix.

Hydrochloric acid (4 M)/Hydrofluoric acid (0.1 M): Add 167 mL 12 M HCl and 50 mL 1 M HF to 200 mL water. Dilute to 500 mL with water and mix well.

Hydrochloric acid (0.1 M)/Hydrofluoric acid (0.05 M)/Titanium (III) chloride (0.02 M): Add 100 mL 1 M HCl and 50 mL 1 M HF to 800 mL water. Dilute to 1 L with water and mix well. Add 1.5 mL 20% $TiCl_3$ per 100 mL of solution just prior to use.

NOTE: It is important to wait to add the $TiCl_3$ just before needed or the reduction of Pu will be incomplete.

Hydrochloric acid (1 M)/Oxalic Acid (0.05 M): Add 42 mL 12 M HCl and 2.25 g of $H_2C_2O_4$ to 200 mL water. Dilute to 500 mL with water and mix well.

Hydrofluoric acid, HF, concentrated, 28 M: **CAUTION: Skin contact with HF causes very severe burns**.

Hydrofluoric acid, 1 M, add 18 mL 28 M HF to 100 mL water. Dilute to 500 mL with water and mix well.

Hydroxylamine hydrochloride, $NH_2(OH)HCl$, 1 M, dissolve 6.9 g in 50 mL water. Filter solution through Supor-450 or equivalent. Dilute to 100 mL with water and mix.

Hydrogen peroxide, H_2O_2, 30-35% (w/v), ACS reagent.

Ln resin, 2 mL pre-packed cartridges.

Nitric acid, HNO_3, concentrated, 16 M.

Nitric acid, 3 M, slowly add 188 mL 16 M HNO_3 to 800 mL water. Dilute to 1 L with water and mix.

Nitric acid, HNO_3, 2 M, slowly add 63 mL 16 M HNO_3 to 200 mL water. Dilute to 500 mL with water and mix.

Nitric acid, HNO_3, 0.1 M, slowly add 25 mL 2 M HNO_3 to 200 mL water. Dilute to 500 mL with water and mix.

Nitric acid (3 M)/Aluminum nitrate (1 M) (Load Solution): Add 188 mL 16 M HNO_3 and 375 g $Al(NO_3)_3 \cdot 9H_2O$ to 200 mL water and dissolve. Filter solution through Supor-450 or equivalent. Dilute to 1 L with water. Scrub solution to remove trace amounts of uranium by pouring solution through UTEVA® resin.

Potassium metabisulfite, $K_2S_2O_5$, anhydrous crystal.

Potassium sulfate, K_2SO_4, anhydrous crystal.

Perchloric acid, $HClO_4$, concentrated, 11.7 M: **CAUTION: Concentrated $HClO_4$ reacts violently with organic material (i.e. paper, skin, alcohol). Hot $HClO_4$ should be used only in rated hoods with wash down after use.**

Potassium ethylenediaminetetraacetic acid, KEDTA, 0.05 M: Dissolve 20.2 g KEDTA in 800 mL water. Using digital pH meter, adjust pH to 10.6 using 10 M KOH. Filter solution through Supor-450 or equivalent. Dilute to 1 L with water.

Potassium hydrogen fluoride, KHF_2, anhydrous crystal.

Potassium hydrogen phthalate, KHP, 0.1 M: Dissolve 10.21 g KHP in 400 mL water. Filter solution through a Supor-450 filter and dilute to 500 mL with water.

Potassium hydroxide, KOH, 10 M: Slowly dissolve 561 g KOH in 400 mL water, in a cold water bath. Filter solution through Supor-450 or equivalent. Dilute to 1 L with water.

Safranin-O, 1% (w/v), Dissolve 1 g safranin-O indicator in 50 mL water. Dilute to 100 mL with water.

Safranin-O, 0.1% (w/v), dilute 10 mL 1% safranin-O indicator to 100 mL with water.

Sodium nitrite, $NaNO_2$, 4 M: dissolve 2.7 g $NaNO_2$ in 10 mL water. **Make fresh daily.**

Sodium sulfate, Na_2SO_4, anhydrous crystal.

Sulfamic acid, H_2NSO_3H, 1.5 M, Dissolve 14.6 g H_2NSO_3H in 75 mL water. Filter solution through Supor-450 or equivalent. Dilute to 100 mL with water and mix. Put the date on the bottle. **Shelf life is 6 months.**

Sulfuric acid, H_2SO_4, concentrated, 18 M.

TEVA® resin, 2 mL pre-packed cartridge.

Titanium (III) chloride, $TiCl_3$, 20% (v/v), ACS reagent.

TRU® resin, 2 mL pre-paced cartridge.

UTEVA® resin, 2 mL, pre-packed cartridge or non pre-packed.

3.0 APPARATUS

Alpha spectrometer
Analytical balance
Beakers
Blast burner
Centrifuge
Centrifuge tubes
Column rack
Double stick tape
Filtering flasks, 1 L
Filters, Supor-450, 25 mm
Filters, Supor-450, 47 mm
Filters, 0.1 :m polypropylene
Fume hood
Hot plate
Petri dish
pH Meter, ORION 520A, or equivalent
Platinum dishes
Polysulfone filtering apparatus
Specimen Cup, 100 mL or equivalent
Stainless Steel Disk, 1.25 inch, taped or plain
Stir bars
Syringe barrels
Teflon filtering apparatus
Tweezers
Vacuum box, Eichrom part # AC-24-BOX

Vacuum manifold
Vacuum pump
Watch glass
White inner tips, Eichrom part # AC-1000-IT
Yellow inner tips, Eichrom part # AC-1000-OT
Yellow plugs

4.0 PROCEDURE

4.1 General Requirements

Before proceeding, you must be certified as indicated in QCP1 of this manual and Section 3 of the Quality Program (QP) Manual. See page three for a copy of the certification record. For a visual flow diagram of the complete procedure (Am, Cm, Pu, Np, Th, and U) see Figure #1.

4.2 Water Sample Preparation

4.2.1 Measure and record sample volume. Typical samples are 0.05 L to 0.25 L. If required, filter the samples through a Supor-450 47 mm filter and pour the samples into an 800 mL beaker. For samples containing visible particulate matter and filtering is **not** requested, evaporate the sample to dryness in a platinum dish and proceed to Step 4.3.2. **See step 4.2.1 of AP11 JHA.**

4.2.2 Add appropriate amounts of tracers (approximately 5 pCi for each tracer) and/or standards. **See step 4.2.2 of AP11 JHA.**

4.2.3 Add 2 mL fusion solution to each sample. **See step 4.2.3 of AP11 JHA.**

4.2.4 Heat sample to dryness on a hot plate. It is important that the sample is taken to COMPLETE dryness.

4.2.5 For analysis requiring uranium only, proceed to Barium Sulfate Precipitation for Uranium Only, section 4.5.

4.2.6 For all other analysis, proceed to Barium Sulfate Precipitation for All Actinides, section 4.6.

4.3 Solid Sample Preparation

4.3.1 Measure the sample in a platinum dish and record the mass. **See step 4.3.1 of AP11 JHA.**

4.3.2 Add appropriate amounts of tracers (approximately 5 pCi for each tracer) and/or standards. **See step 4.3.2 of AP11 JHA.**

NOTE: Since Pt will dissolve in aqua regia, do not add tracers prepared in HNO_3 and HCl to the dish at the same time. The tracers in HNO_3 and the tracers in HCl must be brought to dryness separately.

4.3.3 Dry tracers and/or standards using a hot plate. Proceed to Sample Decomposition for Solid and Unfiltered Samples, section 4.4.

4.4 Sample Decomposition for Solid and Unfiltered Samples

4.4.1 Add ~12-15 g KHF_2 to the sample. **See step 4.4.1 of AP11 JHA.**

4.4.2 Place the platinum dish on a ring stand using a nichrome triangle. **See step 4.4.2 of AP11 JHA**.

4.4.3 Start heating the sample over a blast burner with low flame. Heat until the KHF_2 has completely dried. **See step 4.4.3 of AP11 JHA**.

4.4.4 Use as much heat as possible with limited splattering. Bring the temperature to about 900°C (the color of the Pt dish will turn cherry red). Continue heating until total dissolution occurs. Swirl the hot melt to ensure removal of sample clinging to the sides of the dish. **See step 4.4.4 of AP11 JHA.**

4.4.5 Remove the melt from the burner and swirl the melt gently around the dish to form a thin layer upon cooling. Wait 45 seconds before proceeding to step 4.4.6. (Never set hot platinum on iron). **See step 4.4.5 of AP11 JHA.**

NOTE: IT IS CRITICAL FOR THE FLUORIDE CAKE TO BE SOMEWHAT COOL BEFORE THE ADDITION OF H_2SO_4 TO PREVENT SPLATTERING.

4.4.6 Add ~8 mL concentrated H_2SO_4 to the fluoride cake. Add another ~8 mL. The acid should be added to the edge of the dish and allowed to run to the bottom of the dish. **See step 4.4.6 of AP11 JHA.**

4.4.7 After the addition of H_2SO_4, heat as much as frothing will allow until the fluoride cake is totally dissolved. **See step 4.4.7 of AP11 JHA.**

4.4.8 Remove from heat and add ~3 g anhydrous Na_2SO_4 to the slurry. Place sample over the blast burner with small flame and heat until the slurry begins to turn a golden brown. Slowly increase the temperature until the slurry is completely melted, and then maintain this temperature for approximately 1 minute. **See step 4.4.8 of AP11 JHA.**

4.4.9 Remove the melt from the burner and swirl the melt gently around the

dish to form a thin layer upon cooling. **See step 4.4.9 of AP11 JHA.**

4.4.10 Transfer hardened pyrosulfate cake to a specimen cup by gently bending the dish to crack and loosen the cake. **See step 4.4.10 of AP11 JHA.**

4.4.11 For analysis requiring uranium only, proceed to Barium Sulfate Precipitation for Uranium Only, section 4.5. For all other analyses, proceed to Barium Sulfate Precipitation for All Actinides, section 4.6.

4.5 Barium Sulfate Precipitation for Uranium Only

4.5.1 To either a clean 800 mL beaker (for solid samples) or the 800 mL beaker from step 4.2.6 (for filtered aqueous samples) add 350 mL water, 25 mL 12 M HCl, and a Teflon stirring bar. Cover with a watch glass, place on a hot plate, and begin to bring the solution to a boil. **See step 4.5.1 of AP11 JHA.**

4.5.2 Add 5 g Na_2SO_4 and 10 g K_2SO_4. Proceed to step 4.5.3 once the solids have dissolved. **See steps 4.5.2 through 4.5.5 of AP11 JHA.**

4.5.3 Once the solution begins to boil and for solid and unfiltered aqueous samples, carefully add the pieces of pyrosulfate cake (from step 4.4.10) to the boiling solution. Allow cake to dissolve, then proceed. If precipitate remains, add 25 mL 12 M HCl. Repeat once more if needed. Boil solution for 15 minutes. If precipitate still remains, see Laboratory Manager or designee.

4.5.4 Slowly add ~3 g $K_2S_2O_5$ with stirring and 2 mL 25% ferrous ammonium sulfate (prepared fresh daily). Heat and stir for 15 minutes.

4.5.5 Add 15 mL 0.45% (w/v) $BaCl_2 \cdot 2H_2O$ in five 3 mL portions. Boil for approximately 1 minute after each addition.

4.5.6 Using a Teflon filtering chimney, filter the hot solution through a Supor-450 47 mm membrane filter. Wash the remaining precipitate in the beaker onto the filter using water. Save the filtrate for uranium analysis. Place the filter into the barium solid waste container. **See step 4.5.6 of AP11 JHA.**

4.5.7 Pour the filtrate and rinse from steps 4.5.6 and 4.5.7 into a clean 800 mL beaker.

4.5.8 Cover with a watch glass, heat and stir the solution to boiling.

4.5.9 If polonium separation is requested in the Lab Work Request (LWR), perform Po separation. (see Laboratory Manager or designee for procedure).

4.5.10 Add 4 drops 1% aqueous safranin-O. This should produce a reddish color. **See steps 4.5.10 through 4.5.12 of AP11 JHA.**

4.5.11 Add 20% $TiCl_3$ drop-wise until the reddish color changes to the colorless leuco form. Add 5 more drops $TiCl_3$. If leuco form has not been reached in 10 drops see Laboratory Manager or designee. The uranium is reduced from the VI oxidation state to the IV oxidation state for co-precipitation with $BaSO_4$.

4.5.12 Add 12 mL 0.45% (w/v) $BaCl_2 \cdot 2H_2O$ in four 3 mL portions. Boil approximately 1 minute after each addition.

4.5.13 Using a Teflon filtering chimney, filter the solution through a Supor-450, 47 mm membrane filter. Place the filter in a centrifuge tube. Pour the supernate into the dilute acid waste container. **See step 4.5.13 of AP11 JHA.**

4.5.14 Add 20 mL 0.05 M KEDTA and 2-5 drops 10 M KOH, mix, heat in a boiling water bath until precipitate dissolves (approximately 10 minutes). Remove filter from each tube. For samples that were fused in platinum, some black elemental platinum will not dissolve and this is normal. Remove filter from each centrifuge tube. **See step 4.5.14 of AP11 JHA.**

4.5.156 Add 4 drops 20% $TiCl_3$ and 2 mL 10 M KOH, mix, heat 10 minutes in water bath until the $Ti(OH)_3$ precipitate settles. Centrifuge at 2000 RPM for 5 minutes. Decant and discard supernate in barium waste container. **See step 4.5.15 of AP11 JHA.**

4.5.16 Add 10 mL 3 M HCl, mix, heat in water bath until the $Ti(OH)_3$ has dissolved. **See step 4.5.16 of AP11 JHA.**

4.5.17 Filter through a 25 mm Supor-450 filter using a polysulfone funnel. Collect supernate in a 50 mL centrifuge tube. Wash filter with 1-2 mL reagent water. Save supernate, discard filter. **See step 4.5.17 of AP11 JHA.**

4.5.18 Proceed to Cerium Fluoride Deposition for Uranium, section, 4.10.

4.6 Barium Sulfate Precipitation for All Actinides

4.6.1 To either a clean 800 mL beaker (for solid samples) or the 800 mL beaker from step 4.2.6 (for filtered aqueous samples) add 350 mL reagent water, 25 mL 12 M HCl, and a Teflon stirring bar. Cover with a watch glass, place on a hot plate, and start heating solution to a boil. **See step 4.6.1 of AP11 JHA.**

4.6.2 Add 5 g Na_2SO_4 and 10 g K_2SO_4 and continue heating until the solution boils. Proceed to step 4.5.3 once the solids have dissolved. **See steps 4.6.2 through 4.6.5 of AP11 JHA.**

4.6.3 For solid and unfiltered aqueous samples, carefully add the pieces of pyrosulfate cake (from step 4.4.10) to the boiling solution. Allow cake to dissolve, then proceed. If precipitate remains, add 25 mL 12 M HCl. Repeat once more if needed. If precipitate still remains, see Laboratory Manager or designee. Boil solution for 10 minutes.

4.6.4 Slowly add ~3 g $K_2S_2O_5$ with stirring and boil for 10 minutes.

4.6.5 If requested in LWR, perform Po separation (see Laboratory Manager or designee for procedure).

NOTE: IF ANALYZING FOR Pu ONLY, add 2 mL of 25% $Fe(NH_4)_2SO_4$ and go to step 4.6.8.

4.6.6 Add 4 drops 1% aqueous safranin-O. This should produce a reddish color. **See steps 4.6.6 through 4.6.8 of AP11 JHA.**

4.6.7 Add 20% $TiCl_3$ drop-wise until the reddish color changes to the colorless leuco form. Add 3 more drops $TiCl_3$. If leuco form has not been reached in 10 drops see Laboratory Manager or designee.

4.6.8 Add 21 mL 0.45% (w/v) $BaCl_2 \cdot 2H_2O$ in seven 3 mL portions. Boil approximately 1 minute after each addition.

4.6.9 Using a Teflon filtering chimney, filter the solution through a Supor-450, 47 mm membrane filter. Place filter in a centrifuge tube. Pour supernate into the dilute acid waste container. **See step 4.6.9 of AP11 JHA.**

4.6.10 Add 20 mL 0.05 M KEDTA and 2-5 drops 10 M KOH, vortex, and heat in a boiling water bath until precipitate dissolves, (approximately 10 minutes). For samples that were fused in platinum, some black elemental platinum will not dissolve and this is normal. Remove filter from each centrifuge tube. **See step 4.6.11 of AP11 JHA.**

4.6.11 Add 4 drops 20% $TiCl_3$ and 2 mL 10 M KOH, mix, heat 10 minutes in water bath until the $Ti(OH)_3$ precipitate settles. Centrifuge at 2000 RPM for 5 minutes. Decant and discard supernate in barium waste container. **See step 4.6.11 of AP11 JHA.**

4.6.12 Add 13 mL 3 M HNO_3 /1 M $Al(NO_3)_3$ (load solution, DO NOT EXCEED THE STATED VOLUME), vortex, and heat in a hot water bath until the precipitate dissolves. For samples that were fused in platinum, some black elemental platinum will not dissolve and this is normal. **See step 4.6.12 of AP11 JHA.**

NOTE: Heat the precipitate only long enough to dissolve precipitate. Prolonged heating will cause the $Ti(OH)_3$ to develop "aging" effects which will cause the dissolution process to become extremely difficult.

4.6.13 Remove centrifuge tubes from the hot water bath.

4.6.14 Filter each sample through a 25 mm Supor-450 filter using a polysulfone funnel. Collect supernate in a 50 mL centrifuge tube. Wash filter with 2 mL load solution **(Do not use water).** Apply strong vacuum for one minute to enhance recoveries. Save supernate, discard filter. **See step 4.6.14 of AP11 JHA.**

4.6.15 Proceed to Actinide Separations Using Extraction Chromatography, section 4.7.

NOTE: Do not proceed to step 4.7 unless the rest of section 4.7 can be completed. Need at least 5 hours to complete.

4.7 Actinide Separations Using Extraction Chromatography

4.7.1 Set up of TEVA® and TRU® cartridges in tandem using a vacuum box system (See Figure #2).

NOTE: If analyzing for Cm, use two TRU cartridges to ensure no loss of Cm on the first TRU cartridge.

4.7.1.1 Place the plastic waste container (supplied with the vacuum box) in the vacuum box. Place the lid on the vacuum box.

4.7.1.2 Place the yellow outer tips into all 24 openings of the lid of the vacuum box. Fit a white inner tip into each yellow outer tip.

4.7.1.3 For each sample, put a TRU® cartridge on the inner white tip and a TEVA® cartridge on the top end of the TRU® cartridge.

4.7.1.4 Luer lock a syringe barrel (funnel) to the top end of each TEVA® cartridge.

4.7.1.5 Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

NOTE: The unused openings on the vacuum box need to be sealed with the yellow plugs (supplied with the vacuum box).

4.7.1.6 Add 5 mL 3 M HNO_3 to each funnel to pre-condition the TEVA® and TRU® cartridges. **See step 4.7.1.6 of AP11 JHA.**

4.7.1.7 Adjust vacuum pressure to achieve a flow rate of 1.0 mL/minute.

NOTE: Unless otherwise specified in the procedure, use a flow rate of 1 mL/min for load and strip solutions and 3 mL/min for rinse solutions.

4.7.2 Add 0.5 mL 1.5 M sulfamic acid solution to each sample and mix. **See step 4.7.2 of AP11 JHA.**

NOTE: The sulfamic acid solution has a shelf life of six months. Check the date on the bottle to ensure freshness.

4.7.3 Add 1.5 mL 1.5 M ascorbic acid solution to each sample and mix. Wait 3 minutes before proceeding to step 4.7.4. **See step 4.7.3 of AP11 JHA.**

NOTE: The ascorbic acid solution has a shelf life of approximately one month. Check the date on the bottle to ensure freshness and make sure the solution is not dark yellow.

4.7.4 In a fume hood, **carefully and slowly,** add 2 mL 4 M $NaNO_2$ (made fresh) while mixing sample. **See step 4.7.4 of AP11 JHA.**

4.7.5 Pour the solution through the preconditioned TEVA®/TRU® cartridge and allow solution to drain completely.

4.7.6 Rinse centrifuge tube with 5 mL 3 M HNO_3 and pour through cartridges. Allow solution to drain. **See step 4.7.6 of AP11 JHA.**

4.7.7 Rinse cartridges with 5 mL 3 M HNO_3 and allow solution to drain. Repeat this step twice (for a total of 15 mL rinse). **See step 4.7.7 of AP11 JHA.**

4.7.8 Turn vacuum pump off and separate the TEVA® and TRU® cartridges.

4.7.9 Pour waste into the dilute acid waste container.

4.7.10 Luer lock new syringe barrels (funnels) to the top end of the each TRU® and TEVA® cartridge. Discard used funnels.

4.7.11 Place a centrifuge tube labeled Th under each TEVA® cartridge and a centrifuge tube labeled Am under each TRU® cartridge.

4.7.12 Add 3 mL 9 M HCl to the TEVA® cartridge and collect (do not allow flow rate to exceed 1 mL/min). Combine this with the rinse from step 4.7.14. **See step 4.7.12 of AP11 JHA.**

4.7.13 Elute Am/Cm by adding 15 mL 4 M HCl to the TRU® cartridge and collect. For samples containing a significant amount of lanthanides (i.e. soils), proceed to Americium/Lanthanide Separation, section 4.9. For samples not containing large amounts of lanthanides, proceed to Cerium Fluoride Deposition for Am, Cm, Np, Pu, and Th, section 4.11. For analyses not requiring Am, discard solution to the dilute acid waste stream. **See step 4.7.13 of AP11 JHA.**

4.7.14 Elute Th by adding 30 mL 8 M HCl (1 mL/min) to the TEVA® cartridge and collect in the same tube from step 4.7.12. **See step 4.7.14 of AP11 JHA.**

4.7.15 Pour the solutions from step 4.7.12 and 4.7.14 into a labeled 250 mL Erlenmeyer flask. Rinse centrifuge tube with water and add to flask. Proceed to Organic Destruction for Thorium, section 4.8. For analyses not requiring Th, discard solution to the dilute acid waste stream.

NOTE: The 9 M HCl and 8 M HCl used to elute Th also removes some of the organic material from the TEVA® cartridge. Without the Organic Destruction for Thorium steps, the resolution for Th may be degraded.

4.7.16 Place a centrifuge tube labeled Pu under each TEVA® cartridge and a centrifuge tube labeled waste under each TRU® cartridge.

4.7.17 Elute residual Th on the TRU® cartridge by adding 20 mL 4 M HCl/0.1 M HF to each TRU® cartridge. Discard this rinse into the HF waste stream. **See step 4.7.17 of AP11 JHA.**

NOTE: For step 4.7.18, it is important to add the $TiCl_3$ to the HCl - HF mixture just prior to use to ensure complete reduction of Pu to the +3 oxidation state. Add 1.5 mL 20% $TiCl_3$ per 100 mL HCl - HF solution needed.

4.7.18 See note above. Elute Pu by adding 30 mL 0.1 M HCl/0.05 M HF/0.02 M $TiCl_3$ to each TEVA® cartridge. Proceed to Cerium Fluoride Deposition for Am, Cm, Pu, Np, and Th, section 4.11. For analyses not requiring Pu, discard solution into the HF waste stream. **See step 4.7.18 of AP11 JHA.**

4.7.19 If analyzing for Np, rinse the TRU column with 10 mL of 1M HCl/0.05M $H_2C_2O_4$ to remove any Np that may have been retained on the column. Discard rinse (i.e. TEVA bleed through of Np). **See step 4.7.19 of AP11 JHA.**

4.7.20 Place a centrifuge tube labeled U under each TRU® cartridge. Elute U by adding 20 mL 0.1 M $NH_4HC_2O_4 \cdot ½ H_2O$ to each TRU® cartridge. Proceed to Cerium Fluoride Deposition for Uranium, section, 4.10. For analyses not requiring U, discard solution into the dilute acid waste stream. **See step 4.7.20 of AP11 JHA.**

4.8 Organic Destruction for Thorium

4.8.1 Add 10 mL 16 M HNO_3, 3 mL 11.7 M $HClO_4$, and 2 mL fusion solution to each Th fraction. Carefully heat the solutions to dryness. Allow to cool. **See step 4.8.1 of AP11 JHA.**

4.8.2 Add 10 mL 0.5 M HCl to dissolve the fusion cake. Heat gently, if necessary. **See step 4.8.2 of AP11 JHA.**

4.8.3 Transfer solution to a labeled centrifuge tube. Rinse flask with water and add to the centrifuge tube. Proceed to Cerium Fluoride Deposition for Am, Cm, Pu, Np, and Th, section 4.11.

4.9 Americium/Lanthanide Separation

4.9.1 Place one labeled Ln resin column per sample into column rack. Add 5 mL of the DTPA eluent to each column and allow to drain into a waste container. Repeat. **See Step 4.9.1 of AP11 JHA.**

4.9.2 For each sample from step 4.7.13, add 2 mL Ce carrier and mix. Add 1 drop 30-35% H_2O_2 and immediately add concentrated NH_4OH drop-wise (periodically mixing) until a brown color or brown precipitate remains in the tube (usually about 5-10 mL concentrated NH_4OH is needed). **See step 4.9.2 of AP11 JHA.**

4.9.3 Add 5 more drops concentrated NH_4OH. Allow precipitate to settle for at least 30 minutes. Do not decant supernate until ready to proceed with step 4.9.4. Centrifuge at 2000 RPM for 5 minutes. Carefully decant and discard the supernate into dilute acid waste container.

NOTE: Do not start this part of the procedure if it cannot be completed without interruption. The procedure usually takes three to five hours

4.9.4 Dissolve the precipitate with 12 drops of 2 M HNO_3 and vortex. Heat in a hot water bath. Be sure all precipitate is dissolved and the solution is clear and colorless. **See step 4.9.4 of AP11 JHA.**

NOTE: If the precipitate does not dissolve with 12 drops, an additional 3-4 drops may be added. If the precipitate still will not dissolve, see Laboratory Manager or designee.

4.9.5 Add 2 drops of 1 M hydroxylamine hydrochloride to reduce Ce^{4+} to Ce^{3+}. Mix gently. Add 10 mL DTPA eluent to solution. **See step 4.9.5 of AP11 JHA.**

4.9.6 Pour sample through the pre-conditioned Ln resin column and collect eluent in a labeled centrifuge tube.

4.9.7 Rinse the tube with 5 mL of DTPA eluent and pour through column. Collect in the same centrifuge tube from step 4.9.6. **See step 4.9.7 of AP11 JHA.**

4.9.8 Pour an additional 15 mL of DTPA eluent through column and collect in the same centrifuge tube. **See step 4.9.8 of AP11 JHA.**

4.9.9 Place waste beaker under each Ln resin column. Pour 10 mL 6 M HCl through each column and allow to drain (this removes all lanthanides from the column). Pour two portions of 5 mL 0.1 M HCl and allow to drain.

4.9.10 For each sample from step 4.9.8, proceed to Cerium Fluoride Deposition for Am, Cm, Pu, Np, and Th, section 4.11.

4.10 Cerium Fluoride Deposition for Uranium

4.10.1 To each sample from step 4.5.19 or step 4.7.19, add 1 drop 0.1% safranin-O, and 20% $TiCl_3$ drop-wise until the solution becomes either colorless (U only procedure) or yellow/tan (multiple of actinide procedure). **See steps 4.10.1 through 4.10.2 of AP11 JHA.**

4.10.2 Add 50 µL Ce carrier, mix, and add 2-5 mL 28 M HF. Let stand for at least 15 minutes.

4.10.3 Insert a 0.1 µm filter into a polysulfone filtering apparatus.

4.10.4 Add 2 to 4 mL 95% ethanol to the filter and apply vacuum.

4.10.5 Pour sample onto the filter and allow to drain. **See step 4.10.5 of AP11 JHA**

4.10.6 Rinse centrifuge tube with 3-5 mL water and pour onto filter and drain.

4.10.7 Pour 3-5 mL 95% ethanol onto the filter and drain.

4.10.8 Put filter on a stainless steel disc with double stick tape or pre-taped disc.

4.10.9 Dry filter under a heat lamp for at least 15 minutes. **See step 4.10.9 of AP11 JHA**.

4.10.10 Submit samples for alpha spectrometry counting.

4.11 Cerium Fluoride Deposition for Am, Cm, Pu, Np, and Th

4.11.1 Add 50 µL Ce carrier and 2-5 mL 28 M HF for Am, Cm, Pu, and Np. Use only 1 mL 28 M HF for Th. Let stand for at least 15 minutes. **See steps 4.11.1 through 4.11.4 of AP11 JHA.**

4.11.2 Insert a 0.1 µm filter into a polysulfone filtering apparatus.

4.11.3 Add 2 to 4 mL 95% ethanol to the filter and apply vacuum.

4.11.4 Pour sample onto the filter and allow to drain.

4.11.5 Rinse centrifuge tube with 3-5 mL water and pour onto filter and drain.

4.11.6 Pour 3-5 mL 95% ethanol onto the filter and drain.

4.11.7 Put filter on a stainless steel disc with double stick tape or pre-taped disc.

4.11.8 Dry filter under a heat lamp for at least 15 minutes. **See step 4.11.8 of AP11 JHA.**

4.11.9 Submit samples for alpha spectrometry counting.

5.0 CALIBRATIONS

5.1 Alpha Spectrometer Calibration

Refer to Section 5.0 of CP2 for calibration procedure.

5.2 pH Meter Calibration

5.2.1 Press the Mode key until pH is displayed.

5.2.2 Rinse the electrode with water and place it in the pH 2.40 buffer.

5.2.3 Press the Calibrate key. The date and time of last calibration will be displayed.

5.2.4 Press 3 then "Yes" to select a three buffer calibration.

5.2.5 When "Buffer #1" is displayed, enter the value of the buffer being used and press "Yes".

5.2.6 Remove the electrode from the buffer and rinse with water.

5.2.7 Insert the electrode into the pH 2.60 buffer. When "Buffer #2" is displayed, enter the value of the buffer being used and press "Yes".

5.2.8 Remove the electrode and rinse with water.

5.2.9 Insert the electrode into the pH 2.80 buffer. When "Buffer #3" is displayed, enter the value of the buffer being used and press "Yes". The slope is calculated and shown as a percentage. The meter automatically proceeds into the "Measure" mode.

5.2.10 Rinse the electrode and store in the electrode storage solution.

6.0 CALCULATIONS

The samples analyzed by this technique are spiked with tracer radionuclides which are standardized in this laboratory using NIST traceable materials.

Critical data values will be documented on standard forms and will be maintained as critical records either hard copy or electronically. The following equations define the critical data values. All data will be recorded and reduced according to these calculations.

$$Concentration = \frac{G - B}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi/unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{G + B}}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi/unit$$

$$2\sigma\ TPU = C \cdot 1.96\sqrt{\frac{G + B}{(G - B)^2} + RE^2 + RY^2 + RQ^2} = pCi/unit$$

$$MDC = \frac{3 + 4.65\sqrt{B}}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi/unit$$

To calculate efficiency: $$E = \frac{C_{STD} - B}{(STD\alpha \cdot A \cdot T)}$$

To calculate yield: $$Y = \frac{U - 232_{MA}}{U - 232_{KA}}$$

Where:	A	=	alpha abundance in α/d
	B	=	detector background counts in
	C	=	concentration pCi/units
	C_{STD}	=	standard counts
	E	=	alpha counting efficiency (c/α)
	G	=	sample gross counts
	MDC	=	minimum detectable concentration
	Q	=	sample quantity
	RE	=	1σ relative uncertainty of the efficiency
	RY	=	1σ relative uncertainty of the yield
	RQ	=	1σ relative uncertainty of the quantity
	STDα	=	emission rate of the standard (d/m)
	T	=	count time in minutes
	TPU	=	total propagated uncertainty
	$U\text{-}232_{MA}$	=	measured activity of U-232 tracer
	$U\text{-}232_{KA}$	=	known activity of U-232 tracer
	Y	=	tracer yield
	2.22	=	dpm/pCi conversion

7.0 RECORDS

7.1 Reference QP Manual for general record requirements.

7.2 A system backup to DAT tape or equivalent is performed weekly to protect spectra collected during the previous week.

7.3 A full system backup to DAT tape or equivalent is performed monthly. This backup includes system operating files and all files located on the hard drive.

7.4 Hard copies of assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data sheets show the required data and information. These forms or the equivalent should be completed and retained:

- Alpha Spec Analysis Assignment Form
- Alpha Spec Lab Data Sheet
- Alpha Spec Concentration and Uncertainty Report

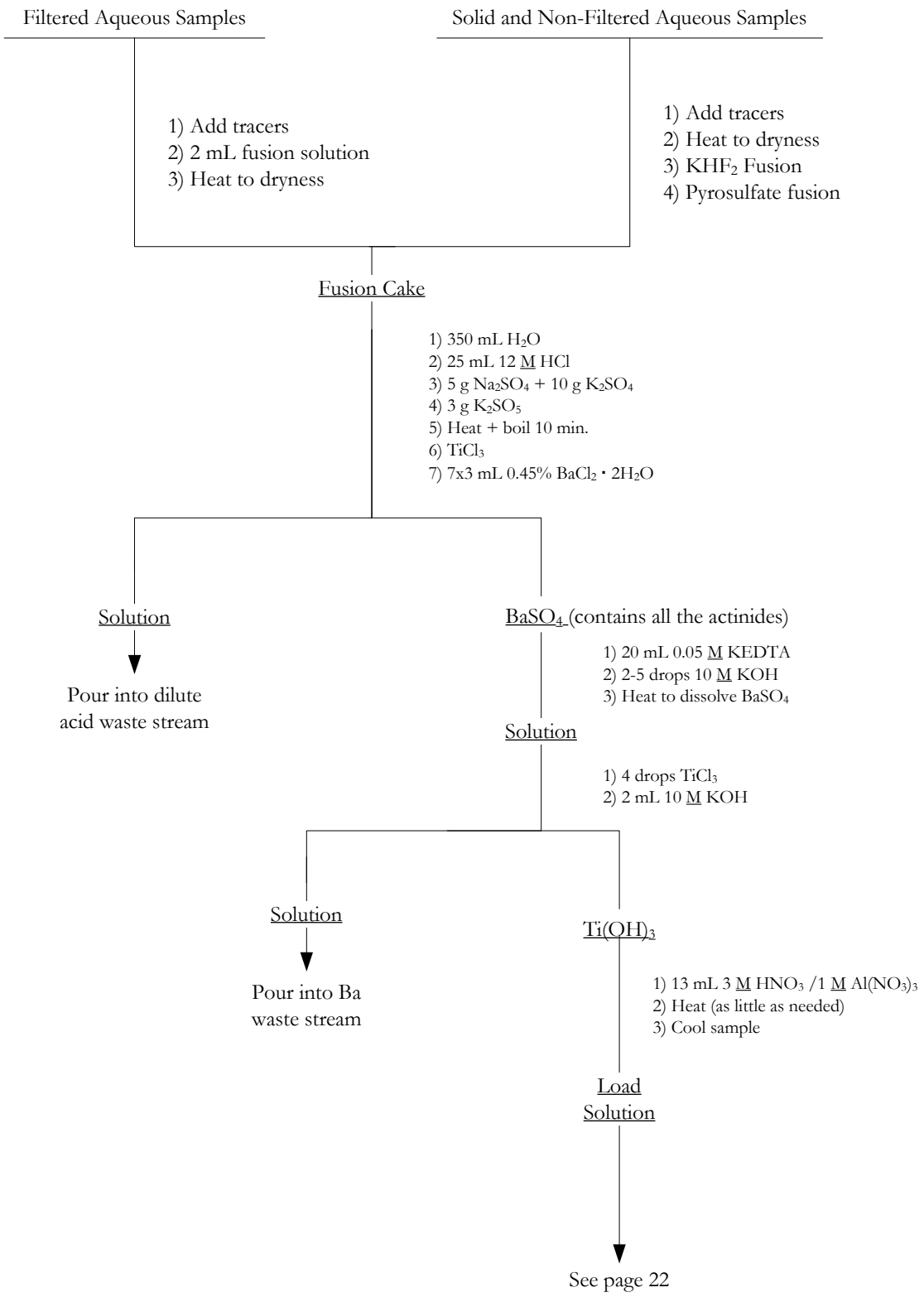


Figure 1: Flow diagram for AP11: Sequential Determination of the Actinides (Am/Cm, Pu/Np, Th, & U) in Environmental Samples Using Total Sample Dissolution and Extraction Chromatography

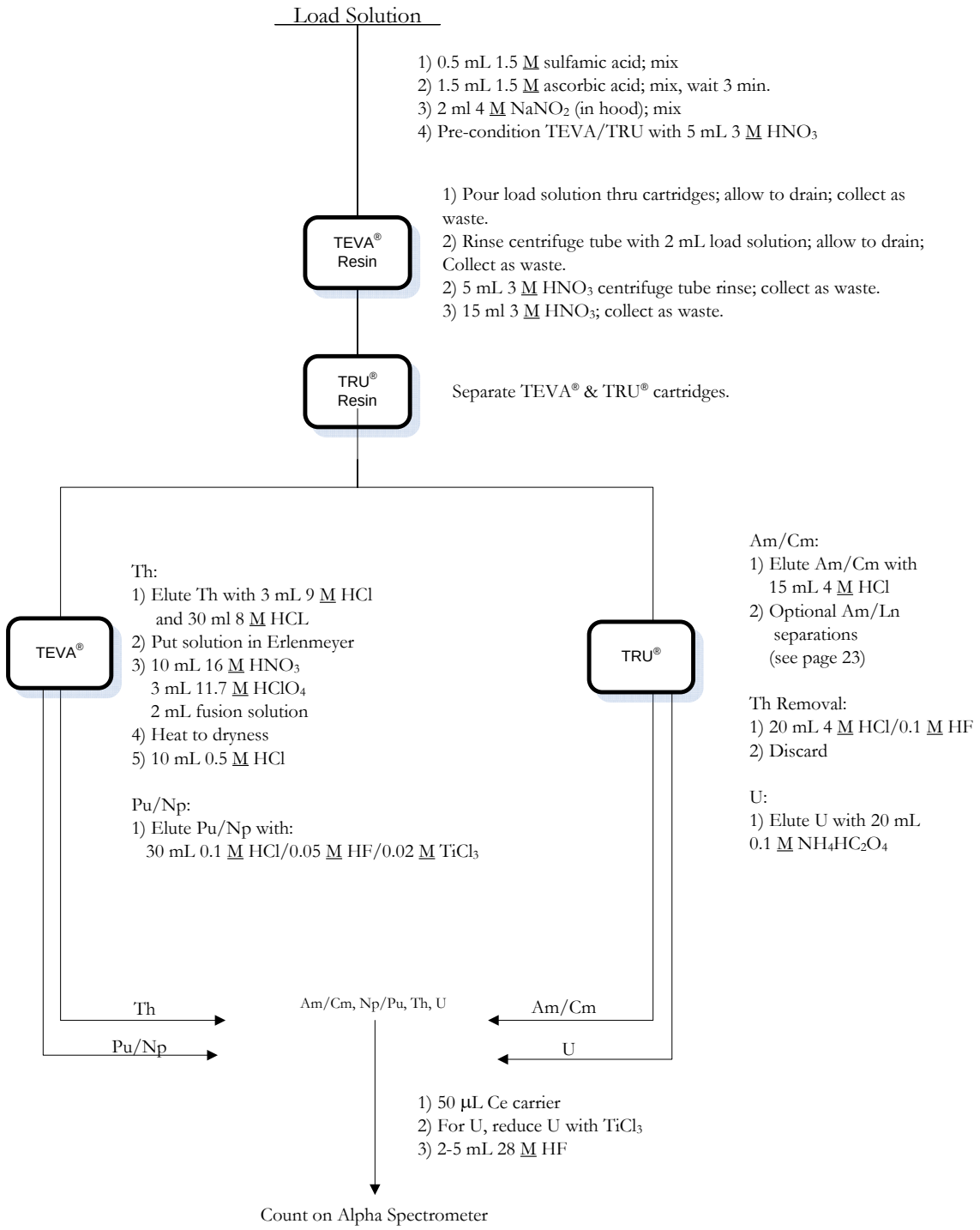
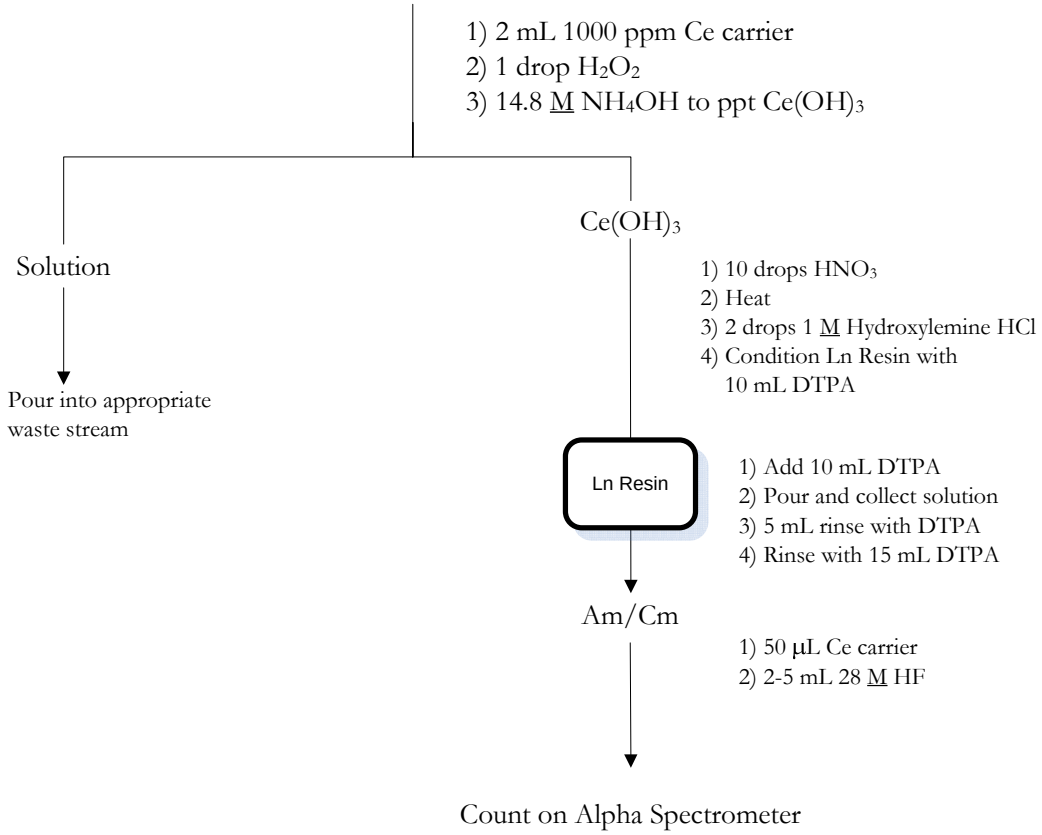


Figure 1 (continued): Flow diagram for AP11: Sequential Determination of the Actinides (Am/Cm, Pu/Np, Th, & U) in Environmental Samples Using Total Sample dissolution and Extraction Chromatography

Am/Ln Separation (optional)



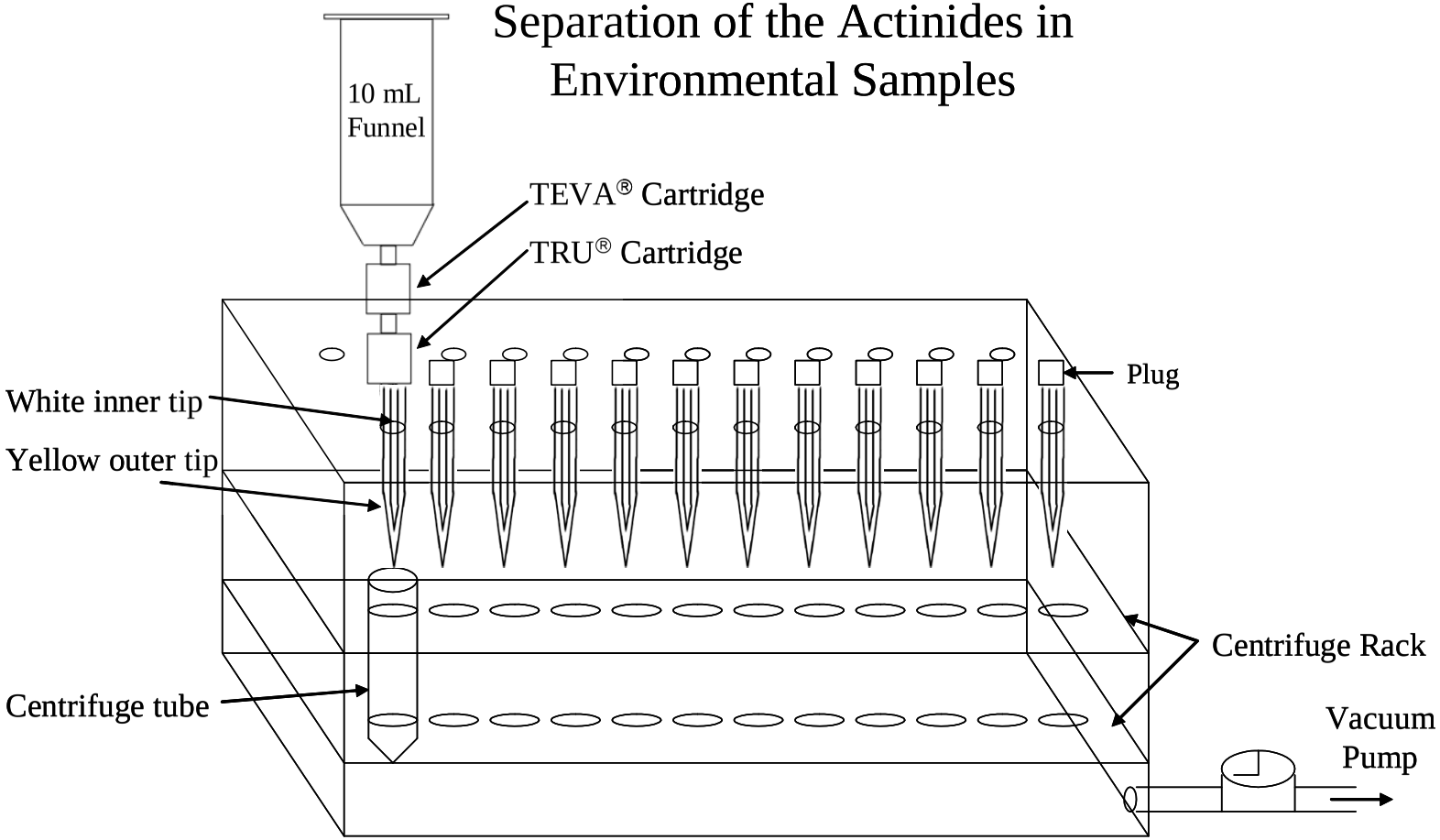


Figure 2: Vacuum Box Set-up for Extraction Chromatography

AP11(Rev 4) - ALPHA SPEC ANALYSIS ASSIGNMENT FORM

Assigned To: _____ **Date:** _____ **Batch:** _____

Task #: _____ **LWR #:** _____ **Activity Level*:** _____

Sample #s: _____

_____

Analysis Required:

					Initials
☐	Am Tracer # _____	Volume _____	Units _____		☐
☐	Pu Tracer # _____	Volume _____	Units _____		☐
☐	Th Tracer # _____	Volume _____	Units _____		☐
☐	U Tracer # _____	Volume _____	Units _____		☐

Pipette # _____ Volume (mL) _____ Weight (g) _____

QC Required:

Blank ☐

					Initials
LCS ☐	Am Std # _____	Quantity _____	Units _____		☐
	Cm Std # _____	Quantity _____	Units _____		☐
	Np Std # _____	Quantity _____	Units _____		☐
	Pu Std # _____	Quantity _____	Units _____		☐
	Th Std # _____	Quantity _____	Units _____		☐
	U Std # _____	Quantity _____	Units _____		☐

Replicate ☐ **Sample #** _____ **# Replications** _____

					Initials
Matrix Spk ☐ **Sample #** _____					
	Am Std # _____	Volume _____	Units _____		☐
	Cm Std # _____	Quantity _____	Units _____		☐
	Np Std # _____	Volume _____	Units _____		☐
	Pu Std # _____	Volume _____	Units _____		☐
	Th Std # _____	Volume _____	Units _____		☐
	U Std # _____	Volume _____	Units _____		☐

SPECIAL INSTRUCTIONS: _____

_____

_____

* If Activity Level is indicated as Moderate or High, perform area survey

COMMENTS: _____

_____

_____

_____

AP11(Rev 4) - ALPHA SPEC LAB DATA SHEET

Sample #								
Sample Quantity								
Quant. Units								
Ash Weight (g)								
Dry/Ash Ratio								

Sample #								
Sample Quantity								
Quant. Units								
Ash Weight (g)								
Dry/Ash Ratio								

Sample #								
Sample Quantity								
Quant. Units								
Ash Weight (g)								
Dry/Ash Ratio								

Procedure AP11 - Revision 4
Alpha Spec Concentration & Uncertainty Report
For Task #:

Batch #: **Acq Date:**

AVERAGE EFFICIENCY:		YIELD:		CORRECTED TRACER:		SAMPLE QUANTITY	
DETECTOR #: 012							
SAMPLE ID	ISOTOPE	Conc. (pCi/t)	TPU (pCi/t)	MDC (pCi/t)	ENERGY (KEV)	SAMPLE COUNTS	DETECTOR BKG
	U-234						
	U-235						
	U-238						
Total U=		TPU Error=					
RATIO OF U-238/U-235=							
RATIO OF U-234/U-235=							
RATIO OF U-238/U-234=							

AVERAGE EFFICIENCY:		YIELD:		CORRECTED TRACER:		SAMPLE QUANTITY	
DETECTOR #: 013							
SAMPLE ID	ISOTOPE	Conc. (pCi/t)	TPU (pCi/t)	MDC (pCi/t)	ENERGY (KEV)	SAMPLE COUNTS	DETECTOR BKG
	U-234						
	U-235						
	U-238						
Total U=		TPU Error=					
RATIO OF U-238/U-235=							
RATIO OF U-234/U-235=							
RATIO OF U-238/U-234=							

Standard	Standard Known Activity (pCi)	Standard Known Uncertainty	Meas./Known Activity Ratio	Meas./Known Uncertainty Ratio
U-234				
U-238				
BLK CORRECT? YES[ ] NO[ ]				
LCS CORRECT? YES[ ] NO[ ]				
YIELDS CORRECT? YES[ ] NO[ ]				
IF NO, SPECIFY REASON:				
			QC Review: (Initials/Date)	

Analyst Review _____ Date _____

Reviewed By _____ Date _____

Given To: _____ Date _____

QC Entered By _____ Date _____