

AP3

ISOTOPIC DETERMINATION OF AMERICIUM, PLUTONIUM, URANIUM, NEPTUNIUM, AND/OR THORIUM IN SOIL, WATER, AIR FILTERS, AND BIOTIC MATERIAL

PART A

PRINCIPLE

Soil samples are dissolved by a combination of potassium hydrogen fluoride and pyrosulfate fusions. The fusion cake is dissolved and all alpha emitters are coprecipitated on barium sulfate. Uranium is separated from the other actinides during a second coprecipitation. The barium sulfate is dissolved and the americium, plutonium, neptunium, and thorium, are separated by liquid-liquid extraction. Uranium, or analyses requiring thorium only, is separated from other actinides using EDTA. All actinides are coprecipitated on cerium fluoride and counted with an alpha spectrometer system.

Water samples are acidified and evaporated to dryness, and the analysis begins with the pyrosulfate fusion. Water samples with high dissolved solids are evaporated to dryness and the residue is treated as soil.

Air filters and biotic material are ashed and the residue is treated as soil.

REFERENCES

1. Claude W. Sill, Kenneth Pupal, and Forest D. Hindman, Anal. Chem. **46**, 1725 (1974).
2. Claude W. Sill and Roger L. Williams, Anal. Chem. **53**, 412 (1981).
3. Claude W. Sill, Anal. Chem. **46**, 1426 (1974).
4. Claude W. Sill, Anal. Chem. **36**, 675 (1964).
5. Roger P. Bernabee, Donald R. Percival, and Forest D. Hindman, Anal. Chem. **52**, 2351 (1980).
6. Annual Book of ASTM, Standards Vol. 11.02, pp. 300-303, pp. 380-381, pp. 407-411.
7. Claude W. Sill, David Sill, Waste Management, Vol. 9, pp 219-229 (1989).
8. EML Procedures Manual, 27th Edition, Volume I, pp 4.5-246, 247 (1992)

Certification Record for

PROCEDURE AP3

ISOTOPIC DETERMINATION OF AMERICIUM, PLUTONIUM, URANIUM, NEPTUNIUM AND/OR THORIUM IN SOIL, WATER, AIR FILTERS AND BIOTIC MATERIAL

CHECKPOINTS

- | | | | |
|----|------------------------|-------|-------|
| 1. | JOB HAZARD ANALYSIS | _____ | _____ |
| 2. | MSDS/HAZARDS DISCUSSED | _____ | _____ |
| 3. | FLUORIDE FUSION | _____ | _____ |
| 4. | PYROSULFATE FUSION | _____ | _____ |
| 5. | BARIUM SULFATE PPT | _____ | _____ |
| 6. | ORGANIC EXTRACTION | _____ | _____ |
| 7. | SAMPLE DEPOSITION | _____ | _____ |

ANALYST SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN RATIO: _____

COMMENTS: _____

PART B

1.0 PURPOSE AND SCOPE

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

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP3 JHA.**

Ammonium hydroxide, NH_4OH , concentrated, ACS reagent.

Barium Chloride solution, 0.45% (w/v): Dissolve 4.5 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 900 mL reagent water. Filter through DM-450 filter. Dilute to 1 L with reagent water.

Bis(2-ethylhexyl)hydrogen phosphate, HDEHP, 15%: Measure 75 mL HDEHP into a 500 mL graduated cylinder. Dilute to 500 mL with n-heptane. Stir to mix.

Carbon Suspension: Fume one 47 mm GA-6 or GA-4 metrical filter in 5 mL 18 M H_2SO_4 . Cool and dilute to 50 mL with water.

Note: This solution is needed only when 0.1 μm filters are not available.

Cerium carrier 1 mg/mL: AA quality Ce solution of 1000 $\mu\text{g/mL}$.

2,5-Di-tert-butylhydroquinone, DBHQ, 0.2 M: Dissolve 11.1 g of purified DBHQ in 200 mL 2-ethyl-1-hexanol. Dilute to 250 mL with 2-ethyl-1-hexanol. Filter through DM-450 filter.

Purification of DBHQ:

1. To a 800 mL beaker add 100 g of reagent DBHQ and a stir bar.
2. Add 500 mL of ethanol. Stir at moderate speed to dissolve solid.
3. Slowly add 100 mL of 0.0006 M HNO_3 in 5 mL intervals. The precipitate will fall out of solution. After all the 0.0006 M HNO_3 has been added, continue to stir for 10 minutes.
4. Filter the solution and precipitate through a 125 cm cumo filter. Break the precipitate cake free from the filter and allow to air dry overnight.
5. Transfer the dried precipitate to a brown plastic bottle and label as "Purified DBHQ".

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. Dilute

solution to 1 L and adjust pH using either concentrated NH_4OH or concentrated HCl to 2.80 ± 0.05 using a pH meter.

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) solution; dissolve 2.5 g $\text{Fe}(\text{NH}_4)\text{SO}_4$ in 10 mL H_2O , prepared fresh daily.

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

Hydrochloric acid, HCl , concentrated, 12 M.

Hydrochloric acid, 3 M: Dilute 250 mL concentrated HCl to 1 L with reagent water.

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

Hydrochloric acid, 0.1 M, add 33 mL 3 M HCl to 900 mL reagent water. Dilute to 1 L with reagent water and mix.

Hydrofluoric acid, HF , concentrated, 48%: **CAUTION: Skin contact with HF causes very severe burns.**

Hydroxylamine Hydrochloride, $\text{NH}_2(\text{OH})\text{HCl}$, 1 M, dissolve 6.9 g in 50 mL reagent water and dilute to 100 mL with reagent water and mix.

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

Hydrazine-Sulfamic Acid Solution, $\text{N}_2\text{H}_2/\text{H}_2\text{NSO}_3\text{H}$: **CAUTION: Handle hydrazine with extreme care. Do not use near open flames. Always perform work in a hood.** Dissolve 97.1 g sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$) in 150 mL reagent water. Add 280 mL 35% hydrazine. Wear gloves and work only in a hood when handling hydrazine. Dilute to 500 mL with reagent water and mix.

Nitric acid, HNO_3 , concentrated, 16 M.

Nitric acid, HNO_3 , 0.0006 M, add 3.15 mL of 0.1 M HNO_3 to 400 mL of reagent water. Dilute to 500 mL with reagent water and mix.

Nitric acid, HNO_3 , 2 M, slowly add 250 mL 4 M HNO_3 to 200 mL water. Dilute to 500 mL with reagent water and mix.

Nitric acid, HNO_3 , 4 M: To 750 mL reagent water, add 250 mL concentrated HNO_3 .

Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, 4% (w/v); dissolve 4 g oxalic acid in 50 mL reagent water. Dilute to 100 mL with reagent water and mix.

Potassium metabisulfite, $\text{K}_2\text{S}_2\text{O}_5$, 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 washdown after use.**

Potassium Ethylenediaminetetraacetic acid, KEDTA, 0.05 M: Dissolve 20.2 g KEDTA in 800 mL reagent water, dilute to 1 L with reagent water. Using digital pH meter, adjust pH to 10.6 using 10 M KOH.

Potassium Hydroxide, KOH, 10 M: Slowly dissolve 561 g KOH in 400 mL reagent water, in a cold water bath. Dilute to 1 L with reagent water.

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

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

Sodium Nitrite, NaNO_2 , 25% (w/v): dissolve 2.5 g NaNO_2 in 10 mL reagent water. Make fresh daily.

Sodium sulfate, Na_2SO_4 , anhydrous crystal.

Substrate Suspension: Dilute 10 mL cerium carrier (1000 $\mu\text{g}/\text{mL}$) and 20 mL 12 M HCl to 250 mL with reagent water. Dilute 8 mL 48% HF to 250 mL with reagent water. Combine the solutions and add 3 mL of carbon suspension. Vigorously shake the substrate solution prior to use. The carbon in the substrate permits visual observation of the area of the otherwise white CeF_3 on the white background of the filter.

Note: This solution is needed only if 0.1 μm filters are not available.

Sulfuric acid, H_2SO_4 , concentrated, 18 M.

Thorium-234 Tracer: See Reference No. 8.

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

3.0 APPARATUS

Equipment lists may be found in references 1 through 5. All procedures require gloves, lab coats and eye protection at all times. All work is performed in fume hoods, with the exception of weighing samples and reagents.

4.0 PROCEDURE

Before proceeding, you must be certified as indicated in QCP1 of this manual and Section 3 of the QA Manual. See page two of this procedure for a copy of the certification record.

4.1 Sample Decomposition

- 4.1.1 Measure and record sample quantity and media. **See step 4.1.1 of AP3 JHA.** Typical samples are 1 g dry soil, 0.25 L water or 10 g dry vegetation. Soil and vegetation are weighed into platinum dishes. If water is dried in platinum go to step 4.1.5; if transferred to a beaker for BaSO_4 precipitation go to step 4.2.1.
- 4.1.2 Wet ash samples with significant organic content, using nitric and sulfuric acids.
- 4.1.3 Add appropriate amounts of tracer. **See step 4.1.3 of AP3 JHA. Do not mix HCl and HNO_3 in platinum.** Dry as needed to avoid mixed acids. For filter and smear samples add tracer(s) directly to filter and dry. Proceed as directed for soil.
- 4.1.4 For filtered water for U only or Th proceed to step 4.2.1.
- 4.1.5 Add ~12 g KHF_2 to the soil. **See step 4.1.5 of AP3 JHA.**
- 4.1.6 Place the platinum dish on a ring stand using a nichrome triangle. **See step 4.1.6 of AP3 JHA.**
- 4.1.7 Start heating the sample over a blast burner with low flame. Increase heat as quickly as possible to dryness. **See step 4.1.7 of AP3 JHA.**
- 4.1.8 Use as much heat as possible, with limited splattering, to bring the temperature to about 900°C . Continue heating until total dissolution

occurs. Swirl the hot melt to ensure removal of sample clinging to the sides of the dish. **See step 4.1.8 of AP3 JHA.**

- 4.1.9 Remove the melt from the burner and swirl gently around the dish to form a thin layer upon cooling. (Never set hot platinum on iron). **See step 4.1.9 of AP3 JHA.**
- 4.1.10 Add ~15 mL concentrated H_2SO_4 to the fluoride cake. The acid should be added to the edge of the cake and allowed to run to the bottom of the dish. **See step 4.1.10 of AP3 JHA.**
- 4.1.11 After the addition of H_2SO_4 , heat as fast as frothing will allow until the fluoride cake is totally dissolved. **See step 4.1.11 of AP3 JHA.**
- 4.1.12 Remove from heat and add ~3.0 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, then maintain this temperature for approximately 1 minute. **See step 4.1.12 of AP3 JHA.**
- 4.1.13 Remove the melt from the burner and swirl gently around the dish to form a thin layer upon cooling. **See step 4.1.13 of AP3 JHA.**
- 4.1.14 Transfer hardened pyrosulfate cake to sample container by gently bending dish to crack and loosen cake. **See step 4.1.14 of AP3 JHA.**

4.2 Barium Sulfate Precipitation to Separate Uranium From Other Actinides

- 4.2.1 To a 800 mL beaker 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 bring the solution to a boil. **See step 4.2.1 of AP3 JHA.**
- 4.2.2 Add 5 g of Na_2SO_4 . If analyzing for Pu, add 10 g K_2SO_4 . Proceed to step 4.2.3 once the solids have dissolved. **See steps 4.2.2 through 4.2.5 of AP3 JHA.**
- 4.2.3 Carefully add the pieces of pyrosulfate cake 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.
- 4.2.4 For analyses requiring Pu, slowly add ~3 g $\text{K}_2\text{S}_2\text{O}_5$ with stirring and 1.0 mL 25% ferrous ammonium sulfate (prepared fresh daily). Heat and stir 30 minutes.

- 4.2.5 Add 15 mL 0.45% (w/v) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in five 3 mL portions. Boil for approximately 1 minute after each addition.
- 4.2.6 Using a teflon filtering chimney, filter the hot solution through a Supor 450 or DM 450 47 mm membrane filter. Save the filtrate for uranium analysis. **See step 4.2.6 of AP3 JHA.**
- Note: If not analyzing for uranium, discard the supernate in the HCl waste container.**
- 4.2.7 Wash the precipitate left in the beaker onto the filter using reagent water.
- 4.2.8 Place the BaSO_4 precipitate in a 250 mL Erlenmeyer flask for combinations of Am, Pu, Th and/or Np; go to Section 4.4.
- 4.2.9 For Th only, place filter in 50 mL centrifuge tube. Go to step 4.3.10.
- 4.2.10 For uranium proceed immediately to step 4.3.2.

4.3 Uranium Precipitation and Deposition

- 4.3.1 If the filtrate from step 4.2.6 cools, filter through a Supor 450 or DM 450 membrane filter in a teflon filtering chimney. Discard filter.
- 4.3.2 Cover with a watch glass and heat the solution to boiling.
- 4.3.3 Perform Po separation if needed (see Laboratory Manager or designee for procedure).
- 4.3.4 Add 4 drops 1% aqueous safranin-O. This should produce a reddish color. **See steps 4.3.4 through 4.3.6 of AP3 JHA.**
- 4.3.5 Add 20% TiCl_3 dropwise until the reddish color changes to the colorless leuco form. Add 3 more drops TiCl_3 . The uranium is reduced from the VI oxidation state to the IV oxidation state for later co-precipitation with BaSO_4 .
- 4.3.6 Add 12 mL 0.45% (w/v) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in four 3 mL portions. Boil approximately 1 minute after each addition.
- 4.3.7 Remove from heat, cool overnight at room temperature, allowing for BaSO_4 precipitate to settle. Go to step 4.3.9. Or while hot, using a teflon filtering chimney filter through a Supor 450 or DM-450 47 mm

membrane filter. Place filter in a centrifuge tube. Pour supernate into the dilute HCl waste container. **See step 4.2.6 of AP3 JHA.** Go to step 4.3.10.

- 4.3.8 Siphon as much liquid as possible without disturbing the precipitate. Transfer precipitate to a centrifuge tube, with reagent water. Centrifuge at 2000 rpm for 10 minutes. Decant and discard supernate in HCl waste container. **See step 4.3.8 of AP3 JHA.**
- 4.3.9 Add 20 mL 0.05 M KEDTA and 2-5 drops 10 M KOH, mix, heat in water bath until precipitate dissolves, (approximately 10 minutes). **See step 4.3.9 of AP3 JHA.**
- 4.3.10 Add 4 drops TiCl_3 and 2 mL 10 M KOH, mix, heat 10 minutes in water bath until the $\text{Ti}(\text{OH})_4$ precipitate settles. Centrifuge at 2000 RPM for 5 minutes. Decant and discard supernate in barium waste container. **See step 4.3.10 of AP3 JHA.**
- 4.3.11 Add 10 mL 3 M HCl, mix, heat in water bath until the $\text{Ti}(\text{OH})_4$ has dissolved. **See step 4.3.11 of AP3 JHA.**
- 4.3.12 Filter through a 25 mm DM-450 filter using a twist lock funnel. Collect supernate in a 50 mL centrifuge tube. Wash filter with 1-2 mL reagent water. Save supernate, discard filter into platinum waste crucible. **See step 4.3.12 of AP3 JHA.** For thorium deposition go to Section 4.5.3.

CERIUM FLUORIDE DEPOSITION FOR URANIUM ONLY

- 4.3.13 Add 1 drop 0.1% safranin-O (red), mix, 1-2 drops 20% TiCl_3 (slight purple), mix, add 50 μL Ce carrier and 2 mL 48% HF. Let stand for 10 minutes. Do not wait over 30 minutes. **See step 4.3.13 of AP3 JHA.**
- 4.3.14 Mount CeF_3 precipitate on a M5PUO25 filter or equivalent in the following manner:
- 4.3.14.1 Insert the M5PUO25 filter into a twist lock funnel.
- 4.3.14.2 Add 2 to 4 mL 95% ethanol to the filter and apply suction.

Note: Go to step 4.3.15.4 when using the recommended filter.

- 4.3.14.3 To the center of the filter, add 5 mL substrate suspension¹ under reduced suction. Apply hard suction² for about 30 seconds in order to firmly seat the substrate on the filter. **See step 4.3.14.3 of AP3 JHA.**
- 4.3.14.4 Apply hard suction, then add a well-shaken sample to the filter. After the sample has been added, reduce the suction to allow the sample to filter slowly. While the sample is filtering, wash the centrifuge tube with 2 to 4 mL reagent water and add to the filtering sample. **See step 4.3.14.4 of AP3 JHA.**
- 4.3.14.5 After the sample has filtered, add 5 mL reagent water, under hard suction, indirectly to the filter. The water helps remove residual HF from the filter.
- 4.3.14.6 After the water has passed, add 2 to 4 mL 95% ethanol under hard suction.
- 4.4 Sequential Extraction of Americium, Plutonium, Neptunium, and/or Thorium. Proceed as Directed for Element(s) Desired.
- 4.4.1 Add 30 mL HClO₄ to the 250 mL Erlenmeyer flask containing the filter. Place on hot plate, using medium heat (setting of 2.5 or 3). Do not agitate flask. As filter dissolves and forms a brown scum, slowly increase heat until acid begins to boil. The brown material should disappear and the solution should become clear. Remove from heat and allow to cool. **See step 4.4.1 of AP3 JHA.**
- 4.4.2 Transfer the solution into a 60 mL separatory funnel containing 10 mL 15% HDEHP. Rinse Erlenmeyer with 5 mL concentrated HClO₄ and add to separatory funnel. Shake 5 minutes. Let the phases separate for 3 minutes. Discard bottom phase in perchloric acid waste container. **See step 4.4.2 of AP3 JHA.**
- 4.4.3 Add 5 mL HClO₄ to separatory funnel. Shake 3 minutes. Let the phases separate for 3 minutes. Discard the bottom layer in perchloric acid waste container. **See step 4.4.3 of AP3 JHA.**

Note: Save perchloric acid waste for disposal by ESH.

¹The substrate should be hand shaken for about 2 minutes before being used with the sample.

²Hard suction is necessary to keep the substrate in place. If the substrate is displaced, the resolution for a sample can be reduced. A degraded spectrum reduces the reliability of the analytical data.

Note: Proceed through each step of procedure until element of interest is extracted. (ex. If analyzing for Pu, you must complete the Am steps first).

- 4.4.4 **Americium:** Add 10 mL 4 M HNO₃ and 1 mL 25% sodium nitrite (prepared fresh). Shake 2 minutes. Let the phases separate for 2 minutes. Drain and save the aqueous phase (bottom layer) in a labeled 250 mL Erlenmeyer flask. Discard excess sodium nitrite into sanitary drain. **See step 4.4.4 of AP3 JHA.**
- 4.4.5 Add 10 mL 4 M HNO₃. Shake 2 minutes. Let the phases separate for 2 minutes. Save and combine the aqueous phase (bottom layer) with preceding wash from step 4.4.4.
- 4.4.6 To the two combined strip solutions from step 4.4.5, add 10 mL of 12 M HCl and 3 mL of 11.7 M HClO₄. Heat on hot plate until fumes of HClO₄. There should be between 10 and 15 mL solution left. **See steps 4.4.6 - 4.4.10 of AP3 JHA.**
- 4.4.7 Pour solution into a centrifuge tube and rinse Erlenmeyer with 10 mL of 0.1 M HNO₃. Add this rinse to the centrifuge tube. (The total volume should be 25-35mL).
- 4.4.8 Add 2 mL of Ce³⁺ carrier (1000 µg/mL) to the centrifuge tube. Mix gently.
- 4.4.9 Add 1 drop 30-35% H₂O₂ and immediately add concentrated NH₄OH drop-wise (periodically mixing) until a brown color or brown precipitate remains in the tube (usually about 5-10 mL concentrated NH₄OH is needed).
- 4.4.10 Add 5 more drops concentrated NH₄OH. Allow precipitate to settle for at least 30 minutes. Centrifuge at 2000 RPM for 5 minutes. Carefully decant and discard the supernate.

Note: Do not start this part of the procedure if it cannot be completed without interruption. Usually takes five hours.

Ln Spec Column Preparation

- a. Pour 10 mL of 6 M HCl through the pre-packed 2mL volume column. **See steps 4.4.10a-c of AP3 JHA.**
- b. Add 5 mL of 0.1 M HCl to the column and allow to drain. Repeat.

- c. Add 5 mL of the DTPA eluent and allow to drain. Repeat.

Note: If analyzing for Am only, drain organic waste that remains in separatory funnel into organic waste container stored under the hood. Do not discard organic if analyzing for other elements.

- 4.4.11 Dissolve the precipitate with 10 drops of 2 M HNO₃. Heat in hot water bath. Be sure all precipitate is dissolved. See step 4.4.11 of AP3 JHA.

Note: If the precipitate does not dissolve with 10 drops, an additional 3-4 drops may be added. If the precipitate still will not dissolve, see Laboratory Manager or designee.

- 4.4.12 Add 2 drops of 1 M hydroxylamine hydrochloride to reduce Ce⁴⁺ to Ce³⁺. Mix gently. Add 10 mL DTPA eluent to solution. See step 4.4.12 of AP3 JHA.
- 4.4.13 Pour sample through the pre-treated column and collect eluent in a labeled centrifuge tube.
- 4.4.14 Rinse the tube with 5 mL of DTPA eluent and pour through column. Collect in the same centrifuge tube from step 4.4.13.
- 4.4.15 Pour an additional 15 mL of DTPA eluent through column and collect in the same centrifuge tube. Go to Section 4.5.4.
- 4.4.16 **Plutonium:** Add 10 mL 4 M HNO₃ and 2 mL hydrazine-sulfamic acid solution to the organic phase. Shake 2 minutes. Let the phases separate for 2 minutes. Discard aqueous phase into the dilute acid waste container. See steps 4.4.16 - 4.4.19 of AP3 JHA.
- 4.4.17 Add 5 mL 0.2 M DBHQ to the organic phase. Gently mix for 1 minute. Add 10 mL 4 M HNO₃ and 2 mL hydrazine-sulfamic acid solution to the organic phase. Shake 5 minutes. Let the phases separate for 2 minutes. Drain and save the aqueous phase (bottom layer) into a labeled 250 mL Erlenmeyer flask.
- 4.4.18 Add 10 mL 4 M HNO₃ and 2 mL hydrazine-sulfamic acid solution to the organic phase. Shake 5 minutes. Let the phases separate for 2 minutes. Save and combine the aqueous phase (bottom layer) with preceding wash from step 4.4.17.
- 4.4.19 Add 10 mL 4 M HNO₃ and 2 mL hydrazine-sulfamic acid solution to the organic phase. Shake 3 minutes. Let the phases separate for 2 minutes. Discard the aqueous phase (bottom layer) into the dilute acid waste container.

- 4.4.20 To the labeled Erlenmeyer flask add 2 mL fusion solution, 2.5 mL HNO₃, 2.5 mL HCl, and glass stir rod to the 250 Erlenmeyer flask. Heat on hot plate (setting 2 or 3) until a yellow color appears. Add 2.5 mL HNO₃, 2.5 mL HCl, and 1 mL HClO₄. Heat to dryness. Cool to room temperature. **See step 4.4.20 of AP3 JHA.** Go to Section 4.5.
- 4.4.21 **Thorium/Neptunium:** Add 15 mL toluene and 15 mL 4% (w/v) oxalic acid. Shake 3 minutes. Let the phases separate for 3 minutes. Drain and save the aqueous phase (bottom layer) into a labeled 250 mL Erlenmeyer flask. **See steps 4.4.21 - 4.4.22 of AP3 JHA.**
- 4.4.22 Add 5 mL 4% (w/v) oxalic acid to the organic phase. Shake 3 minutes. Let the phases separate for 3 minutes. Drain and save the aqueous phase (bottom layer) with the preceding wash from step 4.4.21.
- 4.4.23 Add 2 mL fusion solution, 1 mL HClO₄ to the 250 mL Erlenmeyer flask. Heat to dryness. Cool to room temperature. **See steps 4.4.23 of AP3 JHA.** Go to Section 4.5.
- 4.4.24 Drain organic waste that remains in separatory funnel into organic waste container stored under the hood.

4.5 Cerium Fluoride Deposition for Am, Pu, Np, and Th

- 4.5.1 Dissolve the pyrosulfate crystals in 10 mL 3 M HCl. **See steps 4.5.1 - 4.5.4 of AP3 JHA.**
- 4.5.2 Transfer the solution to a 50 mL centrifuge tube with reagent water. Total volume should be about 12 mL.
- 4.5.3 For Pu, add 1 drop 20% TiCl₃. **See step 4.3.14 of AP3 JHA.**
- 4.5.4 Add 50 µL Ce carrier (1000 µg/mL). **See step 4.3.14 of AP3 JHA.**
- 4.5.5 Add 2 mL 48% HF, mix well, and let stand for 10 minutes. Do not wait over 30 minutes. **See step 4.3.14 of AP3 JHA.** Go to step 4.3.15.

5.0 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 approved assignment and calculation form to 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.

$$\text{Concentration} = \frac{G - B}{T * E * Y * Q} = \text{pCi/unit}$$

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

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

$$\text{MDC} = \frac{3 + 4.65\sqrt{B}}{T * E * Y * Q} = \text{pCi/unit}$$

Where:

- G = Sample gross counts
- B = Detector Background Counts
- T = Count Time in minutes
- E = Alpha Counting Efficiency
- Y = Tracer Yield
- Q = Sample quantity
- TPU = Total Propagated Uncertainty
- MDC = Minimum Detectable Concentration
- RE = 1 σ relative uncertainty of the efficiency
- RY = 1 σ relative uncertainty of the yield
- RQ = 1 σ relative uncertainty of the quantity

6.0 RECORDS

- 6.1 Reference QA Manual for general record requirements.
- 6.2 A system backup to dat tape is performed weekly to protect spectra collected during the previous week.
- 6.3 A full system backup to dat tape is performed monthly. This backup includes system operating files and all files located on the hard drive.

6.4 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 should be completed and retained:

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

AP3(Rev 16) - ALPHA SPEC ANALYSIS ASSIGNMENT FORM

Assigned To: _____ Date: _____ Batch: _____
 Site/Site #: _____ LWR #: _____ Activity Lev*: _____
 Sample #'s: _____

ANALYSIS REQUIRED:

<input type="checkbox"/>	Am Tracer # _____	Volume _____	Units _____	Initials <input type="text"/>
<input type="checkbox"/>	Np Tracer # _____	Volume _____	Units _____	<input type="text"/>
<input type="checkbox"/>	Pu Tracer # _____	Volume _____	Units _____	<input type="text"/>
<input type="checkbox"/>	Th Tracer # _____	Volume _____	Units _____	<input type="text"/>
<input type="checkbox"/>	U Tracer # _____	Volume _____	Units _____	<input type="text"/>
	Pipet # _____	Weight _____	Volume _____	

QC REQUIRED:

Blank	<input checked="" type="checkbox"/>				
Standard	<input checked="" type="checkbox"/>	Am Std # _____	Quantity _____	Units _____	Initials <input type="text"/>
		Np Std # _____	Quantity _____	Units _____	<input type="text"/>
		Pu Std # _____	Quantity _____	Units _____	<input type="text"/>
		Th Std # _____	Quantity _____	Units _____	<input type="text"/>
		U Std # _____	Quantity _____	Units _____	<input type="text"/>
Replicate	<input type="checkbox"/>	Sample # _____	# Replications _____		
Matrix Spk	<input type="checkbox"/>	Sample # _____			
		Am Std # _____	Volume _____	Units _____	<input type="text"/>
		Np Std # _____	Volume _____	Units _____	<input type="text"/>
		Pu Std # _____	Volume _____	Units _____	<input type="text"/>
		Th Std # _____	Volume _____	Units _____	<input type="text"/>
		U Std # _____	Volume _____	Units _____	<input type="text"/>

SPECIAL INSTRUCTIONS: _____

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

AP3(Rev 16) - ALPHA SPEC LAB DATA SHEET

Detector #								
Sample #								
Sample Type**								
Sample Quantity								
Quant. Units								
Ash Weight								
Ash Wt. Units								
Dry/Ash Ratio								

Detector #								
Sample #								
Sample Type**								
Sample Quantity								
Quant. Units								
Ash Weight								
Ash Wt. Units								
Dry/Ash Ratio								

Detector #								
Sample #								
Sample Type**								
Sample Quantity								
Quant. Units								
Ash Weight								
Ash Wt. Units								
Dry/Ash Ratio								

- * If Activity Level is indicated as Moderate or High, perform area survey
- ** Indicate sample type (A=Ashed Soil, S=Unashed Soil, W=Water, X=Other, indicate)

Procedure AP3 - Revision 16
Alpha Spec Concentration & Uncertainty Report
For Site #:

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
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
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				
QC SAMPLES CORRECT? YES[] NO[] IF NO, SPECIFY REASON:				
				QC Review: _____ (Initials/Date)

Analyst Review

Date

Reviewed By

Date