4.5.6 Sequential Analyses

Se-01

ISOTOPIC URANIUM AND RADIUM-226

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to 5 g soil samples, 10 g vegetation and fecal ash samples and ion exchange resin from sampling columns. [Adapted from Fisenne et al. (1980), Hindman (1983), Sill (1961), and Sill and Williams (1981).]

Tracers and carriers are added to the sample which is pretreated with HNO_3-HF, fused with KF, and transposed to pyrosulfate. The cake is dissolved in HCl. Radium/ barium sulfate is precipitated, filtered, and dissolved in alkaline EDTA. The chemical yield for Ra is determined with the γ-emitting tracer ^{133}Ba. Radium-226 is determined by ^{222}Rn emanation.

Uranium is isolated by solvent extraction. The U isotopes are coprecipitated with Nd as the F^- for measurement by α spectrometry.

SPECIAL APPARATUS

1. 100-mL platinum dishes or 250-mL platinum crucibles.

2. Millipore glass filtration chimney, fritted glass support, and metal clamp - 47 mm diameter.

3. Millipore filters - 47 mm diameter, 0.45 μm pore size.

4. Polyethylene dispensing bottle or similar - see Specification 7-11.

5. Mechanical shaker.

6. Special apparatus for the microprecipitation of U are listed under the generic procedure, G-03.

SPECIAL REAGENTS

1. ^{133}Ba tracer solution - about 50 cps per 0.1 g aliquot, prepared in 1:99 HCl.

2. Barium carrier solution (20 mg mL^{-1}) - 30.4 g $BaCl_2$ L^{-1} in 1:99 HCl.

3. EDTA solution - 300 g tetrasodium salt of EDTA L^{-1} in H_2O.

4. Triethanolamine - 1:1 in H_2O.

5. ^{232}U tracer solution - about 0.17 Bq g^{-1} of solution in a dispensing bottle.

6. Alamine-336, tertiary tricaprylyl amine (Henkel Company, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.

SAMPLE PREPARATION

A. Soil and vegetation.

1. Weigh 5 g of soil or 10 g of fecal or vegetation ash into a 100-mL platinum dish. Add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution. Add a weighed aliquot of ^{232}U tracer solution (about 1 g for soil and about 0.5 g for fecal or vegetation ash).

2. Slowly add 10 mL of HNO_3 and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.

3. Continue the analysis as described under **Determination.**

B. Ion exchange resin.

1. Transfer the resin and paper pulp from the collection column (see Specification 7.4) to a 250-mL platinum crucible. Dry under a heat lamp and ash at 500°C in a muffle furnace for 48 h.

2. To the cooled crucible, add a weighed aliquot (about 0.1 g) of ^{133}Ba tracer solution and 1 mL of Ba carrier solution. Add a weighed aliquot (about 0.1 g) of ^{232}U tracer solution.

3. Continue the analysis as described under **Determination.**

DETERMINATION

A. Radium separation.

1. Weigh out 15 g of KF and add to the sample. Press the KF into the sample with a plastic spatula.

Caution: Wear rubber gloves and safety glasses during Steps 2-5.

2. Fuse the sample over an air-fed Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.

3. Using a burette, slowly add 17.5 mL of H_2SO_4 to the melt. Heat the dish on a hot plate until the cake dissolves and evaporate until SO_3 fumes appear.

4. Weigh out 10 g of Na_2SO_4, add to the dish and fuse over a blast burner until a clear melt accompanied by dense fumes is obtained. Cool the melt.

5. Transfer the cake to a 600-mL beaker containing 350 mL of hot water and 25 mL of HCl. Stir the solution to dissolve the cake. Cool for 1 h.

6. Filter the precipitate onto a 47 mm diameter 0.45 μm pore size Millipore filter, police the beaker and wash with H_2O. Reserve the filtrate for U separation.

7. Using a strong stream of H_2O from a wash bottle, transfer the precipitate to a 150-mL beaker. Discard the filter.

8. Add 5 mL of EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 15 min, adding 10 mL of H_2O and stirring occasionally. Reduce the sample volume to about 15 mL.

9. Filter the warm solution by gravity through a Whatman No. 42 filter paper into a 30-mL polyethylene bottle.

10. Wash the beaker and filter with hot water. Discard the filter.

11. Dilute the sample to the same liquid level as a known aliquot (about 0.1 g) of the ^{133}Ba tracer solution diluted to 25 mL in a 30-mL polyethylene bottle.

12. Gamma count the samples and standard to determine the chemical yield of Ba.

13. Transfer the sample to a ^{222}Rn bubbler with H_2O.

14. De-emanate ^{222}Rn by bubbling with forming gas for about 10 min at 100 mL min^{-1} as described in the Emanation Procedure for ^{226}Ra, Ra-03. Record the time as the starting time for ^{222}Rn buildup. Continue the analysis by the emanation technique.

B. Uranium separation.

1. Evaporate the reserved filtrate (**Radium Separation,** Step 6) to a 150-mL volume.

2. Add 150 mL of HCl to the sample solution and stir.

3. Remove the sample from the hot plate and cool to room temperature.

4. Transfer 100 mL of acid washed Alamine-336 into a 500-mL separatory funnel.

5. Transfer the sample solution into the separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.

6. Shake the separatory funnel for 5 min. Allow the phases to separate. Draw off the aqueous (lower) phase and discard.

7. Wash the organic phase four times for 5 min with equal volumes of 1:1 HCl. Discard the washings.

8. Strip the U from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker. Place the organic phase in a suitable container for disposal.

9. Evaporate the strip solution to near dryness.

10. Destroy any residual organic material with dropwise additions of HNO_3.

11. Evaporate the solution to dryness. Dissolve the residue in a few drops of HNO_3.

12. Convert the solution to the chloride with three 5-mL additions of HCl.

13. Add 1-2 mL of 1N HCl, prepared with filtered water (see Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry).

14. Continue the analysis under Procedure G-03, Microprecipitation Source Preparation for Alpha Spectrometry.

LOWER LIMIT OF DETECTION (LLD)*

^{226}Ra		
Counter Efficiency	(2%)	57.5
Counter Background	(cps)	0.0028
Yield	(%)	90
Blank	(cps)	0.0020
LLD (400 min)	(mBq)	3.3
LLD (1000 min)	(mBq)	1.7
Uranium Isotopes		
Counter Efficiency	(%)	40
Counter Background	(cps)	3.33×10^{-6} for ^{238}U 3.33×10^{-6} for ^{234}U
Yield	(%)	85
Blank	(cps)	3.33×10^{-6} for ^{238}U 3.00×10^{-5} for ^{234}U
LLD (400 min)	(mBq)	0.3 for ^{238}U 0.8 for ^{234}U
LLD (1000 min)	(mBq)	0.2 for ^{238}U 0.5 for ^{234}U
(5000 min)	(mBq)	0.1 for ^{238}U 0.2 for ^{234}U

*It is necessary to analyze the reagents used with each batch of samples so that blank corrections can be made for U and ^{226}Ra.

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Se-02

ISOTOPIC URANIUM, ISOTOPIC THORIUM AND RADIUM-226

Contact Person(s) : Isabel M. Fisenne

APPLICATION

The method is applicable to 5 g soil samples, 20 g vegetation ash samples and 50 g bone ash samples.

Soil, vegetation ash and bone ash samples are spiked with ^{229}Th, ^{232}U and ^{133}Ba tracer solutions. The soil and vegetation ash samples are pretreated with HNO_3-HF fused with potassium fluoride and transposed to pyrosulfate. The cake is dissolved in HCl. Bone ash samples are dissolved directly in HCl. Uranium isotopes are isolated by solvent extraction and are coprecipitated with neodymium as the fluoride for alpha spectrometry measurement. Thorium is coprecipitated with calcium as the acidic oxalate. The thorium is separated by solvent extraction and coprecipitated with neodymium as the fluoride for alpha spectrometry measurement. Barium carrier is added and $Ra{\cdot}BaS0_4$ is precipitated, filtered and dissolved in alkaline EDTA. The chemical yield is determined with the γ-emitting tracer ^{133}Ba and ^{226}Ra is determined by radon emanation.

SPECIAL APPARATUS*

1. 100-mL platinum dishes.

2. Polyethylene transfer pipettes.

3. Separatory funnels - 125, 250, 500 and 1000 mL.

* *Special apparatus and special reagents for the microprecipitation of uranium and thorium with neodymium as the fluoride are listed in Microprecipitation of the Actinides, G-03.*

4. Wrist action separatory funnel shaker unit.

5. Millipore filtration unit - 47 mm diameter Pyrex glass filtration chimney, fritted glass support and metal clamp.

6. Millipore filters - 47 mm diameter, 0.45 μm pore size.

7. Radon bubblers - see Specification 7.7.

SPECIAL REAGENTS

1. Uranium-232 tracer solution - about 0.2 Bq g^{-1} of solution in a polyethylene transfer pipette (see **Note 1**).

2. Thorium-229 tracer solution - about 0.2 Bq g^{-1} of solution in a polyethylene transfer pipette.

3. Barium-133 tracer solution - about 10 kBq g^{-1} of solution in a polyethylene transfer pipette. Add 0.1 g of tracer to each sample.

4. Alamine-336, tertiary tricapryl amine (Henkel Corp., 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 3:7 in toluene. Wash twice with an equal volume of 1:1 HCl. Prepare 100 mL of acid-washed 3:7 Alamine-336 for each sample.

5. Aliquat-336, methyltricapryl-ammonium chloride (Henkel Corp., 2430 N. Huachuca Dr., Tucson, AZ 85745-1273) 4:6 in toluene. Wash four times with an equal volume of 2N $HN0_3$ and once with an equal volume of 1:1 $HN0_3$. Prepare 50 mL of acid-washed 4:6 Aliquat-336 for each soil and vegetation ash sample and 100 mL for each bone ash sample.

6. Calcium propionate ($(CH_3CH_2COO)_2Ca$) - solid (see **Note 2**).

7. Oxalic acid (CHO_2COOH) - solid (see **Note 2**).

8. Barium carrier solution (20 mg Ba mL^{-1}) - 30.4 g of $BaCl_2$ L^{-1} of 1:99 HCl.

9. Ammonium sulfate solution (100 mg mL^{-1}) - 100 g of $(NH_4)_2SO_4$ L^{-1} of H_20.

10. EDTA solution - 500 g tetrasodium salt of EDTA L^{-1} of H_20.

11. Triethanolamine - 1:1 with H_20.

SAMPLE PREPARATION

A. Soil, milk, and vegetation ash.

1. Weigh 5 g of soil or up to 20 g of milk or vegetation ash into a 100-mL platinum dish. Add weighed aliquots of ^{133}Ba, ^{229}Th and ^{232}U tracer solutions (see **Note 3**).

2. Slowly add 10 mL of $HN0_3$ and 10 mL of HF to the sample and evaporate on a hot plate to near dryness.

3. Continue the analysis as described under **Sample Dissolution.**

B. Bone ash.

1. Weigh 50 g of ground, dry ashed bone into a 400-mL beaker. Add weighed aliquots of ^{133}Ba, ^{229}Th and ^{232}U tracer solutions (see **Note 3**).

2. Continue the analysis as described under **Sample Dissolution.**

SAMPLE DISSOLUTION*

A. Soil, milk, and vegetation ash.

1. Weigh 15 g of KF and sprinkle over the surface of the sample.

2. Fuse the sample over a Meker burner, gradually increasing the temperature until a clear melt is obtained. Cool the melt.

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* *Based upon Sill (1981).*

3. Slowly add 17.5 mL of H_2S0_4 to the melt. Heat the dish on a high temperature hot plate until the cake dissolves and heat until sulfur trioxide fumes appear.

4. Weigh 10 g of Na_2S0_4, add to the dish and fuse over the Meker burner until a clear melt, accompanied by dense fumes, is obtained. Cool the melt.

5. Transfer the cake to a 600-mL beaker containing 250 mL of hot 1:1 HCl. Stir the solution to dissolve the cake. If necessary, add additional HCl to completely dissolve the cake. Cool for 1 h.

6. Continue the analysis as described under **Uranium Separation.**

B. Bone ash.

1. Add 100 mL of HCl and heat gently on a hot plate for 10 min with occasional stirring.

2. Add 70 mL of water and stir to obtain a clear solution. Cool the solution for 1 h.

3. Continue the analysis as described under **Uranium Separation.**

URANIUM SEPARATION*

1. Transfer 50 mL of acid-washed Alamine-336 into each of two 500-mL separatory funnels.

2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 HCl and add the washings to the funnel.

3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phase into the second separatory funnel. Retain the organic phase in the first funnel.

**Based on Fisenne et al. (1980)*

4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off the aqueous phase into a 2000-mL beaker for subsequent analyses of thorium and radium.

5. Combine the two organic phases in one of the separatory funnels.

6. Wash the organic phase four times for 5 min with an equal volumes of 1:1 HCl. Combine the washings in the 2000-mL beaker (Step 4).

7. Strip the uranium from the organic phase by shaking twice for 5 min with 100-mL portions of 0.1N HCl. Combine the strip solutions in a 400-mL beaker. The organic phase is placed and retrained in a suitable disposal container (see **Note 4**).

8. Add 1 mL of H_2S0_4 to the strip solution and evaporate the solution to sulfur trioxide fumes.

9. Destroy any residual organic material with dropwise additions of $HN0_3$.

10. Evaporate the solution to dryness. Dissolve the residue in a few drops of HCl.

11. Convert the solution to the chloride with three 5-mL additions of HCl.

12. Add 1-2 mL of 1N HCl, prepared with filtered water (see Microprecipitation). Cool to room temperature.

13. Continue the analysis under Microprecipitation of the Actinides, G-03.

THORIUM SEPARATION*

A. Calcium oxalate collections.

1. Add 0.5 g of calcium carrier (2.5 g of calcium propionate) to the sample waste and wash solutions reserved from Steps 4 and 6 in **Uranium Separation**.

Based upon Fisenne and Perry (1978).

Note: DO NOT ADD CALCIUM CARRIER TO BONE ASH OR MILK SAMPLES.

2. Evaporate the solution volume to 100-200 mL.

3. Dilute the solution to 1400 mL with deionized water. Heat the solution to near boiling.

4. Adjust the pH to 2.5 with NH_40H.

5. Add 10 g of oxalic acid to soil, milk, and vegetation ash samples. Add 25 g of oxalic acid to bone ash samples.

6. Stir and heat the solution to a gentle boil. Continue heating for 5 min.

7. Adjust the pH to 2.5 with NH_40H. Gently boil the solution for 10 min.

8. Remove the sample from the hot plate, check the pH and allow the sample to stand overnight at room temperature.

9. Decant the supernate into a 3000-mL beaker and reserve for radium analysis. Reduce the volume of the decanted solution to 500 mL or less.

10. Add 100 mL of $HN0_3$ to the calcium oxalate precipitate and heat to destroy the oxalate. Repeat the $HN0_3$ addition, if necessary.

11. Convert the sample solution to the chloride with three successive additions of 50 mL of HCl.

12. Repeat Steps 5-10 for soil, milk, and vegetation ash samples. Bone ash samples require four calcium oxalate collections to remove most of the phosphate ions.

13. Wet ash the oxalate precipitate with repeated additions of 50-100 mL of $HN0_3$ for soil and vegetation samples. Bone samples initially require 200 mL of $HN0_3$.

14. Reduce the sample solution to near dryness and add 25 mL of 1:1 HNO_3 to the soil and vegetation ash samples. Add 100 mL of 1:1 HNO_3 to the bone ash sample.

15. Warm to dissolve the calcium salts. Cool the solution to room temperature.

B. Solvent extraction separation.

1. For soil and vegetation ash samples, transfer 25 mL of acid-washed Aliquat-336 into each of two 125-mL separatory funnels. For bone ash samples, add 50 mL of acid-washed Aliquat-336 into each of two 250-mL separatory funnels.

2. Transfer the sample to the first separatory funnel. Wash the beaker with 1:1 $HN0_3$ and add the washings to the funnel.

3. Shake the separatory funnel for 5 min. Allow the phases to separate and draw off the aqueous (lower) phrase into the second separatory funnel. Retain the organic phase in the first funnel.

4. Shake the second separatory funnel for 5 min. Allow the phases to separate, draw off the aqueous phase into the beaker with the reserved radium fraction.

5. Combine the two organic phases in one of the separatory funnels.

6. Wash the combined organic phases twice for 5 min with half volumes of 1:1 HNO_3. Add the washings to the reserved radium fraction.

7. Strip the thorium from the organic phase by shaking for 5 min with 25 mL of concentrated HCl. Allow the phases to separate and draw off the aqueous phase into the empty separatory funnel.

8. Repeat Step 7, combining the thorium bearing aqueous phases. The organic phase should be placed and retained in a suitable disposal container (see **Note 4**).

9. Add 25 mL of toluene to the separatory funnel and shake for 5 min.

10. Allow the phases to separate and draw off the aqueous phase into a 150-mL beaker. Discard the organic phase.

11. Heat the solution gently to drive off organic vapors.

12. Reduce the sample solution volume to 10 mL. Wet ash the solution with repeated 10-mL additions of HNO_3 to remove organics. **Caution** - Do not allow the solution to reach dryness.

13. Convert the solution to the chloride with three 5-mL additions of HCl. Reduce the acid volume to near dryness.

14. Add 1-2 mL of 1N HCl, prepared with filtered water (see Microprecipitation of the Actinides, G-03). Cool to room temperature.

15. Continue the analysis under Microprecipitation of the Actinides, G-03.

RADIUM SEPARATION*

1. Add 1 mL of barium carrier (20 mg barium mL^{-1}) to the reserved radium fraction.

2. Reduce the sample solution to dryness and wet ash with repeated 50-100 mL additions of $HN0_3$ to remove organics.

3. Convert the sample to the chloride with repeated 50-100 mL additions of HCl.

4. Dilute the sample solution to 1000 mL with water. Heat and stir to dissolve the salts. Add additional water, if necessary.

5. Adjust the solution pH to 2.5 with NH_40H. Cool the beaker to room temperature in a water bath.

6. Add 5 mL of $(NH_4)_2S0_4$ solution (100 mg $(NH_4)_2SO_4$ mL^{-1}). Stir and let stand at room temperature overnight.

7. Filter the solution through 47 mm diameter, 0.45 μm pore size Millipore filter.

8. Police and wash the beaker with water. Add the washings to the filter chimney. Wash the filter with water.

**Based upon Hallden et al. (1963).*

9. Place the filter with the $Ra.BaS0_4$ in a 150-mL beaker. Discard the filtrate.

10. Add 5 mL of warm EDTA solution and 1 mL of 1:1 triethanolamine to the beaker. Heat on a warm hot plate for about 5 min. Add 10 mL of water and stir occasionally. Continue to heat for 15 min.

11. Gravity filter the warm solution through Whatman No. 42 filter paper into a 30-mL (1 oz) polyethylene bottle.

12. Wash the beaker and filter with hot water. Discard the filter paper.

13. Dilute the sample solution to the same liquid level as a known aliquot of the ^{133}Ba tracer solution diluted to 25 mL in a 30-mL (1 oz) polyethylene bottle.

14. Gamma count the samples and standard to determine the chemical yield of barium.

15. Transfer the sample to a radon bubbler with water.

16. Determine the ^{226}Ra content of the sample as described in Emanation Procedure for Radium-226, Ra-03.

Notes:

1. The ^{232}U decays to ^{228}Th and its daughters. Therefore the activity of the thorium subseries increases with time in the ^{232}U spike. Thus, a blank correction for ^{228}Th from the added ^{232}U tracer is required, resulting in an increasing lower limit of detection (LLD) for ^{228}Th.

2. Calcium compounds and oxalic acid contain variable and measurable quantities of ^{226}Ra. Each lot of these reagents should be checked prior to use to obtain the lowest possible reagent blank value.

3. It is necessary to analyze reagent blank samples along with each batch of samples to determine the proper blank corrections.

4. The organic phase is washed twice for 5 min with an equal volume of water and placed in a suitable disposal container.

LOWER LIMIT OF DETECTION

Based upon Fisenne et al. (1987) and Harley and Fisenne (1990).

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Se-03

AMERICIUM, PLUTONIUM AND URANIUM IN WATER

Contact Person(s) : Anna Berne

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}Am and ^{238}Pu or ^{237}Np and ^{234}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 $H_2C_2O_4 \cdot 2H_2O$ and 7.11 g of $(NH_4)_2C_2O_4 \cdot H_2O$ 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 NH_2SO_3H to 150 mL of water, heat to 70°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 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 HNO_3 to 900 mL of water and dilute to 1 L with water.

13. Nitric acid solution (2M) - add 127 mL of HNO_3 to 800 mL of water and dilute to 1 L with water.

14. Nitric acid solution (3M) - add 191 mL of HNO_3 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_3 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_3. Evaporate to dryness and redissolve in HNO_3 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 3M HNO_3-1.0M $Al(NO_3)_3$. (**Note**: An additional 5 mL may be necessary if the volume of precipitate is large.)

2. Add 2 mL of 0.6M 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 3M 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 3M 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 3M 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 form 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_3 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_3 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_3 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_3 - 0.1M $NaNO_2$ directly into each column, rinsing each column reservoir while adding the 2M HNO_3 - 0.1M $NaNO_2$. (**Note**: Sodium nitrite is used to oxidize Pu^{+3} to Pu^{+4} 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_3 to each column and allow to drain. (**Note**: 0.5M HNO_3 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_3 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 $NH_4HC_2O_4$ to elute plutonium from each column.

17. Evaporate to dryness. Treat with 5 mL HNO_3 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)	3.33×10^{-6} for ^{238}U 6.67×10^{-6} for ^{234}U
Recovery :	(%)	85
LLD (400 min)	(m Bq)	0.2 for ^{238}U 0.3 for ^{234}U
LLD (1000 min)	(m Bq)	0.1 for ^{238}U 0.2 for ^{234}U
LLD (5000 min)	(m Bq)	0.06 for ^{238}U 0.09 for ^{234}U

PLUTONIUM

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

AMERICIUM

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