Plutonium

Environmental Measurements Laboratory
U.S. Department of Energy

Pu-12-RC

PLUTONIUM AND/OR AMERICIUM IN SOIL OR SEDIMENTS

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APPLICATION

This procedure is applicable to soils which contain plutonium and americium deposited from worldwide fallout and some nuclear activities. A total dissolution technique is required for some soil samples for plutonium determination.

Plutonium and americium isotopes are leached and equilibrated with ^{236}Pu and ^{243}Am tracers with nitric and hydrochloric acids from soil samples of up to 100 g in size. Plutonium is isolated and purified by ion exchange. Americium is collected with a calcium oxalate precipitation, isolated and purified by ion exchange. After source preparation by microprecipitation, the plutonium isotopes and americium are determined by alpha spectrometry.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.

2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, ~ 0.15 Bq g^{-1} in a dispensing bottle.

2. Plutonium-236 (^{242}Pu can also be used) tracer solution, ~0.20 Bq g^{-1} in a dispensing bottle.

3. Bio-Rad AG 1-X8 resin (100-200 mesh) - see Specification 7.4.

4. Bio-Rad AG 1-X4 resin (100-200 mesh) - see Specification 7.4.

5. TEVA resin 2 mL ion extraction columns (Aliquat 336, methyltricapryl-ammonium chloride, Henkel Corporation, Tucson, AZ 85745-1273, on Amberchrom resin) or equivalent or can be prepared from TEVA resin, Eichrom Industries, 8205 Cass Ave. Suite 107, Darien, IL 60561) - place a plug of glass wool in the bottom of a 2 mL plastic transfer pipette (see Specification 7.7). Add slurried TEVA resin (0.5 g). Place additional glass wool on the top of the resin.

6. 2M ammonium thiocyanate in 0.1M formic acid solution - dissolve 152 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.

7. 1M ammonium thiocyanate in 0.1M formic acid - dissolve 76 g of NH_4SCN in ASTM Type 2 water, add 4.25 mL formic acid, and dilute to 1 L.

8. Calcium carrier solution, 100 mg mL^{-1} - dissolve 25 g $CaCO_3$ in a minimal amount of concentrated HNO_3, and dilute to 100 mL.

9. Iron carrier, 100 mg mL^{-1} - slowly heat 100 g of iron powder in 500 mL of HCl until reaction ceases. Carefully and slowly add 100 mL of HNO_3 while stirring. Cool and dilute to 1 L.

10. Oxalate wash solution - dissolve 10 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) to make 1 L of solution (~ 1% solution).

11. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$ - solid.

SAMPLE PREPARATION

1. Weigh 1-100 g of soil into an appropriate sized beaker. Add weighed amounts of ^{243}Am and ^{236}Pu tracers.

2. Slowly add 100 mL (**Note**: volumes are based on 100 g sample and should be adjusted if sample size is smaller) of HNO_3 to the beaker. Control the foaming with the addition of a few drops of n-octyl alcohol. Stir sample with a glass stir rod to mix sample and acid. When the reaction subsides, add 30 mL of HCl, and stir. Allow the mixture to react at room temperature, rinse and remove stir rod, cover with a watch glass, then reflux on a low temperature hot plate overnight. Remove from hot plate and cool.

3. Dilute the solution in the beaker with water to 1:1 HNO_3 and filter the solution with vacuum through 9 or 11 cm Whatman No. 42 filter paper on a Büchner funnel into a 1 L flask. Wash with 1:1 HNO_3. Retain the filtrate in a 2-L beaker, evaporate the filtrate until salting out begins to occur. Return the residue and filter to the original beaker using HNO_3 to complete the transfer.

4. Add HNO_3 to the beaker to bring the volume added to 100 mL. Stir with a glass rod to mix sample and acid. Cover with a watch glass and heat until filter is wet ashed. Remove from the hotplate and cool. Add 30 mL of HCl to the beaker, cover with the watch glass, and heat on a low temperature hot plate for about 3 h with occasional stirring. Remove the beaker from the hot plate, and cool.

5. Repeat Step 3; dilute, filter and wash. Combine the filtrates. Return the residue and filter to the original beaker.

6. Repeat Step 4; wet ash filter and leach sample.

7. Repeat Step 3; dilute, filter and wash. Combine the three filtrates in a beaker. Discard the residue and filter paper.

8. Heat the filtrate with repeated 50-mL additions of HNO_3, covering the sample with a watch glass and letting the sample reflux until all organic matter is decomposed. Evaporate the solution to incipient dryness. Redissolve in 50-200 mL of 1:1 HNO_3.

If the solution is not clear, proceed to Step 9, otherwise go to **Plutonium Determination.**

9. If any siliceous matter is present, filter into a flask by gravity through a Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3, and reserve the filtrate.

10. Transfer the filter paper with the residue to the original beaker and wet ash the paper with 100 mL of HNO_3. Repeat wet ashing two or three times, then transfer the residue in the beaker into a 250-mL Teflon beaker, using 1:1 HNO_3. Evaporate to dryness.

11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the beaker and evaporate on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times. Rinse the walls of the Teflon beaker with 1:1 HNO_3 and evaporate, and repeat. Evaporate to dryness. Dissolve with 1:1 HNO_3 and evaporate to dryness.

12. Dissolve the residue in 1:1 HNO_3 and filter by gravity through a Whatman No. 42 filter paper. Add the filtrate to the solution from Step 9. Discard the filter and any residue. Heat the combined solution to incipient dryness. Redissolve in 50-200 mL 1:1 HNO_3.

PLUTONIUM DETERMINATION

Proceed to Plutonium Purification Ion Exchange Technique Procedure *Pu-11-RC*. Save the column effluents for **Americium Determination**.

AMERICIUM DETERMINATION

1. Evaporate the americium effluents to incipient dryness. Redissolve in a minimum amount of 1:1 HNO_3, dilute with four volumes of water.

2. Add 5 mL of calcium carrier solution (500 mg of calcium) and 50 g L^{-1} of oxalic acid to the sample while stirring with a magnetic stirrer. (**Note**: The total volume of the

sample solution can be estimated using the markings on the beaker, and the amount of oxalic acid to be added is calculated using that volume.)

3. Adjust the pH of the solution to 2.0-2.5 with NH_4OH using pH paper as an indicator and continue to stir for 30 min. Remove the magnetic stir bar.

4. Cool the sample and let it stand until precipitate settles and solution clears (for more than 6 h or overnight). Check for completeness of precipitation using a drop of saturated $H_2C_2O_4$ solution. Aspirate (or decant), using a disposable transfer pipette and suction, as much liquid as possible without disturbing the precipitate. Transfer the precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 1**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Decant and discard the supernate.

5. Break up the precipitate with a stirring rod and wash the precipitate with the oxalate wash solution. Centrifuge, decant and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl (the final precipitate should be redissolved in ~200 mL of HNO_3, then proceed to Step 8 below). (**Note**: Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass rod).

6. Transfer the dissolved precipitate to the original 600-mL beaker. Add enough water to make ~ 1M solution. Add 50 g L^{-1} of oxalic acid.

7. Repeat Steps 3 through 6 until supernate is colorless.

8. Transfer the dissolved precipitate to the original beaker and heat to destroy the oxalate ion. Evaporate to near dryness. Dissolve in a minimum of 1:1 HNO_3. Transfer to centrifuge bottle using water to complete the transfer.

9. Add enough water to make ~1M HNO_3. Warm the solution in a 90˚ hot water bath and add 0.2 mL iron carrier solution (20 mg iron).

10. With the centrifuge bottle in the hot water bath adjacent to a hood, adjust the pH of the solution to 8-9 with NH_4OH while stirring with a glass rod. Allow the solution to digest in a hot water bath for 20 min.

11. Cool in a cold water bath, rinse, and remove the glass rod. Balance the bottles on a double pan balance and centrifuge for 40 min at 2000 rpm.

12. Decant (or aspirate) and discard the supernate. Add 10 mL concentrated HCl to dissolve the $Fe(OH)_3$ pellet. Add four drops 30% H_2O_2 to oxidize any Mn present, followed by 100 mL of water and heat in the water bath for 30 min to get rid of excess H_2O_2.

13. Repeat Steps 10 to 12 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be redissolved in HNO_3.

14. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL HNO_3, and evaporate to dryness again.

15. Dissolve the wet-ashed residue in 40 mL 1:1 HNO_3. Cool in an ice-water bath. Add 0.6-1.0 g $NH_2OH \cdot HCl$, dissolve, and let react for 15 min. Cover with a watch glass. Heat on a low temperature hot plate to decompose unreacted $NH_2OH \cdot HCl$, then bring to gentle boil for 1-2 min. Cool and pass the solution through a 1:1 HNO_3 ion-exchange column (see **Note 2**). Collect the effluent in a 400-mL beaker. Wash the column with 150 mL of 1:1 HNO_3 and collect in the beaker.

16. Evaporate the sample in the 400-mL beaker to dryness. Convert to HCl by adding 20-30 mL of HCl at a time, heat to almost dryness, and repeat the HCl addition and evaporation at least three times. Evaporate again and dissolve the final residue in 30 mL of HCl. Pass this solution through a 12N HCl ion exchange column (see **Note 3**). Collect the effluent in a 250-mL beaker. Wash the column with 100 mL of HCl and collect in the 250-mL beaker.

17. Evaporate to dryness. Dissolve the residue in 10 mL 2M NH_4SCN in 0.1M formic acid.

18. Prepare a TEVA column. Equilibrate the resin by adding 3-4 mL 2M NH_4SCN in 0.1M formic acid. Drain to the top of the resin.

19. Transfer the sample to the column. Drain to the top of the resin.

20. Wash the column with 10 mL 1M NH_4SCN in 0.1M formic acid. Discard wash.

21. Elute the americium with 15 mL 2M HCl into a clean 100-mL beaker.

22. Add approximately 10 mL aqua regia to the sample. Gently decompose the thiocyanate solution under a heat lamp. Allow the solution to develop a purple color which will slowly disappear.

23. Heat the sample on a hot plate to near dryness. Dissolve the residue in 3 to 4 mL HNO_3. Evaporate to dryness. Redissolve in HNO_3 and evaporate two more times.

24. Convert to HCl by addition of 3-4 mL HCL. Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing filter paper and precipitate in HNO_3.

2. Preparation of 1:1 HNO_3 column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin, and with the stopcock open allow the water level to reach the top of the upper plug. Pass 150 mL (or enough so that the effluent tests free of Cl^- ion) of 1:1 HNO_3 through the resin bed in three 50-mL portions, allowing the level of each to reach the top of the upper glass wool plug.

3. Preparation of HCl column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with ASTM Type 2 water, 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) to the column and allow it to settle. Place a second plug of glass wool on top of the resin and with the stopcock open allow the water level to reach the top of the upper plug. Pass two 50-mL volumes of HCl through the resin bed and allow each to reach the top of the upper glass wool plug.

MICROPRECIPITATION

See Microprecipitation Source Preparation for Alpha Spectrometry, Procedure G-03.

AMERICIUM
LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	15×10^{-6}
Yield	(%)	50
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.3

PLUTONIUM
LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	25
Counter Background	(cps)	2×10^{-5}
Yield	(%)	75
Blank	(cps)	-
LLD (400 min)	(mBq)	1
LLD (1000 min)	(mBq)	0.5
LLD (5000 min)	(mBq)	0.2