4.5.4 Radiochemical

Americium

Environmental Measurements Laboratory
U.S. Department of Energy

Am-01-RC

AMERICIUM IN SOIL

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APPLICATION

This procedure is applicable to soils which contain americium deposited from worldwide fallout and some nuclear activities.

Americium is leached from the soil with HNO_3 and HCl and simultaneously equilibrated with ^{243}Am tracer. The soil is processed through the plutonium separation steps using ion exchange resin according to Procedure Pu-11-RC. If determination of plutonium is desired, an appropriate plutonium tracer should be added along with the ^{243}Am tracer. Americium is collected with a calcium oxalate precipitation and finally isolated and purified by ion exchange. After source preparation by microprecipitation, the ^{241}Am is determined by alpha spectrometry using ^{243}Am tracer to provide recovery data.

SPECIAL APPARATUS

1. For microprecipitation, see Procedure G-03.

2. Ion-exchange columns - see Specification 7.5.

SPECIAL REAGENTS

1. Americium-243 tracer solution, about 0.15 Bq g^{-1} in dispensing bottle - standardize for total disintegration rate. Measure purity on an α spectrometer.

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

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

4. 4M ammonium thiocyanate solution - dissolve 304 g of NH_4SCN in deionized distilled water and dilute to 1 L. To purify the 4M NH_4SCN, place 4 L of solution in a 5 L polyethylene beaker. Add 25 mL of Bio-Rad AG 1-X4 resin (100-200 mesh) ion exchange resin, and mix for 1 h with a magnetic stirrer. Allow the resin to settle and filter by gravity through Whatman No. 40 filter paper. Repeat the addition of the resin and filtration steps twice more to remove all Fe^{+3} from the 4M NH_4SCN. Store the purified 4M NH_4SCN in a polyethylene bottle.

5. 0.4M NH_4SCN - 0.3M HCl - dilute 100 mL of purified 4M NH_4SCN to 500 mL with water, then add 25 mL HCl and dilute to 1 L. Make 2 L of solution for 10 samples.

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

7. 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.

8. Oxalate wash solution - dissolve 10 g of oxalic acid to make 1 L of solution (~ 1% solution).

SAMPLE PREPARATION

1. Weigh 1000 g of soil into a 4-L beaker. Add a weighed amount (about 0.03 Bq) of ^{243}Am tracer.

2. Slowly add 900 mL of HNO_3. Control the foam with the addition of a few drops of n-octyl alcohol. When the reaction subsides, add 300 mL of HCl. Allow the mixture to react at room temperature, then heat on a low temperature hot plate overnight with occasional stirring.

3. Dilute to 1:1 HNO_3 and filter through Whatman No. 42 filter paper into a 3-L flask. Wash with 1:1 HNO_3. Retain the filtrate. Return the residue and filter to the original beaker.

4. Add 900 mL of HNO_3 and wet ash the filter paper. Maintain the HNO_3 volume. Cool and add 300 mL of HCl to the residue and heat on a low temperature hot plate for about 3 h with occasional stirring. Cool and allow to settle overnight.

5. Filter and wash as in Step 3. Combine the filtrate with the filtrate from Step 3. Return the residue and filter to the original beaker.

6. Repeat Step 4.

7. Filter and wash as in Step 3. Combine the three filtrates and discard the residue.

8. Decompose any organic matter in the extract by heating with repeated additions of HNO_3, covering the sample with a watch cover and letting the sample reflux. Concentrate until salting out begins to occur. Add an equal volume of water. If solution is not clear, proceed to Step 9, otherwise go to Step 14.

9. If any siliceous matter is present, filter by gravity over an 18.5 cm Whatman No. 42 filter paper. Wash the residue with 1:1 HNO_3. Reserve the filtrate.

10. Transfer the filter paper with the residue to the original beaker and ash the paper with 100 mL of HNO_3. Repeat two or three times, then transfer the residue into a 100-mL platinum dish using 1:1 HNO_3.

11. Add 5-25 mL of HF and 5-25 mL of HNO_3 to the platinum dish 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 platinum dish with 1:1 HNO_3 and evaporate. Repeat three times. 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.

13. Heat the combined solution (with the addition of HNO_3 if necessary) to complete the oxidation of any organic materials. Evaporate to near dryness. Redissolve in 1:1 HNO_3 and stir to get a clear solution, adding 1:1 HNO_3 as necessary.

14. Proceed to Procedure Pu-11-RC, ion-exchange purification saving 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. (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 and let 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 (redissolve the precipitate in ~200 mL of HNO_3 a final time and proceed to Step 8). (**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 minimum 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 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. Heat in the water bath for 30 min to get rid of the excess H_2O_2 .

13. Repeat Steps 10 to12 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 the solution 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 a 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 with 100 mL of HCl, and collect in the 250-mL beaker.

17. Evaporate to dryness. Dissolve in 1-2 mL of HCl. Cool thoroughly. Add 40 mL of 4M NH_4SCN and stir immediately. Stir the sample and pass the solution through a 4M NH_4SCN column (see **Note 4**). Discard the effluent.

18. Wash the column with 200 mL of 4N NH_4SCN solution. Discard the wash solution.

19. Elute the americium into a 250-mL beaker with 180 mL of 0.4N NH_4SCN - 0.3N HCl. Evaporate to dryness on a low temperature hot plate overnight. Discard the resin.

19. To remove NH_4^+ salts, place the beaker on an iron tripod and heat slowly with a cool Bunsen flame. After ~ 0.5 h, increase the flame temperature and continue heating to remove all NH_4^+ salts and S, then heat briefly to dull red heat. This step requires ~ 1-1.5 h.

20. Cool to room temperature. Add 25 mL of HNO_3 and boil slowly for a few minutes. **Cautiously** add 1 mL of 30% H_2O_2 and evaporate the solution to dryness.

21. Convert the residue to Cl^- by adding 1 mL of HCl and evaporating to dryness twice and proceed to microprecipitation.

Notes:

1. If a centrifuge is not available, centrifugation can be replaced by filtering and wet ashing the 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 deionized distilled 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 H_2O level to reach the top of the upper plug. Pass 150 mL of 1:1 HNO_3 through the resin bed in three 50-mL portions or enough so that the effluent tests free of Cl^- ion using dilute silver nitrate solution, allowing the level of each portion 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 10 mL of wet settled Bio-Rad AG 1-X4 resin (100-200 mesh) with deionized water 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 H_2O 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.

4. Preparation of NH_4SCN Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer with deionized distilled water, 15 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 H_2O level to reach the top of the upper plug. Pass 100 mL of purified 4M NH_4SCN through the resin bed in two 50-mL portions, allowing the level of each portion to reach the top of the upper glass wool plug.

MICROPRECIPITATION

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

DATA PROCESSING AND ANALYSES

For alpha spectrometry measurements, please see Procedure A-01-R.

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