Am-06-RC

AMERICIUM AND/OR PLUTONIUM IN VEGETATION

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APPLICATION

This procedure is applicable to vegetation which contain americium deposited from worldwide fallout and some nuclear activities. It is most effective when used on dried finely powdered samples of vegetation.

The vegetation is either dry ashed in a ceramic crucible using a muffle furnace or wet ashed with nitric acid. Wet ashing requires considerably more time and must be carefully attended to due to the highly reactive nature of vegetation. The sample is further digested with hydrofluoric acid to dissolve silicate compounds. Plutonium is separated by ion exchange and determined by alpha spectrometry. 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 a dispensing bottle-standardize for total for total disintegration rate (and/or ^{236}Pu tracer solution - a standard solution containing ~0.15 Bq g^{-1} in a dispensing bottle). Measure purity on an α spectrometer.

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

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

4. TRU Resin 2 mL ion extraction columns or equivalent or can be prepared from TRU Resin, Eichrom Industries, Inc., 8205 Cass AV, Suite 107, Darien, IL 60561. Place a plug of glass wool in the bottom of a polyethylene transfer pipette (see Specification 7.7). Add slurried TRU Resin (0.5 g). Assemble immediately before use.

5. 0.5M $Al(NO_3)_3$ in 2M HNO_3 - place 18.76 g of $Al(NO_3)_3 \cdot 9H_2O$ in a 100-mL volumetric flask and add 2M HNO_3 to the mark. Shake to mix thoroughly.

6. 2M HNO_3 - 125 mL nitric acid diluted to 1 L with water.

7. 1M HNO_3 - 62.5 mL nitric acid diluted to 1 L with water.

8. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.

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

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

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

12. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$.

SAMPLE PREPARATION

A. Dry ashing

1. Weigh an aliquot of < 10 g vegetation into a tared 250-mL porcelain crucible. (**Note**: After ashing, several aliquots can be combined to provide adequate sample size.) Place each crucible in a muffle furnace with the crucible cover slightly ajar. Increase the temperature of the furnace at a rate of 0.80˚C min $^{-1}$ to 250˚C. Maintain this temperature for 30 minutes. Increase the temperature at a rate of 10˚C min $^{-1}$ to 600˚C. Maintain the temperature for 960 min to completely ash sample. Cool the crucible and weigh to determine percent ash. Ash content for replicate crucibles should vary by not more than 4%. If the ash content of an individual sample is lower by more than 4%, sample loss should be assumed and that sample discarded.

2. Place a known amount (approximately same amount as ^{241}Am in the sample) of ^{243}Am tracer (and/or ^{236}Pu tracer solution) in a 400-mL beaker containing a small amount of 1:1 HNO_3. Transfer ashed vegetation to the beaker using 1:1 HNO_3 to dissolve the ash and rinse the crucible. Transfer as many aliquots to the beaker as needed to meet the detection requirements.

3. Cover with a watch glass and reflux on a hot plate until there is no evidence of remaining organic matter, adding HNO_3 or H_2O_2 as necessary.

4. Evaporate to near dryness. Add 50 mL 1:1 HNO_3. Filter by gravity through a Whatman No. 42 filter paper, washing with 1:1 HNO_3 into a beaker. Continue with Step 5 below.

B. Wet ashing

1. Weigh an aliquot of vegetation into an appropriate sized beaker. (For a 100-300 g sample, use a 3000-mL beaker.) Add a known amount (approximately the same amount as expected of ^{241}Am in the sample) of ^{243}Am tracer solution (and/or ^{236}Pu tracer solution).

2. Slowly add 500 mL of 1:1 HNO_3. Control the foaming, if necessary, with the addition of a few drops of n-octyl alcohol. Cover with a watch glass and place on a

low temperature hot plate overnight, maintaining a slow reaction and stirring as necessary to break up the foam. Gradually increase the temperature of the hot plate, adding HNO_3 and maintaining refluxing until the reaction is complete as indicated by the lack of brown nitrogen oxide gas.

3. Slowly add enough HCl to equal one third the volume of HNO_3 still in the beaker. Allow the mixture to react at room temperature for 15 min, cover with a watch glass, then heat on a low temperature hot plate overnight with occasional stirring.

4. Remove the sample from the hot plate, add an equal volume of water. Allow the sample to cool to room temperature. Filter by gravity through a large Whatman No. 42 filter paper into a beaker. Wash with 1:1 HNO_3.

5. Retain the filtrate and evaporate to near dryness. Return the residue and filter to the original beaker. Add 100 mL HNO_3, cover with a watch glass and place on a hotplate to reflux until colorless. Change the watch glass to a ribbed watch glass and evaporate to near dryness.

6. Transfer the digested filter with the residue to a 250-mL Teflon beaker using 1:1 HNO_3. Evaporate to dryness. Add 15 mL of HNO_3 and 15 mL of HF to the beaker and evaporate to near dryness on a medium temperature hot plate. Repeat the addition of the HF/HNO_3 and the evaporation process two or three times.

7. Add 30 mL HNO_3 and evaporate to dryness, repeat twice, rinsing the walls of the beaker with acid. Add 20 mL HNO_3. Add 20 mL of water. Cool. Filter by gravity through a Whatman No. 42 filter paper into the beaker with the filtrate from Step 5. Rinse with 1:1 HNO_3.

8. Evaporate filtrate to dryness. Redissolve in 30 mL 1:1 HNO_3. Proceed to Ion Exchange Purification for Plutonium Determination, Procedure Pu-11-RC*,* saving the column effluents for **Americium Determination.**

AMERICIUM DETERMINATION

1. Evaporate the americium containing effluents in a beaker to incipient dryness. Redissolve in a minimum amount (20-100 mL) 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. Check for completeness of precipitation using a drop of saturated $H_2C_2O_4$ solution. Aspirate as much liquid as possible without disturbing the precipitate. Transfer precipitate to a 250-mL centrifuge bottle using oxalate wash solution (see **Note 3**). Balance the bottles on a double pan balance and centrifuge for 10 min at 2000 rpm. Discard the supernate.

5. Wash the precipitate with the oxalate wash solution. Centrifuge and discard the wash. Repeat wash. Redissolve the precipitate in a minimal amount (50-70 mL) of concentrated HCl. (**Note**: Dissolution is easier if the centrifuge bottle is placed in a hot water bath and stirred with a glass stirring rod.)

6. Transfer the precipitate to the original beaker. Add ~3 volumes of water, 50 g L^{-1} of oxalic acid, and reprecipitate the oxalate with NH_4OH at a pH of 2.5-3.5 (see Step 3).

7. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate (repeat Steps 4 and 5).

8. Transfer the solution to original beaker. Add ~3 volumes of water, 50 g L^{-1} of oxalic acid, and reprecipitate the oxalate at a pH of 2.5-3.5 with NH_4OH (see Step 3).

9. Cool the solution, aspirate, transfer to a centrifuge bottle, centrifuge, wash and redissolve the precipitate in ~200 mL of concentrated HNO_3.

10. Transfer the solution to the original beaker and heat to destroy oxalate ion. Evaporate to near dryness. Dissolve in 1:1 HNO_3 and transfer to the centrifuge bottle.

11. Add enough water to make ~1M HNO_3. Warm the solution in a 90˚ hot water bath and add 200 µL iron carrier solution (20 mg iron).

12. Adjust the pH of the solution to 8-9 with NH_4OH, while stirring with a glass rod. Leave the solution in a hot water bath to digest for 20 min.

13. 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.

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

15. Reprecipitate, centrifuge and redissolve. Repeat Steps 12 to 14 three times. Reprecipitate, centrifuge and redissolve. The final precipitate should be dissolved in 1:1 HNO_3.

16. Transfer to a 250-mL beaker, evaporate to dryness, add 20 mL 1:1 HNO_3, and evaporate to dryness again.

17. Dissolve the 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 1**). Collect the effluent in a 400-mL beaker. Wash with 150 mL of 1:1 HNO_3, and collect in the beaker.

18. Evaporate the sample in the 400-mL beaker to dryness and treat several times with concentrated HCl. Dissolve the residue in 30 mL HCl. Pass this solution through a

concentrated HCl ion exchange column (see **Note 2**). Collect the effluent in a 250-mL beaker, and wash with 100 mL of HCl. Evaporate and proceed to microprecipitation if no residue is visible. If residue remains, continue with Step 19.

19. Evaporate to dryness transferring the sample to a 50-mL beaker when volume is sufficiently diminished. Add 10-mL HNO_3 and evaporate to dryness. Add 3 mL 0.5M $Al(NO_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.

20. Prepare a TRU Resin column. Wash the resin with 15 mL 2M HNO_3, and discard the effluent.

21. Load the sample (see Step 19) on the column. Drain to the top of the resin. Wash the beaker with 3 mL 0.5M $Al(NO_3)_3$ in 2M HNO_3 and add to the column. Discard the effluent.

22. Rinse the column with 8 mL 2M HNO_3, followed by 8 mL 1M HNO_3, and discard the effluents.

23. Elute the americium with three 3 mL aliquots of 0.025M HNO_3 into a 50-mL beaker.

24. Evaporate eluate to dryness. Convert the residue to the chloride form by adding 3-4 mL HCl. Evaporate to dryness. Redissolve in HCl and evaporate two more times. Proceed to microprecipitation.

Notes:

1. Preparation of 1:1 HNO_3 Column. Position a plug of glass wool at the base of an 11-mm o.d. column. Transfer 15 mL of wet settled Bio-Rad AG 1-X8 resin (100-200 mesh) to the column with deionized distilled water, and allow 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 (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.

2. 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 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.

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

MICROPRECIPITATION

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

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