4.5.4 Radiochemical

Americium

Environmental Measurements Laboratory
U.S. Department of Energy

Am-01-RC

AMERICIUM IN SOIL

Contact Person(s) : Anne Berne

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

Am-02-RC

AMERICIUM-241 IN SOIL - GAMMA SPECTROMETRY

Contact Person(s) : Colin G. Sanderson

APPLICATION

This procedure is capable of determining small amounts of ^{241}Am in large volume soil samples. The lower limit of detection for 600-800 g of soil in a Marinelli beaker is 0.74 mBq for a 1000-min count.

Americium-241 decays with the emission of γ rays at 11.9, 13.9, 17.8, 20.8, 26.4, and 59.5 keV. The 59.5 keV γ ray, which has an abundance of 35.9%, can be measured in soil with commercially available germanium (Ge) semiconductor γ-ray detectors and 600 mL Marinelli beakers. Gamma-ray attenuation corrections are required if the calibration source and the sample are in a different matrix or are of different densities.

SPECIAL APPARATUS

1. Hyperpure Ge γ-ray detector, shield, and associated electronics.

2. Multichannel analyzer.

3. Marinelli beaker - see Specification 7.22.

SPECIAL REAGENT

Americium-241 calibration solution, about 2.50 Bq mL^{-1}.

SPECTROMETER CALIBRATION

1. Transfer 600 mL of standardized ^{241}Am solution to a Marinelli beaker.

2. Set the spectrometer energy calibrations at 0.5 keV/channel and count the standard until 10,000 or more counts are accumulated in the channels corresponding to 58.0 to 61.5 keV.

3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

SAMPLE PREPARATION

1. Transfer 600 mL of prepared soil to a Marinelli beaker.

2. Accumulate sufficient counts in the 59.5 keV ^{241}Am peak to achieve the desired counting statistics.

3. Record the count time and the channel-by-channel data corresponding to 56.0 to 63.5 keV.

DETERMINATION

If computer calculation techniques are used to determine peak areas from spectral data, the same techniques must be used for both calibration standards and samples. However, in most instances, simple peak integration by channel summing is sufficient.

The net count in the ^{241}Am peak = A - B - C.

where

A = sum of counts in the 8 channels from 58.0 to 61.5 keV

B = sum of counts in the 4 channels from 56.0 to 57.5 keV

C = sum of counts in the 4 channels from 62.0 to 63.5 keV

B and C are the leading and trailing edges of the photopeak and represent the background upon which the photopeak is superimposed.

The net ^{241}Am counts, AmC, corrected for attenuation equals

$$A/e^{-(\mu d \cdot w)}$$

where

A = observed net counts in the ^{241}Am peak,

μd = attenuation constant for Marinelli beaker (see Note below),
for H_2O, $\mu d = 0.000427$ cm^2 g^{-1}
for soil, $\mu d = 0.000533$ cm^2 g^{-1}

w = weight in g of the standard or sample.

The ^{241}Am detector efficiency at 59.5 keV,

$$\text{Efficiency} = (\text{AmC}/t)/(\text{Ac} \cdot 600)$$

where

AmC = net ^{241}Am counts of the standard, corrected for attenuation, and

t = standard count time (sec).

Ac = ^{241}Am activity of standard (Bq mL^{-1}).

The Bq ^{241}Am in the sample = (AmC/t)/Efficiency

where

AmC = net ^{241}Am counts of the sample, corrected for attenuation, and

t = sample count time (sec).

Note:

The Marinelli beaker attenuation constant ($\mu d = 0.000533$ cm^2 g^{-1}) is for soil of normal composition. Soils or ores composed of high atomic number elements will require a different constant. For example, a 1% U ore will attenuate the 59.5 keV γ ray to 7% more than normal soil and the correct μd would be 0.000677 cm^2 g^{-1}.

Am-03-RC

AMERICIUM IN WATER, AIR FILTERS, AND TISSUE

(*see Volume II*)

Am-04-RC

AMERICIUM IN QAP WATER AND AIR FILTERS - EICHROM'S TRU RESIN

Contact Person(s) : Anna Berne

APPLICATION

The following procedure has been applied to the preparation, separation, and analysis of spiked water and air filter samples that contain americium but not lanthanides (Berne, 1996). Lanthanides, if present, will not be removed by this method and will significantly reduce the resolution of the α-spectrograph. Combined with Procedure Pu-11-RC, this procedure allows for the sequential determination of plutonium and americium. Other researchers have applied TRU Resin methods to other matrices (Horowitz et al., 1990). The procedure is used in the EML Quality Assessment Program (QAP; Sanderson and Greenlaw, 1996).

The water and air filters are equilibrated with ^{243}Am and 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. The eluate from the ion exchange column containing americium (and all other ions, except plutonium) is evaporated, redissolved, and loaded onto a TRU Resin extraction column. The americium (and curium, if present) is separated and purified on the column and finally stripped with dilute nitric acid stripping solution. Microprecipitation is used to prepare for α spectrometry.

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. 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.

3. Column feed solution, 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.

4. 2M HNO_3 - 125 mL HNO_3 diluted to 1 L with water.

5. 1M HNO_3 - 62.5 mL HNO_3 diluted to 1 L with water.

6. 0.025M HNO_3 - 25 mL 1M HNO_3 diluted to 1 L with water.

SAMPLE PREPARATION

See Procedure Pu-01-RC, air filters or Procedure Pu-10-RC, water.

AMERICIUM DETERMINATION

1. Collect the sample and the wash effluent from Step 4, **Ion Exchange Separation**, Procedure Pu-11-RC, and evaporate almost to dryness. If necessary, sometime during the evaporation process transfer the solution to a smaller beaker. The final residue should be contained in a beaker not larger than 50 mL. Add 3 mL of 0.5M $Al(NO_3)_3$ in 2M HNO_3 to each residue and heat very gently to dissolve.

2. Prepare an ion extraction column.

3. Wash the resin with 15 mL of 2M HNO_3, and discard the effluent.

4. Load the column with the sample solution from Step 1. Wash the beaker with 3 mL of column-feed solution and add to the column. Discard the effluent.

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

6. Elute the americium fraction with three 3-mL aliquots of 0.025M HNO_3, and collect the eluate in a 50-mL beaker.

7. Evaporate the eluate to dryness. Convert the residue to the chloride form by adding 5 mL of HCl three times and evaporating to dryness at a low temperature.

8. Prepare the sample for α spectrometry by microprecipitation (see Procedure G-03).

DATA PROCESSING AND ANALYSIS

For α spectrometry, see Alpha Radioassay, Procedure A-01-R.

LOWER LIMIT OF DETECTION (LLD)*

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

*Reagent blanks must be analyzed with each set of samples.

REFERENCES

Berne, A.
"Use of EIChrom's TRU Resin in the Determination of Americium, Plutonium and Uranium in Air Filter and water samples."
USDOE Report EML-575, December (1995)

Sanderson, C. G. and P. Greenlaw
"Semi-Annual Report of the Department of Energy, Office of Environmental Restoration and Waste Management, Quality Assessment Program"
USDOE Report EML-581, July (1996)

Am-05-RC

AMERICIUM IN WATER AND AIR FILTERS

(see Volume II)

Am-06-RC

AMERICIUM AND/OR PLUTONIUM IN VEGETATION

Contact Person(s) : Anna Berne

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