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Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

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RAPID RADIOCHEMICAL METHOD FOR AM-241 IN BUILDING MATERIALS FOR ENVIRONMENTAL REMEDIATION FOLLOWING RADIOLOGICAL INCIDENTS

1. Scope and Application
   1.1. The method will be applicable to samples where contamination is either from known or unknown origins.
   1.2. The method is specific for ^{241}Am in building material samples such as concrete, brick, etc. ^{244}Cm may also be determined in the same purified fraction, using ^{243}Am tracer as a yield monitor since curium tracks closely with americium in this method and this is a typical laboratory practice. The specific method parameters (yield, required method uncertainty (u_{MR}), minimum detectable activity, and critical level) for ^{244}Cm would need to be validated by the laboratory.
   1.3. The method uses rapid radiochemical separation techniques for determining alpha-emitting americium isotopes in building materials samples following a nuclear or radiological incident.
   1.4. The method is capable of achieving a required method uncertainty for ^{241}Am of 0.20 pCi/g at an analytical action level of 1.5 pCi/g. To attain the stated measurement quality objectives (MQOs) (see Steps 9.3 and 9.4), a sample weight of approximately 1 g and count time of at least 4 hours are recommended. The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the sample test source, and initial sample weight/volume. The method must be validated prior to use following the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, reference 16.1).
   1.5. The rapid americium method was evaluated following the guidance presented for "Level E Method Validation: Adapted or Newly Developed Methods, Including Rapid Methods" in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, Reference 16.1) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP 2004, Reference 16.2).
   1.6. Multi-radionuclide analysis using sequential separation may be possible using this method in conjunction with other rapid methods (see the appendix of this method). Rapid methods can also be used for routine analyses with appropriate (typically longer) count times.
   1.7. Other solid samples such as soil can be digested using the rapid sodium hydroxide fusion procedure as an alternative to other digestion techniques, but this procedure will have to be validated by the laboratory.

2. Summary of Method
   2.1. This method[1] is based on the use of extraction chromatography resins (TEVA® + DGA® Resins) to isolate and purify americium by removing interfering radionuclides

[1] Concrete and brick samples typically will be fused to digest the samples using *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and*

as well as other matrix components in order to prepare the americium fraction for counting by alpha spectrometry. The method utilizes vacuum-assisted flow to improve the speed of the separations. Am-243 tracer, added to the building materials sample, is used as a yield monitor. The sample test source (STS) is prepared by microprecipitation with CeF_3. Standard laboratory protocol for the use of an alpha spectrometer should be used when the sample is ready for counting.

3. Definitions, Abbreviations, and Acronyms

3.1. Analytical Protocol Specifications (APS). The output of a directed planning process that contains the project's analytical data needs and requirements in an organized, concise form.

3.2. Analytical Action Level (AAL). The term "analytical action level" is used to denote the value of a quantity that will cause the decision-maker to choose one of the alternative actions.

3.3. Discrete Radioactive Particles (DRPs or "hot particles"). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (μm range).

3.4. *Multi-Agency Radiological Analytical Laboratory Protocols Manual* (MARLAP) provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides (Reference 16.2).

3.5. Measurement Quality Objective (MQO). MQOs are the analytical data requirements of the data quality objectives and are project- or program-specific. They can be quantitative or qualitative. MQOs serve as measurement performance criteria or objectives of the analytical process.

3.6. Radiological Dispersal Device (RDD), i.e., a "dirty bomb." This device is an unconventional weapon constructed to distribute radioactive material(s) into the environment either by incorporating them into a conventional bomb or by using sprays, canisters, or manual dispersal.

3.7. Required Method Uncertainty (u_{MR}). The required method uncertainty is a target value for the individual measurement uncertainties, and is an estimate of uncertainty (of measurement) before the sample is actually measured. The required method uncertainty is applicable below an AAL.

3.8. Relative Required Method Uncertainty (φ_{MR}). The relative required method uncertainty is the u_{MR} divided by the AAL and is typically expressed as a percentage. It is applicable above the AAL.

3.9. Sample Test Source (STS). This is the final form of the sample that is used for nuclear counting. This form is usually specific for the nuclear counting technique used in the method such as a solid deposited on a filter for alpha spectrometry analysis.

Uranium Analyses (Reference 16.5), and the americium isotopes were removed from the fusion matrix using iron hydroxide and lanthanum fluoride precipitation steps. Soil samples may also be treated in this manner.

4. Interferences
   4.1. Radiological
      4.1.1. Alpha-emitting radionuclides with irresolvable alpha energies, such as ^{238}Pu (5.50 MeV) and ^{228}Th (5.42 MeV) must be chemically separated to enable measurement. This method separates these radionuclides effectively. The significance of peak overlap will be determined by the individual detector's alpha energy resolution characteristics and the quality of the final precipitate that is counted.
      4.1.2. A thorium removal rinse is performed on DGA® Resin in the event that any thorium ions pass through TEVA® Resin onto DGA® Resin.
      4.1.3. Vacuum box lid and holes must be cleaned frequently to prevent cross-contamination of samples.
      4.1.4. A dilute nitric acid rinse is performed on DGA® Resin to remove calcium (Ca) and lanthanum (La) ions which could end up on the final alpha source filter as fluoride solids. This volume may be increased slightly to better remove Ca and La ions and possibly improve alpha peak resolution, but this will have to be validated by the laboratory.
   4.2. Non-Radiological: Anions that can complex americium such as fluoride and phosphate may lead to lower yields. Boric acid added in the load solution complexes fluoride ions while aluminum complexes both fluoride as well as any residual phosphate that may be present. High levels of calcium can have an adverse impact on americium retention on DGA® Resin. This interference is minimized by increasing the nitrate concentration to lower Ca retention and increase americium affinity on DGA® Resin.

5. Safety
   5.1. General
      5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring, and radiation dose monitoring.
      5.1.2. Refer to your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.
   5.2. Radiological
      5.2.1. Hot particles (DRPs)
         5.2.1.1. Hot particles, also termed "discrete radioactive particles" (DRPs), will be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media and their radiation emissions are <u>not</u> uniform in all directions (anisotropic).
      5.2.2. For samples with detectable activity concentrations of these radionuclides, labware should be used only once due to potential for cross contamination.

5.3. Procedure-Specific Non-Radiological Hazards: Particular attention should be paid to the use of hydrofluoric acid (HF). HF is an extremely dangerous chemical used in the preparation of some of the reagents and in the microprecipitation procedure. Appropriate personal protective equipment (PPE) must be used in strict accordance with the laboratory safety program specification.

6. Equipment and Supplies

6.1. Alpha spectrometer calibrated for use over the range of ~3.5–10 MeV.

6.2. Analytical balance with 10^{-4} g readability, or better.

6.3. Cartridge reservoirs, 10 or 20 mL syringe style with locking device, or columns (empty luer tip, CC-10-M) plus 12 mL reservoirs (CC-06-M), Image Molding, Denver, CO (or equivalent).

6.4. Centrifuge able to accommodate 225 mL tubes.

6.5. Centrifuge flasks, 225 mL capacity.

6.6. 25 mm polypropylene filter, 0.1 µm pore size, or equivalent.

6.7. Stainless steel planchets or other adhesive sample mounts (Ex Environmental Express, Inc. P/N R2200) able to hold the 25 mm filter.

6.8. Tweezers.

6.9. 100 µL, 200 µL, 500 µL and 1 mL pipets or equivalent and appropriate plastic tips.

6.10. 1-10 mL electronic pipet.

6.11. Vacuum pump or laboratory vacuum system.

6.12. Vacuum box tips, white inner, Eichrom part number AC-1000-IT, or PFA 5/32" × ¼" heavywall tubing connectors, natural, Ref P/N 00070EE, cut to 1 inch, Cole Parmer, or equivalent.

6.13. Vacuum box tips, yellow outer, Eichrom part number AC-1000-OT, or equivalent.

6.14. Vacuum box, such as Eichrom part number AC-24-BOX, or equivalent.

6.15. Vortex mixer.

6.16. Miscellaneous laboratory ware of plastic or glass; 250 and 500 mL capacities.

6.17. Heat lamp.

7. Reagents and Standards

NOTES:

All reagents are American Chemical Society (ACS) reagent grade or equivalent unless otherwise specified.

Unless otherwise indicated, all references to water should be understood to mean Type I reagent water (ASTM D1193, Reference 16.4). All solutions used in microprecipitation should be prepared with water filtered through a 0.45 µm (or better) filter.

7.1. Type I reagent water as defined in ASTM Standard D1193 (Reference 16.4).

7.2. Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$).

7.2.1. Aluminum nitrate solution, 2M ($Al(NO_3)_3$): Add 750 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) to ~700 mL of water and dilute to 1 L with water. Low-levels of uranium are typically present in $Al(NO_3)_3$ solution.

7.3. Ascorbic acid (1.5M): Dissolve 66 g of ascorbic acid ($C_6H_8O_6$) in 200 mL of water, warming gently to dissolve, and dilute to 250 mL with water. Shelf life is 30 days or less.

7.4. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6\ H_2O$)

7.4.1. Cerium carrier, 0.5 mg Ce/mL: dissolve 0.155 g cerium (III) nitrate hexahydrate in 50 mL water, and dilute to 100 mL with water.

7.5. DGA® Resin – 2 mL cartridge, 50- to 100-µm mesh size, normal, Eichrom part number DN-R50-S, or equivalent.

7.6. Ethanol, 100%: Anhydrous C_2H_5OH, available commercially, or mix 95 mL 100% ethanol and 5 mL water.

7.7. Graduated cylinders.

7.8. Hydrochloric acid (12M): Concentrated HCl, available commercially.

7.8.1. Hydrochloric acid (0.25M): Add 20.8 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

7.9. Hydrofluoric acid (28M): Concentrated HF, available commercially.

7.10. Hydrogen peroxide (H_2O_2), 30%, available commercially.

7.11. Nitric acid (16M): Concentrated HNO_3, available commercially.

7.11.1. Nitric acid (0.05M): Add 3.2 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.11.2. Nitric acid (0.1M): Add 6.3 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.11.3. Nitric acid (3M): Add 191 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.11.4. Nitric acid (6M): Add 382 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

7.11.5. Nitric acid (3M) - Hydrofluoric acid (0.25M) solution: Add 8.9 mL of concentrated HF and 191 mL of concentrated HNO_3 to 700 mL of water. Dilute to 1 L with water and mix well.

7.12. Americium-243 tracer solution: Add 15–25 dpm of ^{243}Am per aliquant, activity known to at least 5% (combined standard uncertainty of no more than 5%).

NOTE: If count times longer than 1 hour are used, lower levels of tracer activity may be added instead.

7.13. Sodium nitrite, ($NaNO_2$)

7.13.1. Sodium nitrite solution, 3.5M ($NaNO_2$): Dissolve 6.1 g of sodium nitrite in 25 mL of water. Prepare fresh daily.

7.14. Sulfamic acid (H_3NSO_3).

7.14.1. Sulfamic acid solution, 1.5M (H_3NSO_3): Dissolve 72.7 g of sulfamic acid in 400 mL of water and dilute to 500 mL with water.

7.15. TEVA® Resin – 2 mL cartridge, 50 to 100 μm mesh size, Eichrom part number TE-R50-S and TE-R200-S, or equivalent.

8. Sample Collection, Preservation, and Storage
Not Applicable.

9. Quality Control

9.1. Batch quality control results shall be evaluated and meet applicable Analytical Protocol Specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.

9.1.1. A Laboratory Control Sample (LCS) shall be run with each batch of samples. The concentration of the LCS should be at or near the action level or level of interest for the project.

9.1.2. One method blank shall be run with each batch of samples. The laboratory blank should consist of an acceptable simulant or empty crucible blank processed through the fusion procedure (Reference 16.5).

9.1.3. One laboratory duplicate shall be run with each batch of samples. The laboratory duplicate is prepared by removing an aliquant from the original sample container.

9.1.4. A matrix spike sample may be included as a batch quality control sample if there is concern that matrix interferences may compromise chemical yield measurements or overall data quality.

9.2. The source preparation method should produce a sample test source that produces a spectrum with the full width at half maximum (FWHM) of 0.05-0.1 MeV for each peak in the spectrum. Precipitate reprocessing should be considered if this range of FWHM cannot be achieved.

9.3. This method is capable of achieving a u_{MR} of 0.20 pCi/g at or below an action level of 1.5 pCi/g. This may be adjusted if the event specific MQOs are different.

9.4. This method is capable of achieving a required φ_{MR} of 13% above 1.5 pCi/g. This may be adjusted if the event specific MQOs are different.

9.5. This method is capable of achieving a required minimum detectable concentration (MDC) of 0.20 pCi/g.

10. Calibration and Standardization

10.1. Set up the alpha spectrometry system according to the manufacturer's recommendations. The energy range of the spectrometry system should at least include the region between 3 and 8 MeV.

10.2. Calibrate each detector used to count samples according to ASTM Standard Practice D7282, Section 18, "Alpha Spectrometry Instrument Calibrations" (Reference 16.3).

10.3. Continuing Instrument Quality Control Testing shall be performed according to ASTM Standard Practice D7282, Sections 20, 21, and 24.

11. Procedure

11.1. Initial Sample Preparation for Americium

11.1.1. Am isotopes may be preconcentrated from building material samples using procedure *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.5), which fuses the samples using rapid NaOH fusion followed by iron hydroxide and lanthanum fluoride precipitation to preconcentrate Am isotopes from the hydroxide matrix.[2]

11.1.2. This separation can be used with other sample matrices if the initial sample preparation steps result in a column load solution containing ~3M HNO_3-1M $Al(NO_3)_3$.

11.1.3. A smaller volume of the total load solution may be taken and analyzed as needed for very high activity samples, with appropriate dilution factor calculations applied.

11.2. Rapid Americium Separation using TEVA® and DGA® Resins

11.2.1. Perform valence adjustment on column load solutions prepared from the fusion procedure (Reference 16.5) for building materials.

11.2.1.1. If particles are observed suspended in the solution, centrifuge the sample, collect the supernatant solution in small beaker and discard the precipitate.

NOTE: If a smaller volume was taken instead of the total load solutions, this smaller volume should be diluted to ~15 mL with 3M HNO_3 before proceeding with the valence adjustment.

11.2.1.2. Add 0.5 mL of 1.5M sulfamic acid to each solution. Swirl to mix.

NOTE: If ^{237}neptunium (Np) is potentially present in the sample, also add 2mg of Fe as iron nitrate to enhance Np reduction to Np^{4+}. The addition of ascorbic acid will convert Fe^{3+} to Fe^{2+}, which ensures removal of Np on TEVA® Resin.

11.2.1.3. Add 1.25 mL of 1.5M ascorbic acid to each solution. Swirl to mix. Wait 3 minutes.

11.2.1.4. Add 1 mL of 3.5M $NaNO_2$ to each sample. Swirl to mix.

NOTE: Pu, if present, is adjusted to Pu^{4+} to ensure retention and removal on TEVA® Resin. A small amount of brown fumes result from nitrite reaction with sulfamic acid. The solution should clear with swirling. If the solution does not clear (is still dark) an additional small volume of sodium nitrite may be added to clear the solution.

11.2.1.5. Add 1.5 mL concentrated HNO_3 to each sample and swirl to mix.

NOTE: The load solution nitrate concentration is increased after valence adjustment to provide greater retention of Am more effective elution of calcium ions on DGA® Resin.

[2] The fusion procedure provides a column load solution for each sample (consisting of 5 mL 3M HNO_3-0.25M H_3BO_3 + 6 mL HNO_3+7 mL 2M $Al(NO_3)_3$ + 3 mL 3M HNO_3), ready for valence adjustment and column separation on TEVA® Resin.

11.2.2. Set up TEVA® and DGA® cartridges on the vacuum box system.

NOTE: This section deals with a commercially available filtration system. Other vacuum systems developed by individual laboratories may be substituted here as long as the laboratory has provided guidance to analysts in their use. The cartridges may be set up and conditioned with nitric acid so that they are ready for column loading just prior to completion of the valence adjustment steps. More than one vacuum box may be used to increase throughput as needed.

11.2.2.1. Place the inner tube rack (supplied with vacuum box) into the vacuum box with the centrifuge tubes in the rack. Place the lid on the vacuum box system.

11.2.2.2. Place the yellow outer tips into all 24 openings of the lid of the vacuum box. Fit in the inner white tip into each yellow tip.

11.2.2.3. For each sample solution, place a TEVA® plus DGA® cartridge on to the inner white tip (DGA® cartridge below TEVA®).

11.2.2.4. Place reservoirs on the top end of the TEVA® cartridge.

11.2.2.5. Turn the vacuum on (building vacuum or pump) and ensure proper fitting of the lid.

IMPORTANT: The unused openings on the vacuum box should be sealed. Yellow caps (included with the vacuum box) can be used to plug unused white tips to achieve good seal during the separation. Alternately, plastic tape can be used to seal the unused lid holes as well.

11.2.2.6. Add 5 mL of 3M HNO_3 to the column reservoir to precondition the TEVA® cartridges.

11.2.2.7. Adjust the vacuum to achieve a flow-rate of ~1 mL/min.

IMPORTANT: Unless otherwise specified in the procedure, use a flow rate of ~ 1 mL/min for load and strip solutions and ~ 2 -3 mL/min for rinse solutions.

11.2.3. TEVA® and DGA® Resin Separation

11.2.3.1. Transfer each solution from Step 11.2.1.5 into the appropriate reservoir. Allow solution to pass through the stacked TEVA® + DGA® cartridge at a flow rate of ~1 mL/min.

11.2.3.2. Add 5 mL of 6M HNO_3 to each tube/beaker as a rinse and transfer each solution into the appropriate reservoir (the flow rate can be adjusted to ~2 mL/min).

11.2.3.3. Add 5 mL of 6M HNO_3 into each solution into the appropriate reservoir (the flow rate can be adjusted to ~2 mL/min).

11.2.3.4. Turn off vacuum, discard rinse solutions and remove TEVA® cartridges. Discard TEVA® cartridges and place new reservoirs on the DGA® cartridges.

11.2.3.5. If enhanced alpha-peak resolution is needed due to potential rare earth elements or high Ca levels present in the sample matrix, rinse the DGA Resin as follows:

11.2.3.5.1. Add 10 mL of 3M HCl into each reservoir to rinse column (flow rate ~1–2 mL/min).

11.2.3.5.2. Add 3 mL of 1M HNO_3 into each reservoir to rinse column (flow rate ~1–2 mL/min).

11.2.3.6. To DGA® Resin only, add 20 mL of 0.1M HNO_3 into each reservoir to rinse column (flow rate ~1–2 mL/min).

11.2.3.7. Add 10 mL of 0.05M HNO_3 into each reservoir as second column rinse (flow rate ~2 mL/min).

NOTE: The rinses with dilute nitric acid remove U while Am is retained. Using more 0.05M HNO_3 (20 mL) rinse without adding any 0.1M HNO_3 rinse (Step 11.2.3.6) may be an alternative and effective way to remove La/Ca with less total volume, but this will have to be validated by the laboratory.

11.2.3.8. Add 20 mL of 3M HNO_3 – 0.25M HF into each reservoir to remove any Th from DGA® Resin (flow rate ~1–2 mL/min).

11.2.3.9. Add 3 mL of 3M HNO_3 into each reservoir to rinse column of residual fluoride (flow rate ~1–2 mL/min).

11.2.3.10. Ensure that clean, labeled plastic tubes are placed in the tube rack under each cartridge. For maximum removal of interferences during elution, also change connector tips prior to Am elution.

11.2.3.11. Add 10 mL of 0.25M HCl solution to elute americium from each cartridge, reducing the flow rate to ~1 mL/min (or slightly slower).

11.2.3.12. Set americium fraction in the plastic tube aside for cerium fluoride coprecipitation, Step 11.3. Discard the DGA® cartridge.

11.3. Preparation of the Sample Test Source

NOTE: Instructions below describe preparation of a single sample test source (STS). Several STSs can be prepared simultaneously if a multi-channel vacuum manifold system is available.

11.3.1. Pipet 100 µL of the cerium carrier solution into each tube.

11.3.2. Pipet 0.5 mL 30% H_2O_2 into each tube to prevent any residual uranium from precipitating.

11.3.3. Pipet 1 mL of concentrated HF into each tube.

11.3.4. Cap the tube and mix. Allow solutions sit for ~ 15 min before filtering.

11.3.5. Set up a filter apparatus to accommodate a 0.1 micron, 25-mm membrane filter on a microprecipitation filtering apparatus.

Caution: There is no visible difference between the two sides of the filter. If the filter is turned over accidentally, it is recommended that the filter be discarded and a fresh one removed from the box.

11.3.6. Add a few drops of 95% ethanol to wet each filter and apply vacuum. Ensure that there are no leaks along the sides before proceeding.

11.3.7. While vacuum applied, add 2-3 mL of filtered Type I water to each filter and allow the liquid to drain.

11.3.8. Add the sample to the reservoir, rinsing the sample tubes with ~3 mL of water and transfer this rinse to filter apparatus. Allow to drain.

11.3.9. Wash each filter with ~2-3 mL of water and allow to drain.

11.3.10. Wash each filter with ~1-2 mL of 95% ethanol to displace water.

11.3.11. Allow to drain completely before turning the vacuum off.

11.3.12. Mount the filter on a labeled adhesive mounting disk (or equivalent) ensuring that the filter is not wrinkled and is centered on mounting disk.

11.3.13. Place the filter under a heat lamp for approximately 5 minutes or more until it is completely dry.

11.3.14. Count filters for an appropriate period of time by alpha spectrometry.

11.3.15. Discard the filtrate to waste for future disposal. If the filtrate is to be retained, it should be placed in a plastic container to avoid dissolution of the glass vessel by dilute HF.

NOTE: Other methods for STS preparation, such or microprecipitation with neodymium fluoride (NdF_3), may be used in lieu of the cerium fluoride micro-precipitation, but any such substitution must be validated as described in Step 1.5. Nd is typically interchangeable with Ce.

12. Data Analysis and Calculations

12.1. Equation for determination of final result, combined standard uncertainty, and radiochemical yield (if required):

12.1.1. The activity concentration of an analyte and its combined standard uncertainty are calculated using the following equations:

$$AC_a = \frac{A_t \times R_a \times D_t \times I_t}{W_a \times R_t \times D_a \times I_a} \quad (1)$$

and

$$u_c(AC_a) = \sqrt{u^2(R_a) \times \frac{A_t^2 \times D_t^2 \times I_t^2}{W_a^2 \times R_t^2 \times D_a^2 \times I_a^2} + AC_a^2 \times \left(\frac{u^2(A_t)}{A_t^2} + \frac{u^2(W_a)}{W_a^2} + \frac{u^2(R_t)}{R_t^2} \right)} \quad (2)$$

where:

AC_a = activity concentration of the analyte at time of count, in picocuries per gram (pCi/g)

A_t = activity of the tracer added to the sample aliquant at its reference date/time (pCi)

R_a = net count rate of the analyte in the defined region of interest (ROI), in counts per second

R_t = net count rate of the tracer in the defined ROI, in counts per second

W_a = weight of the sample aliquant (g)

D_t = correction factor for decay of the tracer from its reference date and time to the midpoint of the counting period

D_a = correction factor for decay of the analyte from the time of sample collection (or other reference time) to the midpoint of the counting period (if required)

I_t = probability of α emission in the defined ROI per decay of the tracer (Table 17.1)

I_a = probability of α emission in the defined ROI per decay of the analyte (Table 17.1)

$u_c(AC_a)$ = combined standard uncertainty of the activity concentration of the analyte (pCi/g)
$u(A_t)$ = standard uncertainty of the activity of the tracer added to the sample (pCi)
$u(R_a)$ = standard uncertainty of the net count rate of the analyte (s^{-1})
$u(R_t)$ = standard uncertainty of the net count rate of the tracer (s^{-1})
$u(W_a)$ = standard uncertainty of the sample aliquant weight (g)

NOTE: The uncertainties of the decay-correction factors and of the probability of decay factors are assumed to be negligible.

NOTE: The equation for the combined standard uncertainty ($u_c(AC_a)$) calculation is arranged to eliminate the possibility of dividing by zero if $R_a = 0$.

NOTE: The standard uncertainty of the activity of the tracer added to the sample must reflect that associated with the activity of the standard reference material and any other significant sources of uncertainty such as those introduced during the preparation of the tracer solution (e.g., weighing or dilution factors) and during the process of adding the tracer to the sample.

12.1.2. The net count rate of an analyte or tracer and its standard uncertainty are calculated using the following equations:

$$R_x = \frac{C_x}{t_s} - \frac{C_{bx}}{t_b} \quad (3)$$

and

$$u(R_x) = \sqrt{\frac{C_x + 1}{t_s^2} + \frac{C_{bx} + 1}{t_b^2}} \quad (4)$$

where:

R_x = net count rate of analyte or tracer, in counts per second
C_x = sample counts in the analyte or the tracer ROI
t_s = sample count time (s)
C_{bx} = background counts in the same ROI as for x
t_b = background count time (s)
$u(R_x)$ = standard uncertainty of the net count rate of tracer or analyte, in counts per second[3]

If the radiochemical yield of the tracer is requested, the yield and its combined standard uncertainty can be calculated using the following equations:

[3] For methods with very low counts, MARLAP Section 19.5.2.2 recommends adding one count each to the gross counts and the background counts when estimating the uncertainty of the respective net counts. This minimizes negative bias in the estimate of uncertainty and protects against calculating zero uncertainty when a total of zero counts are observed for the sample and background.

$$RY = \frac{R_t}{0.037 \times A_t \times D_t \times I_t \times \varepsilon} \quad (5)$$

and

$$u_c(RY) = RY \times \sqrt{\frac{u^2(R_t)}{R_t^2} + \frac{u^2(A_t)}{A_t^2} + \frac{u^2(\varepsilon)}{\varepsilon^2}} \quad (6)$$

where:

RY	=	radiochemical yield of the tracer, expressed as a fraction
R_t	=	net count rate of the tracer, in counts per second
A_t	=	activity of the tracer added to the sample (pCi)
D_t	=	correction factor for decay of the tracer from its reference date and time to the midpoint of the counting period
I_t	=	probability of α emission in the defined ROI per decay of the tracer (Table 17.1)
ε	=	detector efficiency, expressed as a fraction
$u_c(RY)$	=	combined standard uncertainty of the radiochemical yield
$u(R_t)$	=	standard uncertainty of the net count rate of the tracer, in counts per second
$u(A_t)$	=	standard uncertainty of the activity of the tracer added to the sample (pCi)
$u(\varepsilon)$	=	standard uncertainty of the detector efficiency

12.1.3. If the critical level concentration (L_c) or the minimum detectable concentration (MDC) are requested (at an error rate of 5%), they can be calculated using the following equations: [4]

$$L_c = \frac{\left[0.4 \times \left(\frac{t_s}{t_b} - 1\right) + 0.677 \times \left(1 + \frac{t_s}{t_b}\right) + 1.645 \times \sqrt{\left(R_{ba} t_b + 0.4\right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t \times D_t \times I_t}{t_s \times W_a \times R_t \times D_a \times I_a} \quad (9)$$

$$\mathrm{MDC} = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b}\right) + 3.29 \times \sqrt{R_{ba}\, t_s \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t \times D_t \times I_t}{t_s \times W_a \times R_t \times D_a \times I_a} \quad (8)$$

where:

[4] The formulations for the critical level and minimum detectable concentration are based on the Stapleton Approximation as recommended in MARLAP Section 20A.2.2, Equations 20.54 and 20A.3.2, and Equation 20.74, respectively. The formulations presented here assume an error rate of $\alpha = 0.05$, $\beta = 0.05$ (with $z_{1-\alpha} = z_{1-\beta} = 1.645$) and $d = 0.4$. For methods with very low numbers of counts, these expressions provide better estimates than do the traditional formulas for the critical level and MDC.

R_{ba} = background count rate for the analyte in the defined ROI, in counts per second

12.2. Results Reporting

12.2.1. The following data should be reported for each result: volume of sample used; yield of tracer and its uncertainty; and FWHM of each peak used in the analysis.

12.2.2. The following conventions should be used for each result:

12.2.2.1. Result in scientific notation ± combined standard uncertainty.

13. Method Performance

13.1. Method validation results are to be reported.

13.2. Expected turnaround time per batch of 14 samples plus QC, assuming microprecipitations for the whole batch are performed simultaneously using a vacuum box system:

13.2.1. For an analysis of a 1-g aliquant, sample preparation and digestion should take ~3 h.

13.2.2. Purification and separation of the plutonium fraction using cartridges and vacuum box system should take ~2.5 h.

13.2.3. The sample test source preparation step takes ~1 h.

13.2.4. A four-hour counting time should be sufficient to meet the MQOs listed in 9.3 and 9.4, assuming detector efficiency of 0.2–0.3, and radiochemical yield of at least 0.5. A different counting time may be necessary to meet these MQOs if any of the relevant parameters are significantly different.

13.2.5. Data should be ready for reduction ~7.5 h after beginning of analysis.

14. Pollution Prevention: The method utilizes small volume (2 mL) extraction chromatographic resin columns. This approach leads to a significant reduction in the volumes of load, rinse and strip solutions, as compared to classical methods using ion exchange resins to separate and purify the plutonium fraction.

15. Waste Management

15.1. Types of waste generated per sample analyzed

15.1.1. Approximately 55 mL of acidic waste from loading and rinsing the two extraction columns will be generated.

15.1.2. Approximately 25 mL of acidic waste from the microprecipitation method for source preparation will be generated. The waste contains 1 mL of HF and ~ 5 mL of ethanol.

15.1.3. TEVA® cartridge – ready for appropriate disposal.

15.1.4. DGA® cartridge – ready for appropriate disposal.

15.2. Evaluate all waste streams according to disposal requirements by applicable regulations.

16. References

Cited References

16.1. U.S. Environmental Protection Agency (EPA). 2009. *Method Validation Guide for Radiological Laboratories Participating in Incident Response Activities*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-006, (June 2009). Available at: www.epa.gov/narel.

16.2. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). 2004. EPA 402-B-1304 04-001A, July. Volume I, Chapters 6, 7, 20, Glossary; Volume II and Volume III, Appendix G. Available at: www.epa.gov/radiation/marlap.

16.3. ASTM D7282 "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA.

16.4. ASTM D1193, "Standard Specification for Reagent Water," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA.

16.5. U.S. Environmental Protection Agency (EPA). 2014. Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses. Revision 0, EPA 402-R14-004. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.6. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-007. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.7. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-006. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.8. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-002. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.9. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-001. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.10. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-005. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

Other References

16.11. Maxwell, S., Culligan, B. and Noyes, G. 2010. Rapid method for actinides in emergency soil samples, *Radiochimica Acta*. 98(12): 793-800.

16.12. Maxwell, S., Culligan, B., Kelsey-Wall, A. and Shaw, P. 2011. "Rapid Radiochemical Method for Actinides in Emergency Concrete and Brick Samples," *Analytica Chimica Acta*. 701(1): 112-8.

16.13. VBS01, Rev.1.3, "Setup and Operation Instructions for Eichrom's Vacuum Box System (VBS)," Eichrom Technologies, Inc., Lisle, Illinois (January 2004).

17. Tables, Diagrams, Flow Charts, and Validation Data

17.1. Tables

Table 17.1 Alpha Particle Energies and Abundances of Importance[1]

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance	α Energy (MeV)
^{241}Am	432.6	5.077×10^{-11}	0.848	5.486
			0.131	5.443
			0.0166	5.388
^{243}Am	7.37×10^{3}	2.98×10^{-12}	0.871	5.275
			0.112	5.233
			0.0136	5.181

[1] Only the most abundant particle energies and abundances have been noted here.

17.2. Ingrowth Curves and Ingrowth Factors

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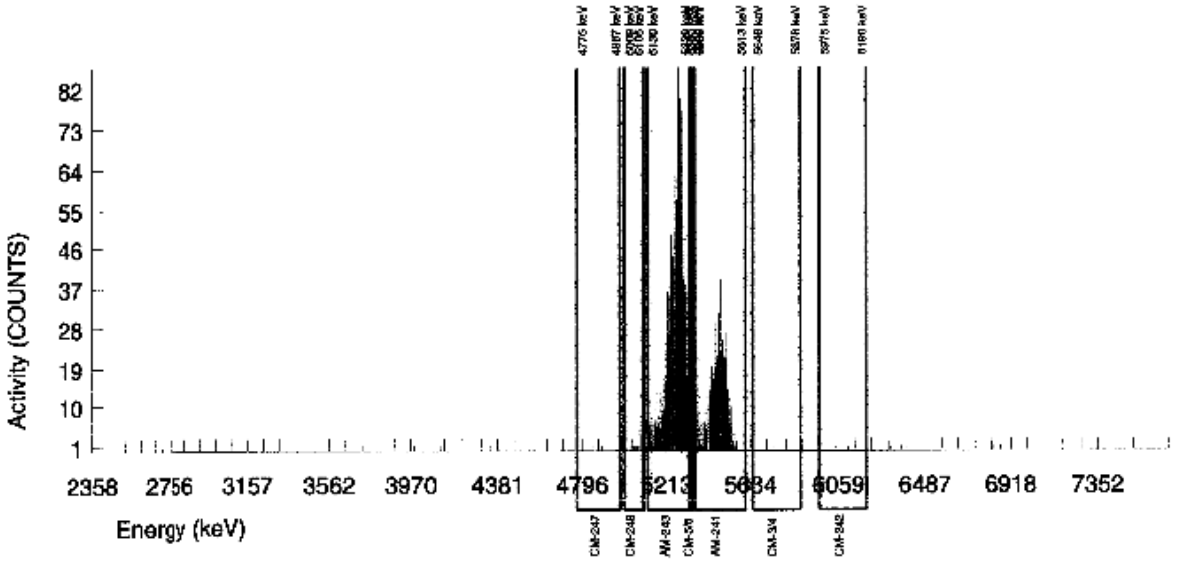
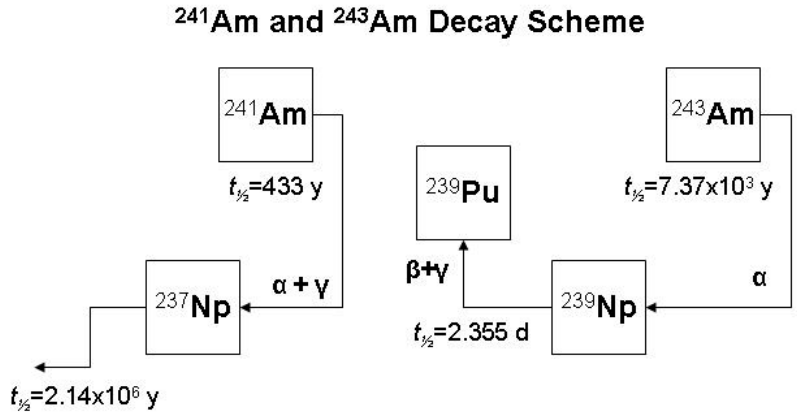
17.3. Spectrum from a Processed Sample

Americium Spectrum

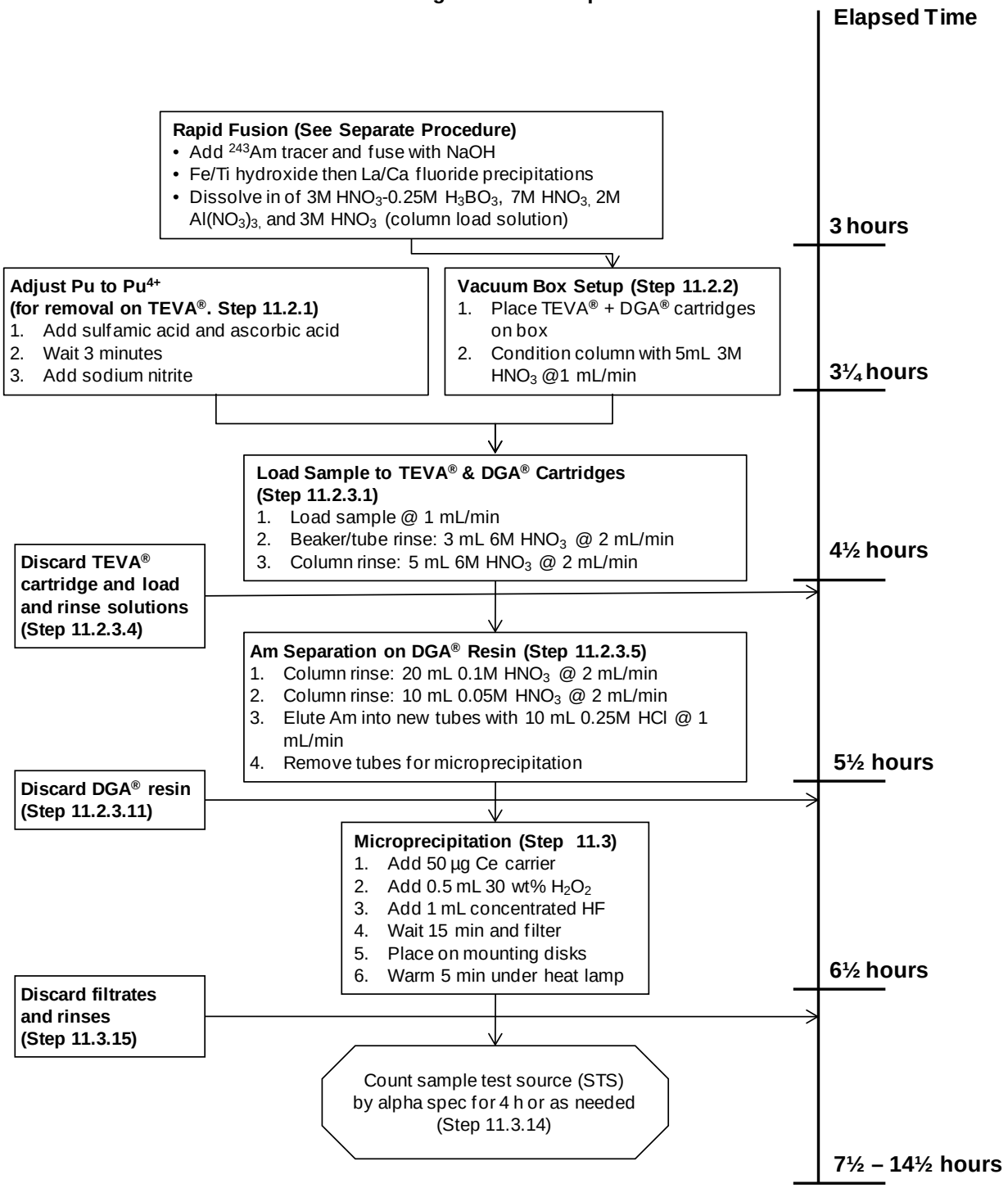


17.4. Decay Scheme



17.5. Flow Chart

Separation Scheme and Timeline for Determination of Am-241 in Building Materials Samples



Appendix:

Example of Sequential Separation Using Am-241, Pu-238+Pu-239/240, and Isotopic U in Building Materials

This sequential combination of rapid procedures for Am-241, Pu-238+Pu-239/240, and isotopic U in building materials (References 16.6, 16.7, and 16.10) has been used by some laboratories, but this sequential approach was not included in this method validation.