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Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents

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RAPID RADIOCHEMICAL METHOD FOR PLUTONIUM-238 AND PLUTONIUM-239/240 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 ^{238}Pu and $^{239/240}$Pu in solid samples such as building materials (concrete, brick, etc.).
   1.3. The method uses rapid radiochemical separation techniques to determine alpha-emitting plutonium isotopes in building material samples following a nuclear or radiological incident.
   1.4. The method cannot distinguish between ^{239}Pu and ^{240}Pu and any results are reported as the total activity of the two radionuclides.
   1.5. The method is capable of achieving a required method uncertainty (u_{MR}) for ^{238}Pu or $^{239/240}$Pu of 0.25 pCi/g at an analytical action level of 1.89 pCi/g. To attain the stated measurement quality objectives (MQOs) (see Sections 9.3 and 9.4), a sample weight of approximately 1 g and count time of at least 3 to 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).
   1.6. The rapid plutonium 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). Note that this method cannot distinguish between ^{239}Pu and ^{240}Pu and only the sum of the activities of these two isotopes can be determined.
   1.7. Multi-radionuclide analysis using sequential separation may be possible using this method in conjunction with other rapid methods (see appendix). Rapid methods can also be used for routine analyses with appropriate (typically longer) count times.
   1.8. 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.
   1.9. This method may also be used in combination with the fusion procedure for RTG (Radioisotope Thermoelectric Generator) materials in water and air filter samples.
   1.10. This method has also been used to determine ^{237}Np by using ^{236}Pu tracer. This was not tested, however, and would require validation by the laboratory.
   1.11. Other methods for sample test source (STS) preparation, such or microprecipitation with neodymium fluoride, may be used in lieu of the cerium fluoride microprecipitation, but any such substitution must be validated as described in Step 1.5.

1.12. Electroplating may not be used with the Pu strip solution containing titanium, which interferes with electrodeposition. A reductant such as rongalite (sodium formaldehyde sulfoxylate) may be used instead of titanium if electrodeposition is used but this must be validated by the laboratory.

2. Summary of Method

2.1. This method is based on the use of TEVA® Resin (Aliquat 336 extractant-coated resin) to isolate and purify plutonium by removing interfering radionuclides as well as other components of the matrix in order to prepare the plutonium fraction for counting by alpha spectrometry. The method utilizes vacuum-assisted flow to improve the speed of the separations. The sample may be fused using the procedure *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.3), with the plutonium isotopes then removed from the fusion matrix using iron hydroxide and lanthanum fluoride precipitation steps. ^{242}Pu or ^{236}Pu tracer, added to the building materials sample, is used as a yield monitor. The 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.

4. Interferences

4.1. Radiological

4.1.1. Alpha-emitting radionuclides with irresolvable alpha energies, such as ^{238}Pu (5.50 MeV), ^{241}Am (5.48 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. Vacuum box lid and holes must be cleaned frequently to prevent cross-contamination of samples.

4.2. Non-Radiological: Very high levels of anions such as phosphates may lead to lower yields due to competition with active sites on the resin and/or complexation with plutonium ions. Aluminum is added in the column load solution to complex interfering anions such as fluoride and phosphate.

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 reservoir 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 tubes, 50 mL and 225 mL capacity.
   - 6.6. Filter manifold apparatus with 25 mm-diameter polysulfone. A single-use (disposable) filter funnel/filter combination may be used, to avoid cross-contamination.
   - 6.7. 25 mm polypropylene filter, 0.1 µm pore size, or equivalent.
   - 6.8. Graduated cylinders, 500 mL and 1000 mL.
   - 6.9. Stainless steel planchets or other adhesive sample mounts (Ex. Environmental Express, Inc. P/N R2200) able to hold the 25 mm filter.
   - 6.10. Tweezers.
   - 6.11. 100 µL, 200 µL, 500 µL and 1 mL pipets or equivalent and appropriate plastic tips.
   - 6.12. 1-10 mL electronic pipet.
   - 6.13. Vacuum pump or laboratory vacuum system.
   - 6.14. Vacuum box tips, white inner, Eichrom part number AC-1000-IT, or PFA 5/32"x 1/4" heavywall tubing connectors, natural, Ref P/N 00070EE, cut to 1 inch, Cole Parmer, or equivalent.
   - 6.15. Vacuum box tips, yellow outer, Eichrom part number AC-1000-OT, or equivalent.
   - 6.16. Vacuum box, such as Eichrom part number AC-24-BOX, or equivalent.
   - 6.17. Vortex mixer.
   - 6.18. Miscellaneous laboratory ware of plastic or glass; 250 and 500 mL capacities.

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 16.5). 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 16.5).
   - 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 liter 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. Ethanol, 100%: Anhydrous C_2H_5OH, available commercially, or mix 95 mL 100% ethanol and 5 mL water.

7.6. Ferric nitrate solution (5 mg/mL): Dissolve 18.1 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9\ H_2O$) in 300 mL water and dilute to 500 mL with water.

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

7.7.1. Hydrochloric acid (0.1M) - Hydrofluoric acid (0.05M) solution: Add 1.8 mL concentrated HF and 8.3 mL concentrated HCl to 500 mL of water. Dilute to 1 liter with water and mix well.

7.7.1.1. Hydrochloric acid (0.1M) - Hydrofluoric acid (0.05M) - $TiCl_3$ (0.01 M): Add 1 mL of 10 wt% solution $TiCl_3$ per 100 mL of hydrochloric acid (0.1M) - hydrofluoric acid (0.05M) solution; prepare fresh daily as needed.

7.7.2. Hydrochloric acid (9M): Add 750 mL of concentrated HCl to 100 mL of water and dilute to 1 L with water.

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

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

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

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

7.11. Plutonium-242 tracer solution: Add 15-25 dpm of ^{242}Pu per aliquant, activity known to at least 5% (combined standard uncertainty of no more than 5%).

NOTE: If it is suspected that ^{242}Pu or ^{237}Np may be present in the sample at levels significant to interfere, ^{236}Pu tracer is an acceptable substitute. The ^{242}Pu (4.90 MeV) tracer peak may overlap slightly with the alpha energy of ^{237}Np (4.78 MeV).

7.12. Sodium nitrite ($NaNO_2$).

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

7.13. Sulfamic acid (H_3NSO_3).

7.13.1. 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.

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

7.15. Titanium (III) chloride solution ($TiCl_3$), 10 wt % solution in 20–30 wt% hydrochloric acid.

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 16.3).
      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. This is typically not required.
   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 0.01-0.1 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 required method uncertainty (u_{MR}) of 0.25 pCi/g at or below an action level of 1.89 pCi/g. This may be adjusted if the event specific MQOs are different.
   9.4. This method is capable of achieving a required relative method uncertainty (φ_{MR}) of 13% above 1.89pCi/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 ~3.5 and 10 MeV.
   10.2. Calibrate each detector used to count samples according to ASTM Standard Practice D7282, Section 18, "Alpha Spectrometry Instrument Calibrations" (Reference16.4).
   10.3. Continuing Instrument Quality Control Testing shall be performed according to ASTM Standard Practice D7282, Sections 20, 21, and 24 (Reference 16.4).

11. Procedure

11.1. Initial Sample Preparation for Plutonium

11.1.1. Pu isotopes may be preconcentrated from building material samples using the procedure *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.3), which fuses the samples using rapid NaOH fusion followed by iron hydroxide and lanthanum fluoride precipitation to preconcentrate Pu isotopes from the hydroxide matrix.[1]

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 Plutonium Separation using TEVA® Resin

NOTE: ^{237}Np is separated along with Pu isotopes using this TEVA® Resin separation. ^{236}Pu has been used as a yield monitor so that ^{237}Np can be determined, but this was not tested as part of the method validation testing.

11.2.1. Perform valence adjustment on column load solutions prepared in *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.3).

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 solution, this smaller volume should be diluted to ~15 mL with 3M HNO_3 before proceeding with the valence adjustment. The amounts of valence adjustment reagents may be adjusted under certain conditions as needed, as long as adequate reduction to Pu^{+3} and oxidation to Pu^{+4} is achieved.

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

11.2.1.3. Add 0.2 mL of 5 mg/mL ferric nitrate solution.

NOTE: Ferric ions are added and are reduced to ferrous ions by ascorbic acid to enhance valence reduction of Pu isotopes.

11.2.1.4. Add 1.25 mL of 1.5M ascorbic acid to each solution, swirling to mix. Wait 3 minutes.

11.2.1.5. Add 1mL 3.5M $NaNO_2$ to each sample, swirling to mix.

NOTE: A small amount of brown fumes result from nitrite reaction with sulfamic acid. The solution should clear with swirling and not remain dark. If the solution does not clear (is still dark) an additional small volume of sodium nitrite may be added to clear the solution.

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

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

NOTE: This section deals with a commercially available vacuum box 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.

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, fit in the TEVA® cartridge on to the inner white tip.

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 must be sealed to have vacuum. 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 needed.

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 ~ 2-4 mL/min for rinse solutions.

11.2.3. TEVA® Resin Separation

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

11.2.3.2. Add 3 mL of 3M HNO_3 to each beaker (from Step 11.2.1.4) as a rinse and transfer each solution into the appropriate reservoir (the flow rate can be adjusted to ~3 mL/min).

11.2.3.3. Add 10 mL of 3M HNO_3 into each reservoir to rinse column (flow rate ~3–4 mL/min).

11.2.3.4. Turn off vacuum and discard rinse solutions.

11.2.3.5. Add 10 mL of 3M HNO_3 into each reservoir to rinse column (flow rate ~3-4 mL/min).

11.2.3.6. Add 20 mL of 9M HCl into each reservoir to remove any Th isotopes present (flow rate ~2-3 mL/min).

11.2.3.7. Add ~3 mL of 3M HNO_3 into each reservoir to reduce bleed-off of organic extraction during Pu strip step (flow rate ~3 mL/min).

NOTE: The 3M HNO_3 added reduces extractant bleedoff that can occur with strong HCl and may improves alpha peak resolution.

11.2.3.8. Turn off vacuum and discard rinse solutions.

11.2.3.9. Ensure that clean, labeled plastic 50 mL centrifuge tubes are placed in the tube rack under each cartridge.

NOTE: For maximum removal of interferences during elution, also change reservoirs and connector tips prior to Pu elution.

11.2.3.10. Add 20 mL of 0.1M HCL-0.05M HF -0.01M $TiCl_3$ solution to elute plutonium from each cartridge, reducing the flow rate to ~1-2 mL/min.

11.2.3.11. Set plutonium fraction in the plastic centrifuge tube aside for cerium fluoride coprecipitation, Step 11.3.

11.2.3.12. Discard the TEVA® 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 (0.5 mg Ce/mL) into each centrifuge tube.

11.3.2. Pipet 0.5 mL 30 wt% H_2O_2 into each tube to prevent any residual uranium ions 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 minutes 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 filter 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 3 to 5 minutes or more until it is completely dry. Do not overheat.

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 microprecipitation, but any such substitution must be validated as described in Section 1.5. Nd is typically interchangeable with Ce.

12. Data Analysis and Calculations

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

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/L)
$u(A_t)$	=	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 weight of sample aliquant (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 shall be calculated by propagating the standard uncertainty 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.

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

$$R_x = \frac{C_x}{t_s} - \frac{C_{bx}}{t_b} \tag{3}$$

and

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

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[2]

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

$$RY = \frac{R_t}{0.037 \times A_t \times D_t \times I_t \times \varepsilon} \tag{5}$$

and

[2] 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.

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

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

12.1.2. 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: [3]

$$L_c = \frac{\left[0.4 \times \left(\frac{t_s}{t_b} - 1\right) + 0.677 \times \left(1 + \frac{t_s}{t_b}\right) + 1.645 \times \sqrt{\left(R_{ba} t_b + 0.4\right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t \times D_t \times I_t}{t_s \times W_a \times R_t \times D_a \times I_a} \quad (7)$$

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

where:

[3] 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 $d = 0.4$, a constant in equation 20.54 (the z value of 1.645 reflects the 1-α and 1-β quantiles of the normal distribution when α= β=0.05). 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 quality control (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 sample 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 ~2.25 h.

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

13.2.4. A one-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 ~7.25 h after beginning of analysis, depending on the MQOs. In order to meet the MQOs for the method validation process, a counting time of four hours was required.

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 65 mL of acidic waste from loading and rinsing the extraction column will be generated. These solutions may contain an unknown quantity of radionuclides such as Am, U, and Th isotopes if present in the sample originally.

15.1.2. Approximately 45 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. Used resins and columns should be considered radioactive waste and disposed of in accordance with restriction provided in the facility's radioactive materials license and any prevailing local restrictions.

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

16. References

Cited References

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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

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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})	Emission Probability (Abundance)[2]	α Energy (MeV)
^{238}Pu	87.7	2.50×10^{-10}	0.7091	5.499
			0.2898	5.456
$^{239/240}$Pu (Total)[3]	2.411×10^{4}	9.110×10^{-13}	0.9986	(All at same peak)
^{239}Pu	2.411×10^{4}	9.110×10^{-13}	0.7077	5.157
			0.1711	5.144
			0.1194	5.105
^{240}Pu	6.561×10^{3}	3.348×10^{-12}	0.7280	5.168
			0.2710	5.124
^{242}Pu	3.735×10^{5}	5.881×10^{-14}	0.7649	4.902
			0.2348	4.858

[1] Only the most abundant particle energies and abundances have been noted here.
[2] Unless individual plutonium isotopes are present, the alpha emissions for $^{239/240}$Pu or separately for ^{238}Pu, should use an abundance factor of 1.0.
[3] Half-life and λ are based on ^{239}Pu.

17.2. Ingrowth Curves and Ingrowth Factors

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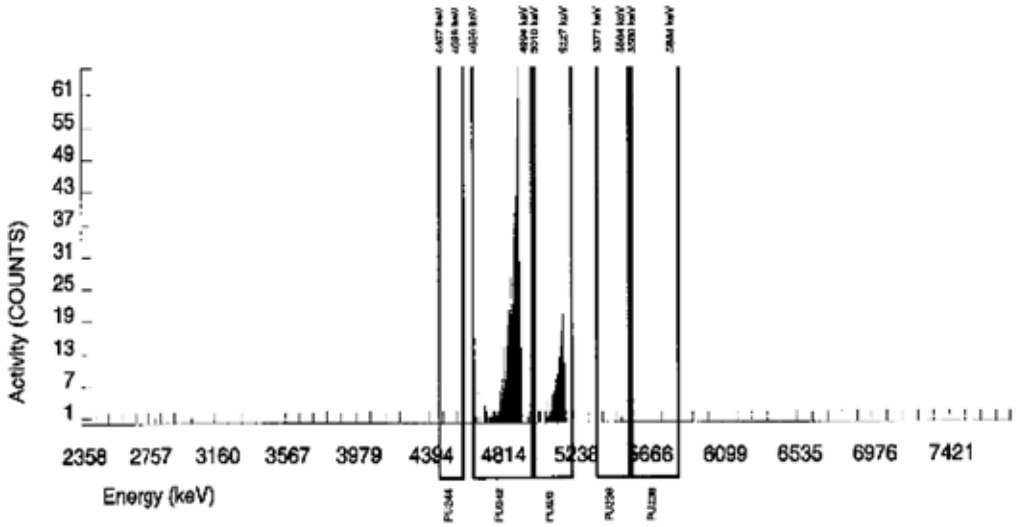
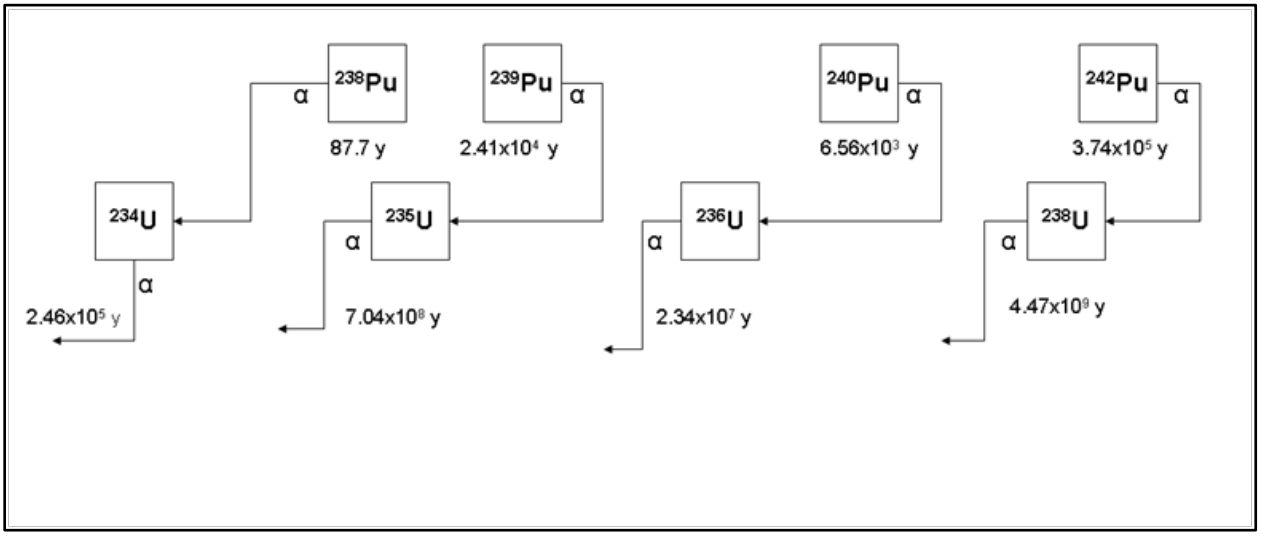
17.3. Spectrum from a Processed Sample

Plutonium Spectrum



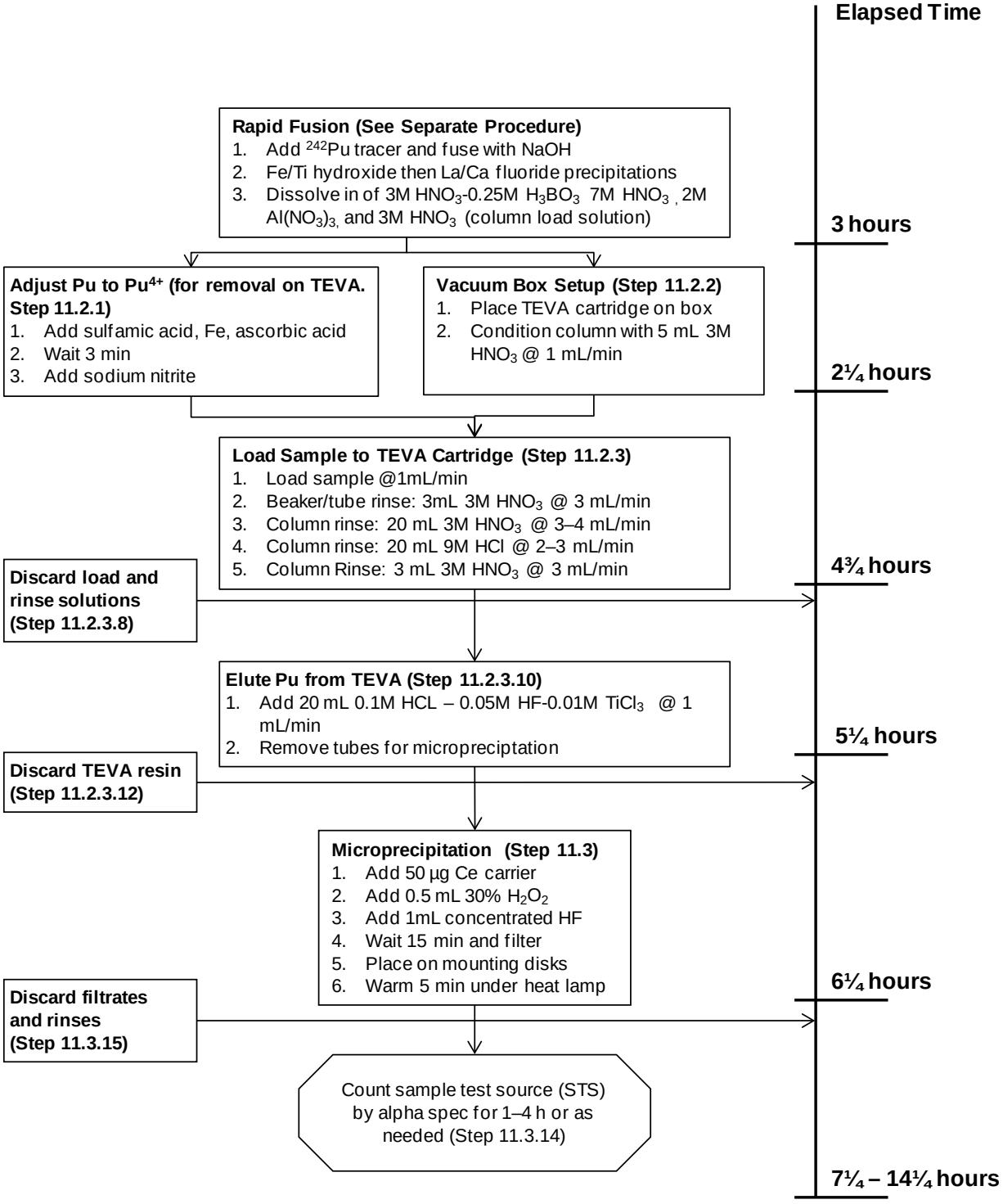
17.4. Decay Scheme

Plutonium Decay Scheme



17.5. Flow chart

Separation Scheme and Timeline for Determination of Pu Isotopes 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 16.1, 16.2, and 16.5) has been used by some laboratories, but this sequential approach was not included in this method validation.