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# Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents

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## Revision History

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**RAPID RADIOCHEMICAL METHOD FOR ISOTOPIC URANIUM 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 $^{238}U$, $^{235}U$, and $^{234}U$ in building materials such as concrete, brick, etc.
   1.3. The method uses rapid radiochemical separation techniques for determining alpha-emitting uranium isotopes in building material samples following a nuclear or radiological incident.
   1.4. The method is capable of achieving a required method uncertainty for $^{238}U$, $^{235}U$, and $^{234}U$ of 1.9 pCi/g at an analytical action level of 14.7 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 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 (STS), 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* (Reference 16.1).
   1.5. The rapid isotopic uranium 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* (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 Appendix B). 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 is based on the use of extraction chromatography resins to isolate and purify uranium isotopes by removing interfering radionuclides as well as other components of the matrix in order to prepare the uranium fraction for counting by alpha spectrometry. The method utilizes vacuum-assisted flow to improve the speed of the separations. The sample was fused using *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents* (16.3) and then the uranium isotopes were removed from the fusion matrix using iron hydroxide and lanthanum fluoride precipitation steps. U-232 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 decisionmaker 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 ($\varphi_{MR}$). 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. Spectral Overlap: Alpha-emitting radionuclides (or their short-lived decay progeny) with peaks at energies that cannot be adequately resolved from the tracer or analyte (e.g., $^{210}$Po (5.304 MeV), $^{228}$Th (5.423 MeV, 5.340 MeV), and $^{243}$Am (5.275 MeV, 5.233 MeV)) must be chemically separated to enable radionuclide-specific measurements. This method separates these radionuclides effectively. The significance of peak overlap will be determined by the individual detector's alpha

energy resolution characteristics, the quality of the final precipitate that is counted and the amount of the interfering radionuclide present.

4.1.1. Polonium-210 ($^{210}$Po), in particular, must be effectively removed from the uranium fraction because it cannot be distinguished from $^{232}$U. Its presence can result in high tracer recoveries and negatively biased U isotopic results.

4.1.2. Thorium (Th) isotopes are removed on TEVA® Resin. Any residual Th that makes it to TRU Resin is removed with a rinse step. If extremely high levels of Th isotopes are still present, the 4M HCl-0.2M-0.002M $TiCl_3$ rinse volume may be increased for difficult samples containing high levels of interferences.

4.1.3. Nepunium-237 ($^{237}$Np) (4.78 MeV) can interfere with $^{234}$U (4.77 MeV) analyses due to overlapping alpha energies so $^{237}$Np must be effectively removed.

4.1.4. It may be possible, if very high levels of interferences are present on the final STS filter, to redissolve the radionuclides in 15 mL of warm 3M $HNO_3$-0.25M boric acid and perform the column separation again without digesting another concrete aliquant. This reprocessing step to remove extremely high levels of Th isotopes, for example, will have to be validated by the laboratory.

4.1.5. Higher levels of uranium may require more cerium (Ce) to quantitatively precipitate uranium (150–200 µL [75–100 µg] instead of 100 µL (50 µg) if $^{238}$ U is 10 pCi or more in final purified fraction). There is a slight alpha peak broadening but complete precipitation is more probable. When very high activities are suspected, additional Ce should be added and/or aliquant size reduced.

4.1.6. Fe present in samples and used to preconcentrate samples after the fusion procedure can interfere slightly with U retention on TRU Resin. The cerium fluoride ($CeF_3$) precipitation step typically removes iron (Fe) effectively.

4.1.7. Vacuum box lid and holes must be cleaned frequently to prevent cross-contamination of samples.

4.2. Non-Radiological: Anions such as fluoride and phosphate that complex uranium ions may cause lower chemical yields. Aluminum that is added in the column load solution complexes fluoride present as well as any residual phosphate that may be present. Lanthanum, added to preconcentrate uranium from the sample matrix as lanthanum fluoride, can have a slight adverse impact on uranium retention on TRU Resin, but this impact is minimal with the level added. $Fe^{3+}$ can also have an adverse impact on uranium retention on TRU Resin, but the residual Fe levels after preconcentration steps are acceptable.

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 not 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. Stainless steel planchets or other adhesive sample mounts (Ex. Environmental Express, Inc., P/N R2200) able to hold the 25 mm filter.

6.9. Tweezers.

6.10. 100 µL, 200 and 500 pipette or equivalent and appropriate plastic tips.

6.11. 1-10 mL electronic pipet or manual equivalent.

6.12. Vacuum pump or laboratory vacuum system.

6.13. 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 Inc., or equivalent.

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

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

6.16. Vortex mixer.

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

6.18. 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): 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.

**NOTE: For low-level measurements, trace uranium contamination in the aluminum nitrate may be removed by passing ~250 mL of 2M $Al(NO_3)_3$ through a large column containing ~7 mL of UTEVA® Resin or TRU Resin (Eichrom Technologies, Lisle, Il) that has been previously preconditioned with ~5 mL of 3M $HNO_3$.**

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. Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$)

7.4.1. Ammonium bioxalate solution (0.1M): Dissolve 6.3 g of oxalic acid and 7.1 g of ammonium oxalate in 900 mL of water, filter, and dilute to 1 liter with water.

7.5. Barium chloride (~0.45%): Dissolve 4.5 grams of barium chloride ($BaCl_2 \cdot H_2O$) in 500 mL of water and dilute to 1000 mL with water.

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

7.6.1. 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.

7.7. Ethanol, 100%: Anhydrous $C_2H_5OH$, available commercially.

7.7.1. Ethanol (~95% v/v): Commercially available or mix 95 mL 100% ethanol and 5 mL water.

7.8. Ferric nitrate solution (5 mg/mL): Dissolve 18.1-g ferric nitrate in 300 mL water and dilute to 500 mL with water.

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

7.9.1. Hydrochloric acid (4M): Add 333 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

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

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

7.10.1. Hydrochloric acid (4M): Hydrofluoric acid (0.2M) solution: Add 7.14 mL concentrated HF to 1000 mL 4M HCl and mix well.

7.10.2. Hydrochloric acid (4M): Hydrofluoric acid (0.2M) - 0.002M $TiCl_3$ solution: Add 0.2 mL of 10 percent by mass (wt%) solution $TiCl_3$ per 100 mL; prepare fresh daily as needed.

7.11. Hydrogen peroxide, ($H_2O_2$), 30%, available commercially.

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

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

7.12.2. Nitric acid (8M): Add 510 mL of concentrated $HNO_3$ to 300 mL of water and dilute to 1 L with water.

7.13. Oxalic acid ($H_2C_2O_4 \cdot 2\ H_2O$), available commercially.

7.14. Potassium sulfate ($K_2SO_4$), available commercially.

7.15. Sodium nitrite, ($NaNO_2$).

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

7.16. Sulfamic acid ($H_3NSO_3$)

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

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

7.18. TRU Resin – 2 mL cartridge, 50 to 100 μm mesh size, Eichrom part number TR-R50-S and TR-R200-S, or equivalent.

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

7.20. Sodium sulfate ($Na_2SO_4$), available commercially.

7.21. Sulfuric acid ($H_2SO_4$), 18M concentrated, available commercially.

7.22. Uranium-232 tracer solution: Add 15-25 dpm of $^{232}U$ 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. Self-cleaning tracer to remove the $^{228}Th$ daughter from the $^{232}U$ tracer as described in Appendix A reduces the chance of $^{228}Th$ contamination in the purified uranium fraction, which could overlap with the $^{232}U$ tracer peak if levels are high enough.**

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 fusion procedure.

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 $^{238}U$ $u_{MR}$ of 1.9 pCi/g at or below an action level of 14.7 pCi/g. This may be adjusted if the event specific MQOs are different.

9.4. This method is capable of achieving a required $^{238}U$ $\varphi_{MR}$ of 13% above 14.7 pCi/g. This may be adjusted if the event specific MQOs are different.

9.5. This method is capable of achieving a required $^{238}U$ minimum detectable concentration (MDC) of ~0.5 pCi/g with a counting time of 180 minutes.

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" (Reference 16.5).

10.3. Continuing Instrument Quality Control Testing shall be performed according to ASTM Standard Practice D7282, Sections 20, 21, and 24 (Reference 16.5).

11. Procedure

11.1. Initial Sample Preparation for Uranium

11.1.1. U 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 U isotopes from the hydroxide matrix.[1]

[1] The fusion procedure provides a column load solution for each sample (consisting of 5mL 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.

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.

**NOTE: It should be noted that the $LaF_3$ matrix removal step in the fusion procedure (Reference 16.3) following the sodium hydroxide fusion removes Fe to minimal levels that will not interfere with TRU Resin as $Fe^{3+}$. If this column method is used on solid samples (soil, etc.) with high Fe levels without the $LaF_3$ matrix removal, there may be a significant adverse impact on U retention on TRU Resin.**

11.2. Rapid Uranium Separation using TEVA® and TRU Resins

11.2.1. Perform valence adjustment on column load solutions prepared from the fusion procedure for building materials (Reference 16.3).

**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.**

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

**NOTE: Pu, if present, is valence adjusted to $Pu^{4+}$ to ensure retention and removal on TEVA® Resin.**

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

11.2.1.3. Add 0.1 mL of 5 mg/mL ferric nitrate solution.

**NOTE: Ferric ions are added and are reduced to ferrous ion s by ascorbic acid to enhance valence reduction of Pu isotopes and $^{237}Np$.**

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 1 mL of 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.**

11.2.1.6. Add 1.5 mL of concentrated $HNO_3$ to each sample, swirling to mix.

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

**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 onto 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. Place a TEVA® cartridge above a TRU cartridge and place on vacuum box.

11.2.2.4. Place reservoirs into top of stacked TEVA®+TRU Resin cartridges, inserting reservoir into top of 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® and TRU 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® and TRU Resin Separation

11.2.3.1. Transfer each solution from Step 11.2.1.5 into the appropriate reservoir by pouring or by using a plastic transfer pipette.

11.2.3.2. Allow solution to pass through the stacked TEVA® + TRU cartridges at a flow rate of ~1 mL/min.

11.2.3.3. Add 3 mL of 3M $HNO_3$ to each tube (from Step 11.2.1.5) as a rinse and transfer each solution into the appropriate reservoir (the flow rate can be adjusted to ~1 to 2 mL/min).

11.2.3.4. Add 10 mL of 3M $HNO_3$ into each reservoir to rinse column (flow rate ~2 mL/min).

11.2.3.5. Turn off vacuum, discard rinse solutions. Remove and discard the TEVA® cartridges.

11.2.3.6. To the TRU Resin cartridge only, add 15 mL of 4M HCl-0.2M HF-0.002M $TiCl_3$ into each reservoir as second column rinse (flow rate ~1–2 mL/min) to remove Am, Th and Po.

11.2.3.7. Add 5 mL of 8M $HNO_3$ into each reservoir as second column rinse (flow rate ~1–2 mL/min) to reduce bleed-off of organic extractant.

11.2.3.8. 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 U elution.**

11.2.3.9. Add 15 mL of 0.1M ammonium bioxalate ($NH_4HC_2O_4$) to elute the uranium from each cartridge, reducing the flow rate to ~1 mL/min.

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

11.2.3.11. Discard the TRU cartridge.

11.3. Preparation of the Sample Test Source

**NOTE: Additional Ce (200 µL) is typically needed if the $^{238}$U is greater than 10-15 pCi in the final purified solution to ensure complete precipitation and prevent lower chemical yields. If it is not known that the $^{238}$U is < 10-15 pCi in the final purified solution, 200 µL Ce (100 µg Ce) should be added instead of 100 µL Ce.**

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

11.3.2. Pipet 0.5 mL 10 wt% $TiCl_3$ into each tube to reduce uranium to $U^{4+}$.

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 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 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. 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/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) |

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

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

**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[2] |

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

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

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) |
| $\varepsilon$ | = | detector efficiency, expressed as a fraction |
| $u_c(RY)$ | = | combined standard uncertainty of the radiochemical yield |

[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.

$u(R_t)$ = 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: [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:

$R_{ba}$ = 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.

[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.

13.2.2. Purification and separation of the uranium 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 3 to 4 hour counting time should be sufficient to meet the MQOs listed in 9.3, 9.4, and 9.5, 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 ~9.5 to 10.5 hours 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 uranium 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. 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.

15.1.4. TRU 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.

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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 – Decay and Radiation Data

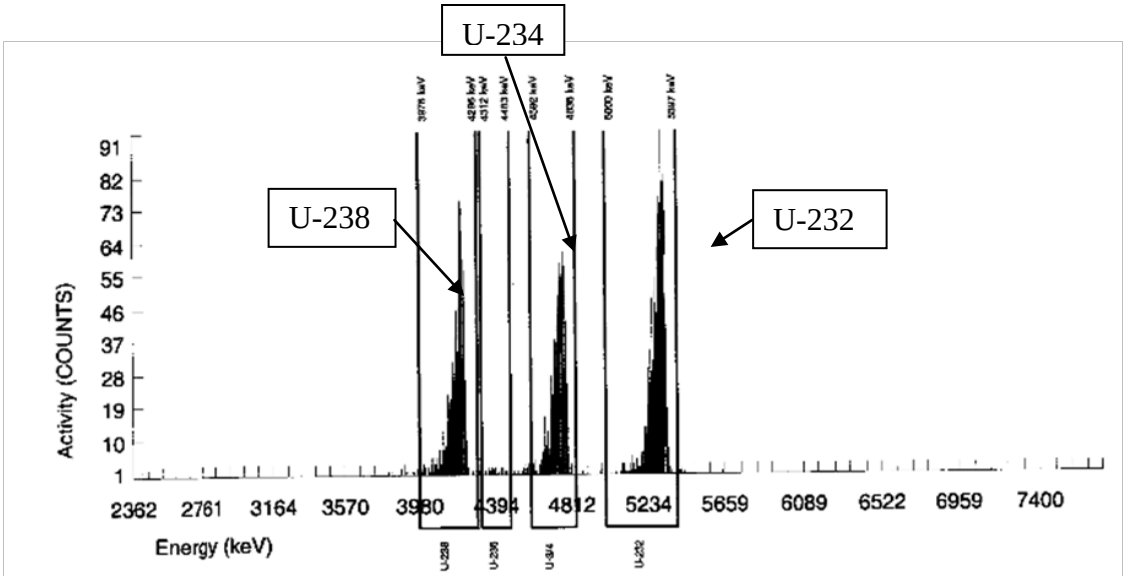
| Nuclide | Half-Life (Years) | λ ($s^{-1}$) | Abundance | α Energy (MeV) |
|---|---|---|---|---|
| $^{238}U$ | $4.468\times10^{9}$ | $4.916\times10^{-18}$ | 0.79 | 4.198 |
| | | | 0.21 | 4.151 |
| $^{235}U$ | $7.038\times10^{8}$ | $3.121\times10^{-17}$ | 0.050 | 4.596 |
| | | | 0.042 | 4.556 |
| | | | 0.0170 | 4.502 |
| | | | 0.0070 | 4.435 |
| | | | 0.0210 | 4.414 |
| | | | 0.55 | 4.398 |
| | | | 0.170 | 4.366 |
| $^{234}U$ | $2.457\times10^{5}$ | $8.940\times10^{-14}$ | 0.7138 | 4.775 |
| | | | 0.2842 | 4.722 |
| | | | 0.002 | 4.604 |
| $^{232}U$ | 68.9 | $3.19\times10^{-10}$ | 0.6815 | 5.320 |
| | | | 0.3155 | 5.263 |

17.2. Ingrowth Curves and Ingrowth Factors

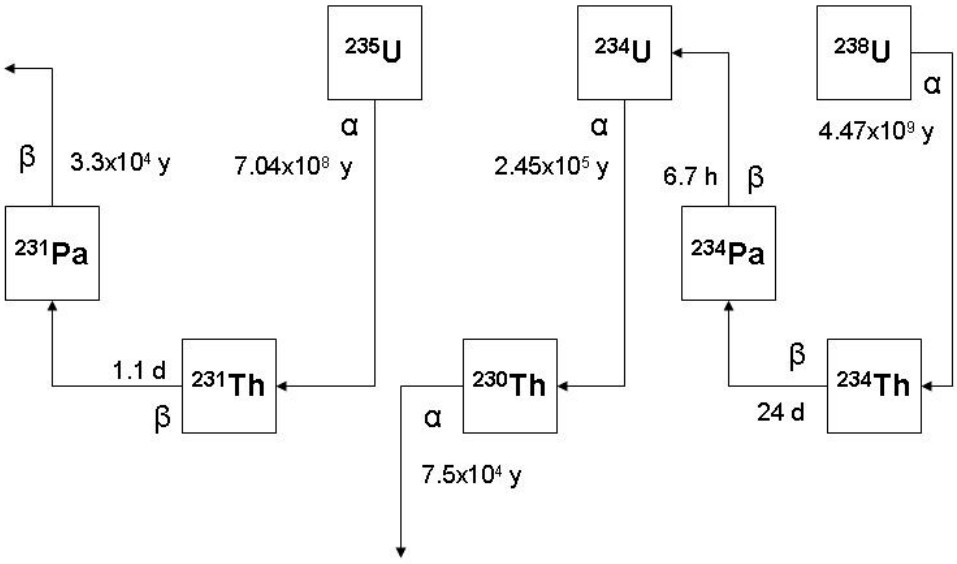
*This section intentionally left blank*

17.3. Spectrum from a Processed Sample

**Uranium Spectrum**

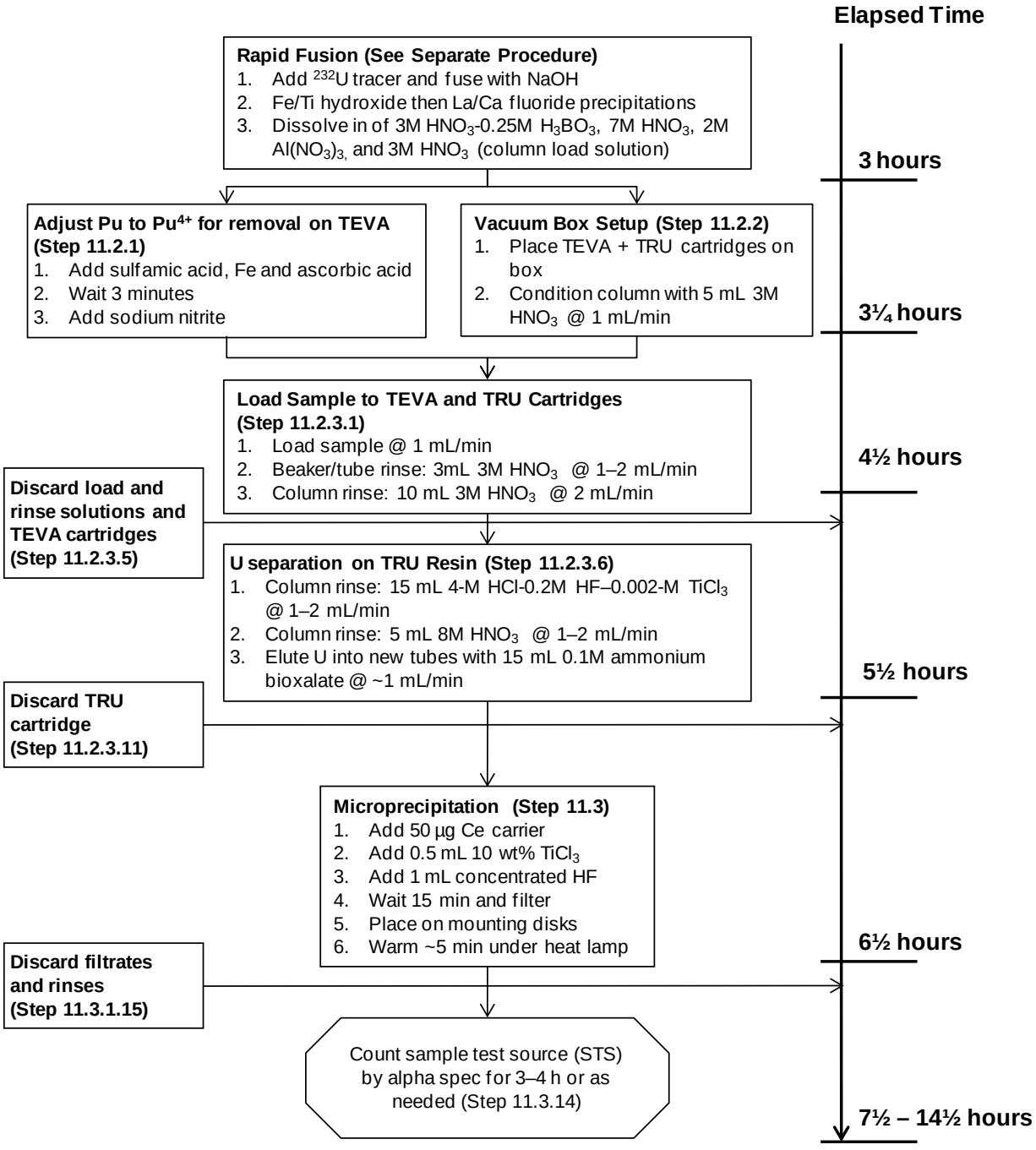


17.4. Decay Scheme: Ingrowth is not generally a large concern with this analysis unless one is running sequential analysis for uranium and plutonium with $^{236}$Pu tracer (due to ingrowth of $^{232}$U tracer) or sequential analyses for uranium and thorium (due to $^{228}$Th tracer ingrowth in the $^{232}$U tracer).



## 17.5. Flow Chart

**Separation Scheme and Timeline for Determination of Uranium Isotopes in Building Materials Samples**



# Appendix A:

## Preparation of Self-Cleaning $^{232}U$ Tracer

**NOTE: $^{228}Th$ daughter is removed continually using barium sulfate precipitation to minimize $^{228}Th$ when using this tracer.**

1. Add 45 g $K_2SO_4$, 20 g $Na_2SO_4$ and 20 mL conc. $H_2SO_4$ to a 1 L Erlenmeyer flask.
2. Pipet the volume prescribed from a $^{232}U$ stock solution into the flask to prepare the desired concentration of $^{232}U$ tracer.
3. Heat solution on a hot plate on medium heat until the tracer solution is evaporated and fumes of $H_2SO_4$ begins to form.
4. Heat until a thick sulfate solution forms with minimal fumes.
5. Remove flask from the hot plate with tongs and swirl flask until the sulfate fusion cake forms.
6. Dissolve the fusion cake in 250 mL water and 31.8 mL conc. $HNO_3$, using heat as needed.
7. Add 3 mL 30% $H_2O_2$ to the flask. Swirl to mix.
8. With heating and stirring, add six 10 mL portions 0.45% $BaCl_2$, waiting 1 minute between each addition.
9. Remove flask from hotplate.
10. Cool flask to room temperature.
11. Transfer solution and solids to 1,000 mL volumetric flask. Rinse initial flask with water and transfer rinse to the volumetric flask.
12. Dilute volume to 1000 mL with water.
13. Mix standard well.
14. Transfer standard with solids to a 1 L plastic bottle.
15. When volumes of this standard are transferred to smaller containers, make sure that solids are transferred along with the liquid by swirling prior to transfer.

    **NOTE: The smaller bottles of $^{232}U$ tracer used in the lab may be used with or without periodic shaking and allowing the solids to settle. Tracer volumes should not be taken when volumes are low enough such that suspended solids (containing $^{228}Th$) will also be pipetted. $^{228}Th$ levels remain low with or without shaking and either way is acceptable for this method, which contains Th removal steps. For maximum Th removal, however, shaking and settling should be performed within 1 week of use. Ex. If the tracer is also used for sequential work where U and Th separations are performed sequentially, maximum $^{228}Th$ removal is essential for accurate $^{228}Th$ assay in samples.**

## Appendix B:

### 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 $^{241}$Am, $^{238}$Pu+$^{239/240}$Pu, 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.