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Rapid Method for Sodium Hydroxide/Sodium Peroxide Fusion of Radioisotope Thermoelectric Generator Materials in Water and Air Filter Matrices Prior to Plutonium Analyses for Environmental Remediation Following Radiological Incidents

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Rapid Method for Sodium Hydroxide/Sodium Peroxide Fusion of Radioisotope Thermoelectric Generator Materials in Water and Air Filter Matrices Prior to Plutonium Analyses

1. Scope and Application

1.1. This method is applicable to the total dissolution of refractory radioisotope thermoelectric generator (RTG) materials in water and air samples collected following a radiological or nuclear incident. The fusion is rapid, rigorous, and effectively dissolves refractory radionuclide particles present in waters and air filter matrices.

1.2. This method is a sample dissolution and pretreatment technique used prior to other separation and analysis methods. It was validated together with the chemical separation and analysis process described in *Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.1).

1.3. Highly refractory ("high-fired") plutonium in particulate material isolated from water samples by filtration is less likely to be absorbed in the digestive tract (and is therefore determined separately) than the more bioavailable plutonium isolated in the aqueous sample filtrate. Results for the two fractions may be reported separately, or they may be combined mathematically and reported as a single result for activity and associated combined uncertainty.

1.4. The user should refer to project-specific requirements for the determination of applicable measurement quality objectives (MQOs). In the absence of project-specific guidance, MQOs for water and air samples may be based on the Analytical Action Levels (AALs) and required method uncertainties (u_{MR} and φ_{MR}) found in the *Radiological Sample Analysis Guide for Incidents of National Significance — Radionuclides in Water* (Reference 16.4), and *Radiological Sample Analysis Guide for Incidents of National Significance — Radionuclides in Air* (Reference 16.5).

1.5. For air filters, this method is capable of meeting a required method uncertainty of 1.9 pCi/filter at and below the AAL of 15.0 pCi/filter, and a required relative method uncertainty of 13% above the AAL. This assumes that the filter sample is split following acid dissolution with one-half of the sample being processed through chemical separations and a 360 minute count duration. With a 68 m^3 air volume, this would equate to a required method uncertainty of 0.028 pCi/m^3 at the action level of 0.22 pCi/m^3. Minimum detectable concentration (MDC) values of 0.20 pCi/filter or below may be achieved with the same aliquant and a count time of 240 minutes. Assuming a 68 m^3 air volume, the method would be capable of meeting a required MDC of 0.003 pCi/m^3 or below.

1.6. For water samples (filtered solids, filtrate, or combined result), this method is capable of satisfying a required method uncertainty of 2.1 pCi/L at and below an AAL of 16.3 pCi/L, and a required relative method uncertainty of 13% above the AAL. This assumes a 1 liter aliquant and a count duration of 360 minutes. Required MDCs of 0.23 pCi/L may be achieved with the same aliquant and a count time of 240 minutes.

1.7. Application of this method must be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (Reference 16.3) or the protocols for method validation published by a recognized standards organization. The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the final counting form and initial sample volume.

1.8. Although this method may be applicable to other matrices that potentially contain RTG material, such as soils, concrete, or brick after destruction of organics in the sample, it is the laboratory's responsibility to perform method validation on the modified method prior to use.

2. Summary of Method

2.1. Air filters: The method is based on total dissolution of RTG materials in water or air filter samples. The air filter is fused using rapid sodium hydroxide/sodium peroxide at 700 °C.

2.2. Water samples: refractory RTG particles are collected on a 0.45-µm filter using vacuum. RTG activity remaining in the aqueous filtrate is preconcentrated using calcium phosphate precipitation. The filtered solids fraction and the filtrate fraction are processed separately by fusing with sodium hydroxide/sodium peroxide prior to subsequent chemical separation and alpha spectrometric analysis.

2.3. The fusion method requires approximately one hour per batch of twenty samples using multiple furnaces. Preconcentration steps to eliminate the alkaline fusion matrix and collect the radionuclides and require approximately two hours.

2.4. Plutonium (Pu) is separated from the fusion matrix using a lanthanum/calcium fluoride matrix removal step in preparation for separation and analysis using the *Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.1).

3. Definitions, Abbreviations and Acronyms

NOTE: Common laboratory and chemical acronyms and abbreviations not included

3.1. AAL – analytical action level

3.2. APS – analytical protocol specifications

3.3. CSU – combined standard uncertainty

3.4. DRP – discrete radioactive particle

3.5. FWHM – full-width-at-half-maximum

3.6. keV – kilo electron volt

3.7. LCS – laboratory control sample

3.8. MCE – mixed cellulose ester

3.9. MeV – mega electron volt

3.10. MDC – minimum detectable concentration

3.11. MQO – measurement quality objective

3.12. MARLAP – *Multi-Agency Radiological Analytical Laboratory Protocol Manual* (Reference 16.6).

3.13. QC – quality control

3.14. RTG – radioisotope thermoelectric generator

3.15. ROI – region of interest

3.16. S_c – critical level concentration

4. Interferences and Limitations

4.1. Organic-based vs. Glass-fiber Filters

4.1.1. Organic-based filters, such as cellulose nitrate or cellulose acetate filters, may react vigorously upon addition of peroxide or during charring steps. Wet-ashing with nitric-acid and hydrogen peroxide is needed to destroy organic constituents in the air filter matrix prior to fusion.

4.1.2. Glass fiber filter samples may be fused without any wet-ashing.

4.2. Samples with elevated activity or samples that require multiple analyses from a single RTG sample may need to be split after dissolution.

4.2.1. Tracer or carrier amounts added for radiochemical yield determinations should be increased so that the split being processed contains the normal amount of tracer or carrier.

4.2.2. For very high activity samples, the addition of the tracer or carrier may be postponed until following the sample split. Special care must be taken to ensure that isotopic exchange of the sample with the radiochemical yield tracer is achieved (i.e., following total dissolution and initial valence adjustment). This deviation from the method must be thoroughly documented and reported in the case narrative.

4.2.3. When this method is employed as written, the entire volume of sample is fused and processed through subsequent chemical separation method. The original sample size is used in all calculations.

4.2.4. In cases where the sample is split or diluted prior to analysis, the fractional size of splits and dilutions may be used determine the chemical yield and possibly the size of the sample aliquant. Therefore, the mass/volume of the respective split fraction(s) and dilutions must be measured accurately. The calculation of sample aliquant size and the tracer activity for chemical yield are described in Section 12, below.

4.3. Analytical parameters, such as the duration of the sample count and the aliquant size, should be modified to achieve optimal throughput while leveraging those resources available to the laboratory. For example, longer count times combined with smaller

aliquant sizes may achieve optimal throughput when facilities and equipment are more limited than instrumentation. If instrumentation is limiting, however, higher throughput might be achieved with larger aliquant sizes and shorter count times. In either case, the laboratory must validate the method using those analytical parameters that will be employed when in analyzing samples.

4.4. Batch quality control samples (blanks, laboratory control samples (LCS), duplicates, and if required, matrix spikes) shall be created as early in the process as possible and subjected to the same processes as associated field samples, including filtration, tracer/carrier addition, sample dissolution and splitting, chemical separations, source preparation and counting.

4.5. Centrifuge speeds of 3000 rpm or greater are suggested, but lower centrifuge speeds, down to 2500 rpm, would be acceptable as long as the supernatant solution can be effectively removed.

4.6. Valence control of plutonium is very important, both in the preconcentration steps and column separation steps used in this method. Pu^{+6} typically forms when plutonium oxide is fused using sodium peroxide. All plutonium must be reduced to Pu^{+4} or Pu^{+3} before isotopic exchange with the tracer can be achieved with reasonable certainty. Additionally, only Pu^{+4} or Pu^{+3} will precipitate in the lanthanum fluoride/calcium fluoride preconcentration step. Although peroxide may reduce Pu^{+6} to Pu^{+4}, the Pu valence must be controlled with certainty. The alkaline fusion cake is dissolved using HCl. The solution is allowed to stand for a sufficient period of time for peroxide ions to react with the HCl minimizing residual peroxide present prior to adjusting the valence of plutonium with titanium (III) chloride. The iron added facilitates removal of peroxide that may be present. Valence controls also ensure that plutonium will be present in the Pu^{+4} form prior to separation on TEVA Resin ™ in the *Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials* (Reference 16.1)

4.7. Although this method was validated using ^{242}Pu tracer, ^{236}Pu tracer may be used assuming traceable material can be obtained with sufficient purity. Pu-242 is the optimal tracer to use for samples expected to contain little or no activity since tailing counts from the tracer peak will not fall in analyte peaks of higher energy. In contrast, ^{236}Pu offers an advantage for samples expected to contain high activities of plutonium since its energy falls above ^{238}Pu and $^{239/240}Pu$ and the tracer peak is not be affected by tailing from high levels of analyte in samples. Typically, a total of 2–10 pCi of tracer is added for each sample test source depending on the count time and the total tracer counts desired. The tracer activity and count time may be adjusted, however, if the sample is split or diluted, depending on count times, and the total number tracer counts needed to meet method uncertainty requirements.

4.8. The alpha spectrometry regions of interest (ROIs) should encompass the entire ^{242}Pu peak. ROIs for ^{238}Pu, $^{239/240}Pu$, and ^{242}Pu tracer peak should be of similar width, and should ideally capture all peak counts. If high activities of ^{238}Pu are present, the ^{238}Pu alpha peak may tail into the $^{239/240}Pu$ region of interest, even in samples with very good resolution. Although efforts should be made to minimize peak overlap, if $^{239/240}Pu$ is known not to be present in the sample (e.g., RTG material consisting of pure ^{238}Pu),

tailing of ^{238}Pu into $^{239/240}$Pu ROI may not be a large concern. When peak overlap compromises sample quantitation, sample test sources may need to be reprocessed or reprepared.[1]

4.9. Zirconium crucibles used in the fusion process may be reused.

4.9.1. It was found that fused RTG material may be lost on crucible walls and that additional rinsing with HCl at the point of dissolving the fusion cake will enhance removal of residual material from the crucible.

4.9.2. The laboratory must have a process for cleaning and contamination assessment of the reused zirconium crucibles. The crucibles should be cleaned using soap and water, followed by warm nitric acid (multiple rinses) and water. Blank measurements should be monitored to ensure effective cleaning.

4.9.3. Segregation of crucibles used for low- and high-activity samples is needed to minimize the risk of cross-contamination.

4.9.4. The heating of crucibles at 700 °C will oxidize the zirconium metal over time and the crucibles will need to be replaced.

4.10. Although this fusion and preconcentration method was validated for ^{238}Pu, it could be modified for use in determining most actinides in refractory air and water samples. Chemical yield tracers appropriate to the respective determinations of actinides would be added in place of, or in addition to ^{242}Pu. The product of the fusion and preconcentration would then be processed according to an appropriate chemical separation scheme for the radionuclide(s) of concern.

5. Safety

5.1. General

5.1.1. Refer to the laboratory safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.

5.1.2. Refer to the laboratory chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

5.2. Radiological

5.2.1. Discrete Radioactive Particles (DRPs or Hot Particles)

5.2.1.1. Hot particles will be small, on the order of 1 mm or less. DRPs are typically not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic).

NOTE: Information regarding DRPs should accompany the samples during processing as well as be described in the case narrative that accompanies the sample results.

[1] Reprocessing might include redissolving the sample from the sample test source and repurifying using the Pu separation procedure to remove chemical or radioactive impurities.

5.3. Procedure-Specific Non-Radiological Hazards:

5.3.1. The sodium peroxide/sodium hydroxide fusion is performed in a furnace at 700 °C. The operator should exercise extreme care when using the furnace and when handling the hot crucibles. Long tongs are recommended. Thermal protection gloves are also recommended when performing this part of the method. The fusion furnace should be used in a ventilated area (hood, trunk exhaust, etc.).

6. Equipment and Supplies

6.1. Adjustable temperature laboratory hotplates.

6.2. Balance, top loading or analytical, readout display of at least ± 0.01 g.

6.3. Beakers, 1000 mL or as needed.

6.4. Centrifuge able to accommodate 225-mL tubes.

6.5. Centrifuge tubes, 50 mL and 225-mL (or 250 mL) capacity.

6.6. Crucibles, 250 mL, zirconium, with lids. (e.g., low-form 250-mL crucibles, P/N 10-0250LF and 10-0250C lid from Metal Technology, Inc., Albany, or equivalent).

6.7. Filters, 0.45 micron mixed cellulose ester (e.g., MCE) filter, Millipore HA, or equivalent.

6.8. 100-µL, 200-µL, 500-µL, and 1-mL pipets or equivalent and appropriate plastic tips.

6.9. 1 mL-10 mL electronic/adjustable pipet.

6.10. Muffle furnace capable of reaching at least 700 ^{o}C.

6.11. Reusable vacuum filter units to hold 47mm filters with 500-mL receivers or equivalent filter apparatus. (e.g., Thermo Scientific Nalgene Reusable Filter Holders, P/N 300-4050, transparent polysulfone; capacity: upper chamber 500 mL, receiver 500 mL, or equivalent).

6.12. Tongs for handling crucibles (small and long tongs).

6.13. Tweezers or forceps.

6.14. Vacuum, building vacuum source or portable pump.

6.15. Vortex stirrer.

7. Reagents and Standards

Note: Unless otherwise indicated, all references to water should be understood to mean Type I Reagent water (ASTM D1193; Reference 16.7).

NOTE: All reagents are American Chemical Society grade or equivalent unless otherwise specified.

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

7.1.1. Aluminum nitrate solution, 2M ($Al(NO_3)_3$): Dissolve 750 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9\ H_2O$) in ~700 mL of water and dilute to 1 L with water.

7.2. Ammonium hydrogen phosphate (3.2 M): Dissolve 106 g of $(NH_4)_2HPO_4$ in 200 mL of water, heat gently to dissolve and dilute to 250 mL with water.

7.3. Ammonium hydroxide (NH_4OH), concentrated.

7.4. Boric Acid, H_3BO_3.

7.5. Calcium nitrate (1.25M): Dissolve 147 g of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) in 300 mL of water and dilute to 500 mL with water.

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

7.6.1. Hydrochloric acid (0.01 M): Add 0.83 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.

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

7.6.3. Hydrochloric acid (6 M): Add 500 mL of concentrated HCl to 400 mL of water and dilute with water to 1 L.

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

7.8. Iron carrier (50 mg/mL): dissolve 181 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 300 mL 997 water and dilute to 500 mL with water.

7.9. Lanthanum carrier, 1.0 mg La/mL: add 1.56 g lanthanum (III) nitrate hexahydrate [$La(NO_3)_3 \cdot 6\ H_2O$] in 300 mL water, diluted to 500 mL with water.

7.10. Nitric acid (15.8 M): Concentrated HNO_3, available commercially.

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

7.10.2. Nitric acid–boric acid solution, 3 M–0.25 M: add 15.4 g of boric acid and 190 mL of concentrated HNO_3 to 500 mL of water, heat to dissolve, and dilute to 1 L with water.

7.10.3. Nitric acid (7 M): Add 443 mL of concentrated HNO_3 to 400 mL of water and dilute to 1 L with water.

7.11. Phenolphthalein solution: dissolve 1 g of phenolphthalein in 100 mL 95% ethanol and dilute with 100 mL water.

7.12. Sodium Hydroxide (NaOH) pellets.

7.13. Sodium Peroxide (Na_2O_2) pellets.

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

7.15. Radioactive tracers/carriers (used as radiochemical yield monitors) and spiking solutions. Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Tracers/carriers that are used to monitor radiochemical/chemical yield should be added at the beginning of this procedure. This

allows for monitoring and correction for of chemical losses in the combined dissolution process, as well as in the chemical separation method. Carriers used to prepare sample test sources but not used for chemical yield determination (e.g., cerium added for microprecipitation of plutonium), should be added where indicated.

8. Sample Collection, Preservation, and Storage

8.1. Samples should be collected in 1-L plastic containers.

8.2. No sample perseveration is required if sample is delivered to the laboratory within 3 days of sampling

8.3. If separate dissolved and/or suspended concentrations of plutonium are sought, the insoluble fraction r

8.4. If the sample is to be held for more than three days, HNO_3 shall be added until pH<2.

9. Quality Control

9.1. Where the subsequent chemical separation technique requires the addition of carriers and radioactive tracers for chemical or radiochemical yield determinations, these are to be added prior to beginning the fusion procedure, unless there is good technical justification for doing otherwise.

9.2. The source preparation method should produce a sample test source with full-width-at-half-maximum values (FWHM) of less than 100 keV for the tracer peak.[2] Precipitate reprocessing should be considered if this range of FWHM cannot be achieved.[3]

9.3. Quality control samples shall be analyzed with each batch of twenty or fewer samples and shall be created as early in the process as possible. They shall be subjected to the same processes as associated field samples, including filtration, tracer/carrier addition, sample dissolution and splitting, chemical separations, source preparation, counting, and calculation of sample activities.

9.3.1. One laboratory control sample (LCS) shall be run with each batch of samples. The LCS consists of analyte-free matrix (where available) spiked with a known quantity of radionuclide spiking solution. The concentration of the LCS should be at or near the action level or level of interest for the project.

9.3.2. One blank shall be run with each batch of samples. The reagent blank should consist of the analyte-free matrix (where available).

9.3.3. One sample duplicate that is equivalent in size to the original aliquant should be analyzed with each batch of samples. If sample volumes are limited, an LCS duplicate may be substituted for the sample duplicate.

9.3.4. A matrix spike is not required with this method.

[2] This is a rule of thumb that works for Pu, Am, and U determinations but would be problematic for ^{229}Th, which consists of numerous lower abundance peaks distributed across a wider energy range.

[3] Reprocessing might include redissolving the sample from the sample test source and repurifying using the Pu separation procedure to remove chemical or radioactive impurities.

9.4. Efforts should be made to obtain analyte-free quality control (QC) materials that have similar composition as the samples to be analyzed (e.g., deionized water or a blank air filter from the same lot of filters as the samples). A reagent blank shall be substituted for analyte-free matrix when analyte-free matrix is not available.

9.5. 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 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.

10. Calibration and Standardization.

10.1. Set up the alpha spectrometry system consistent with manufacturer recommendations following laboratory quality manual specifications. 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 16.8).

10.3. Continuing instrument QC testing shall be performed according to ASTM Standard Practice D7282, Sections 20, 21, and 24 (Reference 16.8).

11. Procedure

11.1. RTG Materials in Water Samples

11.1.1. Acidify the water sample with concentrated HNO_3 to a pH of < 2.0 by adding enough HNO_3 (usually about 2 mL of concentrated HNO_3 per 1,000 mL of sample).

11.1.2. Perform screening analysis of the water sample using an appropriate gross alpha/gross beta counting technique such as liquid scintillation counting or gas proportional counting per laboratory protocol. Mix the sample well prior to removing the screening aliquant to minimize the risk of removing a non-representative sample.

11.1.3. Place a 47-mm membrane filter (0.45 micron mixed cellulose ester filter) on a clean, reusable filter unit with a 500 mL reservoir (or alternate volume as needed).

NOTE: For very high level water samples where a small aliquant volume must be used, a filter unit with a smaller collection reservoir may be used.

11.1.4. Filter the entire water sample using vacuum to collect any RTG particles on the filter.

11.1.5. Rinse the sample container with 10-15 mL of water and add to the filter. Rinse the sample reservoir above the filter with ~10 to 15 mL of water.

11.1.6. Remove the filter containing the filtered solids and place in a labeled 250 mL zirconium crucible.

11.1.7. Pour the filtrate into a large beaker. Rinse collection container well with ~10 mL of water and transferring the rinse volumes to the beaker.

11.1.8. Add appropriate tracer to the crucible or beaker to determine radiochemical yield as needed.

NOTE: For plutonium analysis, 2–10 pCi of ^{242}Pu or ^{236}Pu tracer are typically added depending on the count time, the total tracer counts desired to meet the required method uncertainty, and any sample splits or dilutions that will be performed.

11.1.9. Add 10 mL of concentrated nitric acid and 3–4 mL of hydrogen peroxide to the zirconium crucible to wet ash the filter. Heat on medium heat to dryness and remove from heat.

NOTE: The filter contains cellulose and needs to be digested to destroy organics since sodium peroxide will be used in the fusion process.

11.1.10. Proceed to section 11.3 for fusion of the filtered solids of the water sample

11.1.11. Add 1.5 mL of 1.25 M calcium nitrate solution, 3 mL of 3.2 M ammonium hydrogen phosphate solution and about ~5-10 drops of phenolphthalein indicator to the beaker containing the sample filtrate.

11.1.12. Add enough concentrated NH_4OH to the beaker to reach a dark pink phenolphthalein end point.

11.1.13. Heat the beaker on a hot plate for ~15 minutes to help aggregate precipitate. Remove beaker and allow precipitate to settle so that enough clear supernatant solution can be poured off. The remaining supernate with the precipitate is added to a 225 mL centrifuge tube.

11.1.14. Centrifuge the sample for at least 6 minutes at 3000 rpm or more.

11.1.15. Decant supernate from the centrifuge tube. Discard supernate to waste.

11.1.16. Add enough concentrated NH_4OH to the centrifuge tube to reach a dark pink phenolphthalein end point.

11.1.17. Add 10 mL concentrated HNO_3 to the centrifuge tube. Cap and mix well to dissolve the precipitate, and transfer to a 250 mL zirconium crucible.

11.1.18. Rinse the tube twice more with ~5 mL of concentrated HNO_3 and transfer to the zirconium crucible.

11.1.19. Evaporate the rinse solutions to dryness using medium heat and remove crucibles from hotplate.

11.1.20. Proceed to Step 11.3 for fusion of the precipitate from the water sample filtrate.

11.2. RTG Materials in Air Filter Samples

11.2.1. Perform appropriate screening analysis of the air filter sample using an appropriate hand held alpha/beta monitoring probes.

11.2.2. Place a sample filter into a 250 mL zirconium (Zr) crucible.

11.2.3. Add appropriate activity of tracer to the crucible to determine radiochemical yield. If activity levels are too high, do not add yield tracer to the sample aliquant until a smaller aliquant can be taken after the fusion and preconcentration steps. Additional care should be taken to avoid losses of sample material until an aliquant of suitable activity is obtained and equilibrated with tracer.

NOTE: For plutonium analysis, 2–10 pCi of ^{242}Pu or ^{236}Pu tracer are typically added depending on the count time, the total tracer counts desired to meet the required method uncertainty, and any sample splits or dilutions that will be performed. For example, it is often desirable to reserve ½ the final dissolved air filter solution for the event that analytical rework is required. If this is approach is planned, twice the normal amounts of Pu tracer may be added to compensate for analyzing only one-half of the dissolved filter.

11.2.4. Add 10 mL of concentrated nitric acid and 3–4 mL of hydrogen peroxide to the zirconium crucible to wet ash the filter.

11.2.5. Heat on medium heat to dryness and remove from heat.

11.2.6. Proceed to Step 11.3 for fusion.

11.3. Fusion

11.3.1. Prepare the crucible from Step 11.1 (water sample) or Section 11.2 (air filter sample) for fusion.

11.3.2. Add 8 g of sodium hydroxide and 4 g of sodium peroxide to the crucible.

11.3.3. Place the crucible with lid in the 700 °C furnace using tongs.

11.3.4. Heat the crucible for ~30 minutes or longer as needed to obtain a clear melt.

11.3.5. Using tongs, very carefully remove crucible containing hot liquid melt from furnace and transfer to hood. Allow the crucible to cool for 8–10 minutes (or longer).

11.3.6. Add ~25 mL of water to the crucible and allow the sample to react with water until the fusion cake is dissolved. Place the crucible on a hot plate at medium heat to help in dissolving the fusion cake. Transfer the solution to a labeled 225-mL centrifuge tube rinsing the crucible with water.

11.3.7. Rinse the crucible with a 25-mL portion of 6 M HCl. Warm on a hotplate, and then carefully pour each rinse into the 225 mL centrifuge tube. Pour rinse slowly to prevent splattering of the sample. Repeat two more times.

11.3.8. Dilute the sample to ~170 mL with deionized water and swirl to mix.

11.3.9. Allow sample solution to cool for 40 minutes in the open centrifuge tube.

11.3.10. Cap centrifuge tube and place in ice bath for 3 minutes to cool solution to room temperature.

11.4. Preconcentration of Pu from Fusion Matrix

NOTE: These steps also preconcentrate other actinides besides plutonium from the fusion matrix. For example, if the appropriate tracers are added, americium and uranium isotopes may be assayed using *Rapid Radiochemical Method for ^{241}Am in Building Materials* and *Rapid*

Radiochemical Method for Isotopic Uranium in Building Materials **respectively (available at** www.epa.gov/narel**). It is the laboratory's responsibility, however, to validate these methods prior to use.**

11.4.1. Pipet 10 mL of 1 mg La/mL into the centrifuge tube, swirling to mix.

11.4.2. Pipet 1 mL of iron carrier (50 mg/mL) into the centrifuge tube, swirling to mix.

11.4.3. For water sample solids, pipet 1.5 mL of 1.25M calcium nitrate into the centrifuge tube. The water sample filtrate fraction does not need additional calcium. For air filter samples, add 1.5 mL of 1.25M calcium nitrate into the centrifuge tube. Swirl to mix.

11.4.4. Pipet 10 mL of 20 wt %. $TiCl_3$ into the centrifuge tube and cap to mix.

11.4.5. Add 24 mL of concentrated HF to the centrifuge tube and cap to mix. Shake well to mix.

11.4.6. Thoroughly mix and allow the sample to sit for 10 minutes. .

11.4.7. Centrifuge the sample for ~6 minutes at 3000 rpm or more as needed.

11.4.8. Pour off supernatant liquid and discard to waste.

11.4.9. Pipet 5 mL of 3 M HNO_3-0.25 M boric acid into the 225 mL centrifuge tube containing the calcium/lanthanum precipitate.

11.4.10. Cap, mix and transfer contents of the 225 mL centrifuge tube into a new, labeled 50 mL centrifuge tube.

11.4.11. Add 6 mL of 7 M HNO_3 and 10 mL of 2 M aluminum nitrate into the 225 mL tube, cap and mix, and transfer rinse to 50 mL centrifuge tube.

11.4.12. Pipet 5 mL of 3 M HNO_3 directly into the 50 mL centrifuge tube.

11.4.13. Mix the sample load solution in a 50 mL centrifuge tube using a vortex stirrer to dissolve residual precipitate.

11.4.14. Centrifuge the sample at 3000 rpm or higher for 6 minutes to remove any traces of solids. These may not be visible prior to centrifuging. Transfer the solution to labeled 50 mL centrifuge tubes for further processing. If undissolved solids are present, rinse the solids with 5 mL of 3M HNO_3 and vortex to dissolve. Centrifuge the tube with residual solids (if any) and add the supernate to the sample solution.

NOTE: For samples that will be split such that ½ is held in reserve, the tracer added to the initial air filter in Step 11.1.8 should have been increased accordingly (e.g., if one-half the sample is taken, the tracer amount would be doubled). The fractional splitting of the sample will be accounted for properly in the calculations.

11.4.15. For air filter samples, set aside one-half of the sample by carefully splitting the dissolved filter, either by mass or volume, into a labeled 50-mL centrifuge tube.

11.4.16. For Pu analysis, follow Steps 11.1.2 through 11.3.15 of the *Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials*

(Reference 16.1), incorporating steps in Sections 6, 7, and 10 as they support Section 11, and making the following adjustments:

- Change Step 11.2.1.4 to: Add 1.5 mL of 1.5M ascorbic acid to the solution, swirling to mix. Wait 3 min.
- Change Step 11.2.1.5 to: Add 1.5 mL 3.5M $NaNO_2$ to the sample, swirling to mix.
- Change Step 11.2.3.2 to: Add 5 mL of 3M HNO_3 to the beaker (from Step 10.2.1.5) as a rinse. Transfer the solution into the appropriate reservoir (the flow rate may be adjusted to ~3 mL/min).
- Change Step 11.2.3.7 to: Add 5 mL of 3M HNO_3 to the reservoir to reduce bleed-off of organic extraction during Pu strip step (flow rate ~3 mL/min).
- Change Step 11.3.3 to: Pipet 2 mL (or alternately 1 mL) of concentrated HF into the centrifuge tube.

12. Data Analysis and Calculations

12.1. Equations for calculating final results for the activity (concentration) and associated combined standard uncertainty, the radiochemical yield (if required), the critical level, and the MDC are found below. Ensure that the units used for the aliquant, and for reporting are consistent with those established in analytical protocol specifications.

12.1.1. If the sample is split or serially diluted, the actual activity of tracer added to the sample is used for calculations. The aliquant size used for calculations, W_a, must be the effective amount of sample in the aliquant into which the tracer is added. It is calculated as follows:

$$W_a = W_s \times d_1 \times d_2 \times d_3 \qquad \text{(Eq. 1)}$$

Where

$$d_1 = \frac{D_{a1}}{D_{s1}}, d_2 = \frac{D_{a2}}{D_{s2}}, and\ d_3 = \frac{D_{a3}}{D_{s3}}$$

and

W_s = initial size of the sample aliquant taken for fusion in the units designated in analytical protocol specifications (e.g., 0.020 L, or 67 m^3, 0.500 filter).

$D_{a\#}$ = mass or volume of the aliquant taken (i.e., the redissolved fusion cake or subsequent dilution thereof) where # denotes the respective number of the serial dilution from *i* to *n*, (e.g., 5.0 mL, etc.).

$D_{s\#}$ = mass or volume of the dissolved residues of fusion, or the dilution thereof, from which $D_{a\#}$ is taken, where # denotes the number of the respective serial dilution from *i* to *n* (e.g., 20 mL, etc.).

NOTE: $D_{a\#}$ and $D_{s\#}$ must use the same units of mass or volume. If no splits or dilutions are performed, $W_s = W_a$. If fewer than three splits or dilutions are made, not all three of the d_1, d_2, or d_3 terms will be needed. A factor of one (1) may be substituted for the unused terms.

12.1.2. The actual activity of tracer added to the sample is used in the calculation of the final sample results as described in 12.1.1. If the sample has been split or diluted, the tracer activity used to calculate the radiochemical yield must be modified to reflect the activity of tracer that would be present theoretically in the final sample test source assuming 100% radiochemical yield. It is calculated as follows:

$$A_{t-yld} = A_t \times d_1 \times d_2 \times d_3 \quad \text{(Eq. 2)}$$

Where

$A_{t\text{-}yld}$ = theoretical activity in sample test source assuming 100% radiochemical yield.

A_t = activity of the tracer added to the sample aliquant at the reference date/time for the tracer.

and

d_1, d_2 and d_3 are defined as described in 12.1.1.

NOTE: $D_{a\#}$ and $D_{s\#}$ must use the same units of mass or volume. If fewer than three splits/dilutions are made, a factor of one (1) is substituted for the unneeded D_a and D_s terms. If no splits or dilutions are performed, $A_{t\text{-}yld} = A_t$

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

$$AC_a = \frac{A_t \times R_a \times D_t \times I_t}{W_a \times R_t \times D_a \times I_a} \quad \text{(Eq. 3)}$$

and

$$u_c(AC_a) = \sqrt{u^2(R_a) \times \frac{A_t^2 \times D_t^2 \times I_t^2}{W_a^2 \times R_t^2 \times D_a^2 \times I_a^2} + AC_a^2 \times \left(\frac{u^2(A_t)}{A_t^2} + \frac{u^2(W_a)}{W_a^2} + \frac{u^2(R_t)}{R_t^2} \right)} \quad \text{(Eq. 4)}$$

where:

AC_a = activity concentration of the analyte at time of count, in picocuries per liter, cubic meter or sample (pCi/L, pCi/m^3, or pCi/filter)

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 = the size of the sample aliquant from Eq. 2, consistent with units required in analytical protocol specifications (L, m^3, or filter, as appropriate)

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)

$u(W_a)$ = standard uncertainty of the volume of sample aliquant (L, m^3, or filter, as appropriate)

$u(R_a)$ = 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})

NOTE: Since the tracer is used as the basis for quantitation, terms for the chemical yield and efficiency do not appear in the equations for activity, uncertainty, critical level, and minimum detectable concentration.

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 of the activity concentration ($u_c(AC_a)$) 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 tracer 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.

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

$$R_x = \frac{C_x}{t_s} - \frac{C_{bx}}{t_b} \qquad \text{(Eq. 5)}$$

and

$$u(R_x) = \sqrt{\frac{C_x + 1}{t_s^2} + \frac{C_{bx} + 1}{t_b^2}} \quad \text{(Eq. 6)}$$

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[4]

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

$$RY = \frac{R_t}{0.037 \times A_{t\text{-yld}} \times D_t \times I_t \times \varepsilon} \quad \text{(Eq. 7)}$$

and

$$u_c(RY) = RY \times \sqrt{\frac{u^2(R_t)}{R_t^2} + \frac{u^2(A_{t\text{-yld}})}{A_{t\text{-yld}}^2} + \frac{u^2(\varepsilon)}{\varepsilon^2}} \quad \text{(Eq. 8)}$$

where:

RY	=	radiochemical yield of the tracer, expressed as a fraction
R_t	=	net count rate of the tracer, in counts per second
$A_{t\text{-yld}}$	=	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

[4] 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

$u(A_{t\text{-}yld})$ = standard uncertainty of $A_{t\text{-}yld}$ (pCi)

$u(\varepsilon)$ = standard uncertainty of the detector efficiency

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

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

$$\text{MDC} = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b}\right) + 3.29 \times \sqrt{R_{ba}\, t_s \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t \times D_t \times I_t}{t_s \times W_a \times R_t \times D_a \times I_a} \quad \text{(Eq. 10)}$$

where:

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

12.3. If required for water samples, the results of the filtered RTG solids) and the filtrate (coprecipitated on calcium phosphate) are mathematically combined as follows:

$$\text{AC}_{water} \pm u_c(\text{AC}_{water}) = \left[\text{AC}_{filtrand} + \text{AC}_{filtrate}\right] \pm \sqrt{u_c^2(\text{AC}_{filtrand}) + u_c^2(\text{AC}_{filtrate})} \quad \text{(Eq. 11)}$$

where:

AC_{water} = the summed activity concentration of the water sample (i.e., filtered solids + filtrate)

$u_c(AC_{water})$ = the combined standard uncertainty of the summed activity concentration of the water sample (i.e., filtered solids + filtrate)

$AC_{filtrand}$ = the activity concentration for the filtered solids in pCi/L of original sample from Eq. 3

$u_c(AC_{filtrand})$ = the combined standard uncertainty (CSU) of $AC_{filtrand}$ in pCi/L of original sample from Eq. 4 (k=1)

[5] 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 $z_{1-\alpha} = z_{1-\beta} = 1.645$, where $z_{1-\alpha}$ and $z_{1-\beta}$ are the $1-\alpha$ and $1-\beta$ quantiles of the standard normal distribution function) 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.

$AC_{filtrate}$ = the activity concentration of filtrate (pCi/L of original sample from Eq. 3

$u_c(AC_{filtrate})$ = the CSU of $AC_{filtrate}$ in pCi/L of original sample from Eq. 4 (k=1)

12.4. Results Reporting

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

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

12.4.2.1. Result ± combined standard uncertainty.

12.4.2.2. For water samples, report results as specified in the analytical protocol specifications. If no guidance is provided, the results for each of the two fractions (or the mathematically combined result) may be reported as pCi/L of original sample. For example:

$^{239/240}$Pu for Sample 12-1-99:

Filtrate Result: $(1.28 \pm 0.15) \times 10^1$ pCi/L

Filtered Residue Result: $(2.50 \pm 0.32) \times 10^0$ pCi/L

12.4.2.3. For air filter samples, report results as specified in the analytical protocol specifications. If no guidance is provided, the results should be reported as pCi/m^3. For example:

$^{239/240}$Pu for Sample 12-1-99:$(1.28 \pm 0.15) \times 10^1$ pCi/m^3

13. Method Performance

13.1. Results of method validation performance are to be archived and available for reporting purposes.

13.2. Estimates of turnaround times for fusion and preconcentration steps assume that batches of twenty samples are processed together with associated QC.

13.2.1. For water samples, initial filtration and preparation for the fusion require approximately 1.75 hours per batch.

13.2.2. For water and air filter samples, the fusion requires approximately 1.75-2.75 hours per batch.

13.2.3. The preconcentration, chemical separation and source preparation steps require approximately 2.5 hours per batch.

13.2.4. Sample count duration may vary depending on the validated configuration of the method.

NOTE: Turnaround times for the subsequent chemical separation methods are given in those methods for batch preparations.

14. Pollution Prevention

This method inherently produces no significant pollutants. The sample and fusion reagents are retained in the final product and are carried into the ensuing chemical separation techniques, which marginally increases the salt content of the effluent waste. It is noted that

if the sampled particulates include radionuclides which may be volatile under the fusion conditions, these constituents will be exhausted through fume hood system.

15. Waste Management

15.1. Refer to the appropriate chemical separation methods for waste disposal information.

16. References

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17. Tables, Diagrams, and Flow Charts

17.1. Tables

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

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance[2]	Alpha Emission Energy (MeV)
^{236}Pu	2.858	9.685×10^{-9}	0.691	5.768
			0.308	5.721
^{238}Pu	87.7	2.50×10^{-10}	0.7091	5.499
			0.2898	5.456
^{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
$^{239/240}Pu$ (combined)[3]	2.411×10^{4}	9.110×10^{-13}	0.9986	~5.16
^{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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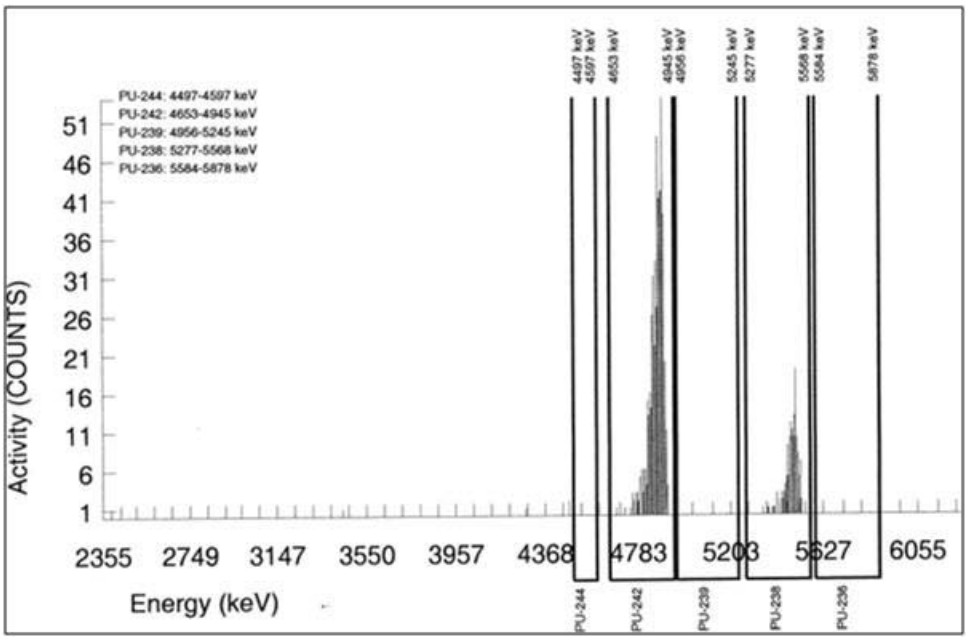
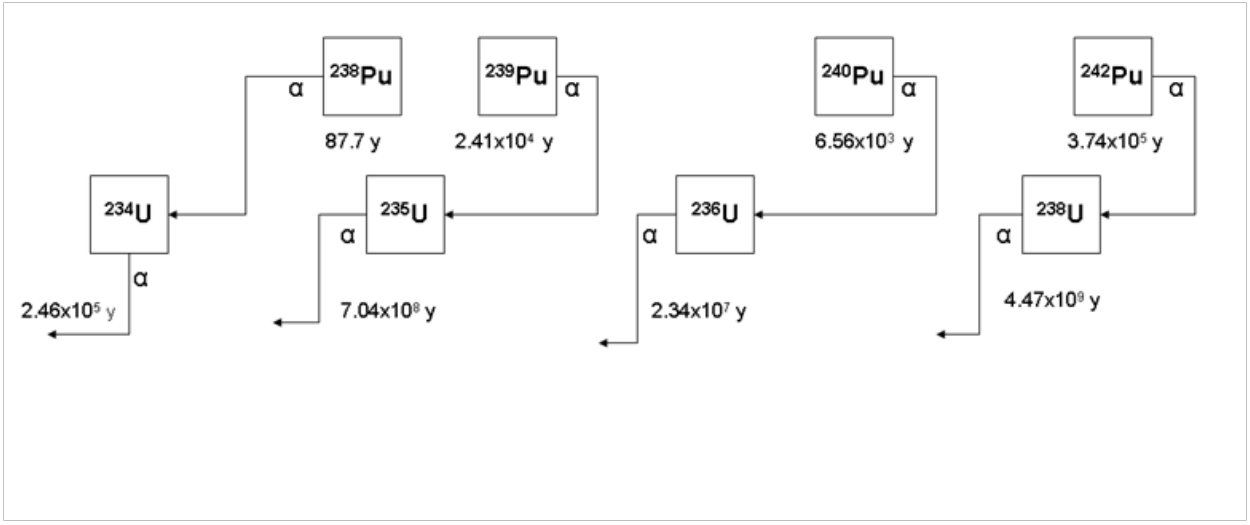
17.3. Spectrum from a Processed Sample

Plutonium Spectrum



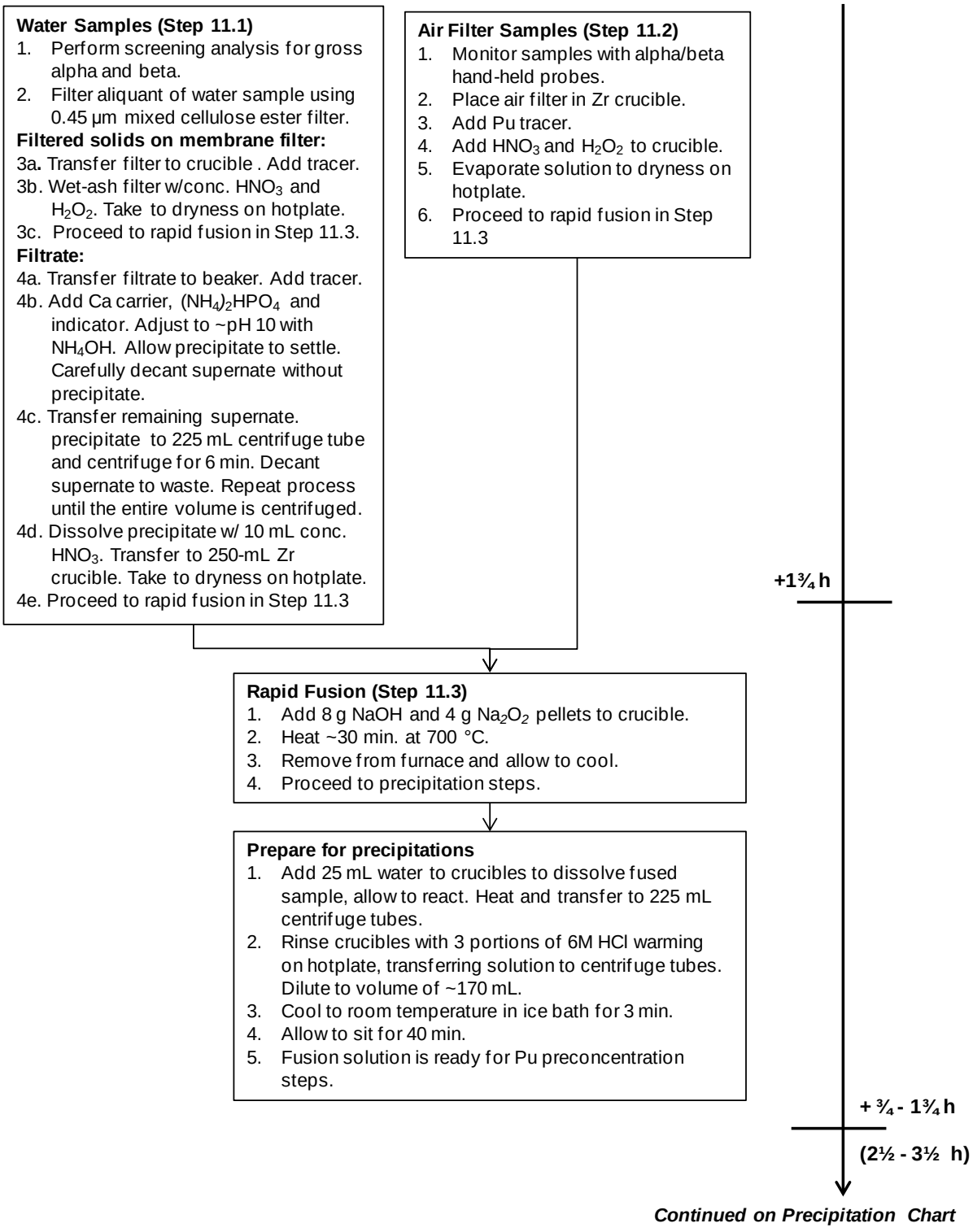
17.4. Decay Scheme

Plutonium Decay Scheme



17.5. Fusion Method Flow Chart

Timeline for Rapid Fusion and Preparation of Radioisotope Thermoelectric Generator Samples for Precipitation and Analysis



Plutonium Precipitation Procedure