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Validation of Rapid Radiochemical Method for Californium-252 in Water, Air Particulate Filters, Swipes and Soils for Environmental Remediation Following Radiological Incidents

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RAPID RADIOCHEMICAL METHOD FOR CALIFORNIUM-252 IN WATER, AIR PARTICULATE FILTERS, SWIPES, AND SOILS FOR ENVIRONMENTAL REMEDIATION FOLLOWING RADIOLOGICAL INCIDENTS

1. Scope and Application
   1.1. This method provides for the determination of californium-252 (^{252}Cf) in water, air particulate filters, swipes and soil samples.
      1.1.1. Californium-250 emits alpha particles that are isoenergetic with ^{252}Cf. Measurement results should therefore be reported in terms of the activity of $^{252/250}$Cf.
      1.1.2. The presence of other isotopes of californium, especially the longer-lived ^{250}Cf, mixed in unknown proportions with relatively shorter-lived ^{252}Cf impacts the accuracy of decay correction of measured results. See further discussion in Section 4.
   1.2. The method uses americium-243 (^{243}Am) tracer as the basis for quantification of ^{252}Cf, and as a radiochemical yield monitor.
   1.3. A sample test source is prepared by microprecipitation. The test source is counted by alpha spectrometry for ^{252}Cf.
   1.4. MQOs:
      1.4.1. Water:
         1.4.1.1. This method is capable of achieving a required method uncertainty for ^{252}Cf of 2.0 pCi/L at an analytical action level of 15.3 pCi/L. To attain this measurement quality objective (MQO), a sample volume of 0.2 L and count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background.
         1.4.1.2. This method is capable of achieving a required minimum detectable concentration (MDC) for ^{252}Cf of 1.5 pCi/L. To attain this MQO, a sample volume of 0.2 L and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background.
      1.4.2. Air Particulate Filter:
         1.4.2.1. This method is capable of achieving a required method uncertainty for ^{252}Cf of 0.57 pCi/filter at an analytical action level of 4.37 pCi/filter. To attain this MQO, a sample aliquant of one filter and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background. The concentration in air (i.e., pCi/m^3) to which this MQO corresponds will vary according to the volume of air sampled on the filter.

1.4.2.2. This method is capable of achieving a required MDC for ^{252}Cf of 0.44 pCi/filter. To attain this MQO, a sample aliquant of one filter and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background. The concentration in air (i.e., pCi/m^3) to which this MQO corresponds will vary according to the volume of air sampled on the filter.

1.4.3. Swipe or Organic-Polymer-Based Air Particulate Filter:

1.4.3.1. This method is capable of achieving a required method uncertainty for ^{252}Cf of 0.12 pCi/swipe or filter at an analytical action level of 0.89 pCi/swipe or filter. To attain this MQO, a sample aliquant of one swipe and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background. For swipes, the surface concentration activity (i.e., pCi/cm^2) to which this MQO corresponds will vary according to the area sampled on the swipe. Similarly for air filters, the concentration in air (i.e., pCi/m^3) to which this MQO corresponds will vary according to the volume of air sampled on the filter.

1.4.3.2. This method is capable of achieving a required MDC for ^{252}Cf of 0.15 pCi/swipe or filter. To attain this MQO, a sample aliquant of one filter and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background. For swipes, the surface concentration activity (i.e., pCi/cm^2) to which this MQO corresponds will vary according to the area sampled on the swipe. Similarly for air filters, the concentration in air (i.e., pCi/m^3) to which this MQO corresponds will vary according to the volume of air sampled on the filter.

1.4.4. Soil:

1.4.4.1. This method is capable of achieving a required method uncertainty for ^{252}Cf of 0.18 pCi/g at an analytical action level of 1.38 pCi/g. To attain this MQO, a sample weight of 1 gram and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background.

1.4.4.2. This method is capable of achieving a required MDC for ^{252}Cf of 0.14 pCi/g. To attain this MQO, a sample weight of 1 gram and a count time of at least 4 hours are recommended. Sample count times may vary based on differences in instrument parameters such as detection efficiency and background.

1.5. This ^{252}Cf method was single-laboratory 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, Reference16.1)) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (EPA 2004, Reference 16.2).

1.5.1. Since curium (Cm) and americium are chemical analogs that track closely with californium through the chemical separation, it may be possible not only to determine other isotopes of californium, but also those of americium (e.g., ^{241}Am) and curium (e.g., $^{244/243}$Cm) that may be present in the sample test source.

1.5.2. 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.

1.5.3. Multi-radionuclide analysis using sequential separation may be possible using this method in conjunction with other rapid methods (see Appendix A of this method). Rapid methods can also be used for routine analyses with appropriate (typically longer) count times.

1.5.4. The method, as implemented at the laboratory, 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).

2. Summary of Method

2.1. This method is based on the use of extraction chromatography resins (TEVA® + DGA resins) to isolate and purify californium by removing interfering radionuclides as well as other matrix components. The method utilizes vacuum-assisted flow to improve the speed of the separations. Am-243 tracer equilibrated with the sample is used as a yield monitor.

2.1.1. Water samples are concentrated using a calcium phosphate [$Ca_3(PO_4)_2$] coprecipitation. The calcium phosphate precipitate is dissolved in a load solution containing ~3 molar (M) nitric acid (HNO_3) - 1 M aluminum nitrate [$Al(NO_3)_3$] before continuing with chemical separations.

2.1.2. Glass-fiber or cellulose-based air particulate filter samples are wet-ashed with repeated additions of nitric and hydrofluoric acids and hydrogen peroxide. The residues are treated with nitric-boric acid, and dissolved in a load solution containing 3 M HNO_3 - 1 M $Al(NO_3)_3$ before continuing with chemical separations.

2.1.3. Cotton-twill swipe and organic-polymer-based air particulate filter samples are dry-ashed in a beaker for 30-60 minutes using a ramped program to minimize the risk of flash-ignition. The residue is transferred to a Teflon beaker with nitric acid and hydrogen peroxide, digested with hydrofluoric acid, and taken to dryness. The residues are wet-ashed with nitric acid and hydrogen peroxide and taken to dryness before being treated with nitric-boric

acid and dissolved in a load solution containing 3 M HNO_3 - 1 M $Al(NO_3)_3$ for chemical separations.

2.1.4. Soils are finely ground before being fused with NaOH in zirconium crucibles. The fusion cake is dissolved in water and californium preconcentrated from the alkaline matrix using an iron/titanium hydroxide precipitation (enhanced with calcium phosphate precipitation) followed by a lanthanum fluoride matrix removal step. The fluoride precipitate is dissolved with nitric-boric acid and diluted in nitric acid and aluminum nitrate to yield a load solution containing ~3 M HNO_3-1 M $Al(NO_3)_3$.

2.1.5. The size of the sample aliquant may need to be decreased for samples containing high alpha activity. This may require delay of addition of the tracer after the sample has been dissolved and split, and would require that the appropriate dilution factor be applied.

2.2. Extraction chromatography resins (TEVA® + DGA resins) are then used to isolate and purify californium and americium by removing interfering radionuclides and other matrix components. Following chemical separation of Cm and Am, the sample test source (STS) is prepared by microprecipitation with CeF_3.

2.3. The alpha emissions from the source are measured using an alpha spectrometer and used to calculate the activity of ^{252}Cf in the sample.

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 [micron (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 (EPA 2004, Reference 16.22).

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. 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.

3.7. Required Relative 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.

3.8. 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 emissions from ^{250}Cf fall in the same region as ^{252}Cf and cannot be differentiated from those of ^{252}Cf using alpha spectrometric determinations. Alpha spectrometry measurements should be reported in terms of the activity of $^{252/250}$Cf.

4.1.1.1. If alpha spectrometry measurements show activity in the region of interest for ^{252}Cf, confirmatory measurements of ^{252}Cf may be possible based on fission fragment analysis using an internal gas ionization detector with bias voltage set below the point where alpha particles result in measureable signal (e.g., 5-20 volts).

4.1.1.2. Fresh californium sources routinely contain significant quantities of ^{250}Cf with a half-life of 13.08 years (typical levels in a fresh source are 10%). As californium sources age, however, longer-lived isotopes contribute more to the relative activity of the mixture.

4.1.2. Since alpha spectrometry measurements does not differentiate between ^{250}Cf and ^{252}Cf, decay corrections based on the half-life of ^{252}Cf will impart a positive bias to results as mixtures age. The effect can be minimized by keeping the time between the activity reference date (i.e., collection or standard reference date) short, or, if acceptable to the user of the data, by reporting the activity at the time of the measurement. It is recommended that QC sample known values be updated frequently (e.g., every month) to minimize the effect on the evaluation of method performance. Americium and curium are chemical analogs of californium and are not separated from californium using the separation scheme in this method. Several americium and curium isotopes emit alpha particles in the same energy region of interest (ROI) as does ^{252}Cf. These include ^{242}Cm, ^{243}Cm, and ^{244}Cm which have also alpha emissions outside of the ROI for ^{252}Cf. While these radionuclides are not normally present in californium sources, if their presence is suspected, the alpha spectrum may be monitored for their alpha emissions outside the ^{252}Cf region of interest and data qualified or corrections made as appropriate.

4.1.3. Radionuclides of other elements (or their short-lived progeny) that emit alpha particles that are isoenergetic with ^{252}Cf (e.g., Bismuth-212 (^{212}Bi) at 6.1 MeV supported by ^{228}Th and/or ^{224}Ra) must be chemically separated to prevent positive interference with the measurement. This method effectively separates these radionuclides. For example, a thorium removal rinse is performed on DGA resin in the event that any thorium ions pass through TEVA® Resin onto DGA resin.

4.1.4. DGA has very high affinity for both Cf and Am. The retention of californium on DGA, however, is higher than that of Am. The use of the ^{243}Am tracer for quantification assumes that both californium and americium are quantitatively removed from the column at the time of elution. The separation scheme employed is designed to ensure that two constituents, nitrates and lanthanum (La), will not interfere with this elution.

4.1.4.1. Residual nitric acid can increases the affinity of californium relative to americium. Hydrochloric acid rinsing prior to and during elution flushes residual nitrate from the column prior to elution and to facilitate complete elution of californium and americium.

4.1.4.2. The bioxalate elution step very reliably strips all californium and americium from DGA. If residual lanthanum is still present on the column when the bioxalate is added, however, there is a chance that lanthanum will precipitate, physically trapping californium and americium on the column. Late-eluting californium could preferentially be retained on the resin and a bias could result. The method for soil samples therefore contains steps designed to effectively flush lanthanum from the column prior to elution with the bioxalate. The method pertaining to soil samples, therefore, contains steps designed to effectively flush La from the column prior to elution with the bioxalate.

4.1.5. The dilute nitric acid rinse performed on DGA resin for soil samples is designed to remove Ca and lanthanum (La) ions which could end up on the final alpha source filter and coprecipitate with cerium fluoride. If elevated full width at half maximum (FWHM) values for the tracer indicate degraded resolution, it is possible that this is due to inadequate decontamination from La or Ca. Slightly increasing the volume of the lanthanum rinse steps would help remove Ca and La ions and improve alpha peak resolution. Such changes, however, should be validated by the laboratory.

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

4.1.7. Zirconium crucibles used in the furnace ashing and fusion process may be reused.

4.1.7.1. Before reuse, the crucibles should be cleaned very well using soap and water, followed by hot nitric acid (multiple rinses) and then water. Blank measurements should be monitored to ensure effective cleaning and control against cross-contamination.

4.1.7.2. Segregation of crucibles used for low and high activity samples is recommended to minimize the risk of cross-contamination while maximizing the efficient use of crucibles.

4.2. Non-Radiological:

4.2.1. Anions that can complex californium and americium, including fluoride and phosphate, may lead to depressed yields. Boric acid added to the load solution will complex residual fluoride ions, while aluminum in the load solution will complex phosphate ions that may be present.

4.2.2. High levels of Ca present in soil samples may have an adverse impact on retention of californium and americium retention on DGA resin. The method is designed to minimize Ca interference and enhance californium and americium affinity by increasing the nitrate concentration in the load and initial rinse solutions. A dilute nitric acid rinse is performed on the DGA resin to minimize residual Ca which could otherwise end up on the sample test source as the fluoride. For samples containing especially elevated con333centrations of Ca, it may be advisable to slightly increase the volume of this rinse step to better remove Ca ions and possibly improve alpha peak resolution. This modification must be validated by the laboratory prior to use with samples.

5. Safety

5.1. General

5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring, and radiation safety manual for 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, usually much smaller than 1 mm. Typically, DRPs are not evenly distributed in the media and their radiation emissions are anisotropic (i.e., not uniform in all directions).

5.2.1.2. Samples containing measureable activity of ^{252}Cf may have DRPs. If suspended solids are removed by filtration, they should be checked for potential radioactivity.

5.2.1.3. Californium present in DRPs may not be chemically available, and will not be determined, unless it is dissolved prior to chemical separation.

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 a range that includes 4.5 and 7 MeV.

6.2. Analytical balance with 10^{-2} g readability.

6.3. Centrifuge tubes, 225-mL, 50-mL capacity, or equivalent.

6.4. Centrifuge, to accommodate centrifuge tubes.

6.5. Crucibles, 250-mL, zirconium, with lids.

6.6. Heat lamp.

6.7. Hot Plate.

6.8. Laboratory ware of plastic, glass, or Teflon; 150-, 250-, 500- and 1,000-mL capacities, as needed.

6.9. Oven capable of temperatures ranging from 100-600 °C.

6.10. Pipettor, electronic, and appropriate plastic tips, 1-10 mL as needed.

6.11. Pipettors, manual, and appropriate plastic tips, 100- microliter (µL), 200-µL, 500-µL and 1-mL, or equivalent, as needed.

6.12. Sample test source mounts:

6.12.1. Polypropylene filter, 0.1-µm pore size, 25-mm diameter, or equivalent.

6.12.2. Stainless steel planchets, adhesive backed disks (e.g., Environmental Express, Inc. P/N R2200) or equivalent (calibrated for 25-mm filter geometry).

6.13. Tweezers.

6.14. Vacuum box system

6.14.1. Vacuum box/rack (e.g., Eichrom Technologies, Inc., Lisle, IL part number AC-24-BOX), or equivalent.

6.14.2. Cartridge reservoirs, 10- or 20-mL syringe style with locking device, or columns (e.g., empty Luer-lock tip, Image Molding, Denver, CO, part number CC-10-M) plus 12-mL reservoirs (e.g., Image Molding, Denver, CO part number CC-06-M), or equivalent.

6.14.3. Vacuum box tips, white inner, Eichrom Technologies, Inc., Lisle, IL part number AC-1000-TUBE-PE, or PFA 5/32" × ¼" heavy wall tubing connectors, natural, Cole Parmer Instrument Company, LLC, Vernon Hills, IL, part number 00070EE, cut to 1 inch, or equivalent.

6.14.4. Vacuum box tips, yellow outer, Eichrom Technologies, Inc., Lisle, IL part number AC-1000-OT, or equivalent.

6.14.5. Laboratory vacuum source.

6.15. Vortex mixer.

7. Reagents and Standards

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

NOTE: 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.

NOTE: Low-levels of uranium are typically present in $Al(NO_3)_3$.

7.1. Aluminum nitrate solution, 2 M: Add 750 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9\ H_2O$) to ~500 mL of water and dilute to 1 liter with water.

7.2. Americium-243 tracer solution – 10-40 dpm of ^{243}Am per aliquant.

7.3. Ammonium bioxalate solution, 0.1M: Dissolve 6.3 g of $H_2C_2O_4 \cdot 2\ H_2O$ and 7.1 g of $(NH_4)_2C_2O_4 \cdot H_2O$ in 900 mL of water, filter, and dilute to 1 liter with water.

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

7.5. Ammonium hydroxide, 15M: Concentrated NH_4OH.

7.6. Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4 \cdot H_2O$.

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

7.8. Calcium nitrate, 1.25M: Dissolve 73.8 g of $Ca(NO_3)_2 \cdot 4\ H_2O$ in 100 mL of water and dilute to 250 mL with water.

7.9. Californium-252 tracer solution – 10-40 dpm of ^{252}Cf per aliquant.

7.10. Cerium carrier, 0.5 mg Ce/mL: dissolve 0.16 g $Ce(NO_3)_3 \cdot 6\ H_2O$ in 50 mL water and dilute to 100 mL with water.

7.11. DGA resin, normal, 2-mL cartridge, 50- to 100-µm mesh size, Eichrom Technologies, Inc., Lisle, IL part number DN-R50-S, or equivalent.

7.12. Ethanol, 95%: Reagent C_2H_5OH, or mix 95 mL 100% ethanol and 5 mL water.

7.13. Hydrochloric acid, 12M: Concentrated HCl.

7.13.1. Hydrochloric acid, 0.01M: Add 0.83 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

7.13.2. Hydrochloric acid, 0.25M: Add 21 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

7.13.3. Hydrochloric acid, 1.5M: Add 125 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

7.13.4. Hydrochloric acid, 3M: Add 250 mL of concentrated HCl to 500 mL of water and dilute with water to 1 L.

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

7.14. Hydrofluoric acid, 28M: Concentrated HF

7.15. Hydrogen peroxide, 30 weight percent (wt.%) (H_2O_2).

7.16. Iron carrier, 4 mg/mL: Dissolve 14 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9\ H_2O$) in 300 mL water and dilute to 500 mL with water.

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

7.18. Lanthanum carrier, 1.0 mg La^{3+}/mL: Dissolve 1.56 g lanthanum (III) nitrate hexahydrate [$La(NO_3)_3 \cdot 6\ H_2O$] in 300 mL water and dilute to 500 mL with water.

7.19. Nitric acid, 16M: Concentrated HNO_3.

7.19.1. Nitric acid, 0.075M: Add 4.7 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

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

7.19.3. Nitric acid, 1M: Add 63 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.19.4. Nitric acid, 3M: Add 190 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.19.5. Nitric acid, 6M: Add 380 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

7.19.6. Nitric acid, 7M: Add 443 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

7.20. Nitric acid – boric acid, 3M–0.25M: Add 15.5 g of H_3BO_3 and 190 mL of concentrated HNO_3 to 500 mL of water, heat to dissolve, and dilute to 1 liter with water.

7.21. Nitric acid, 3M – hydrofluoric acid, 0.25M: Add 8.9 mL of concentrated HF and 190 mL of concentrated HNO_3 to 700 mL of water. Dilute to 1 liter with water and mix well.

7.22. Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\ H_2O$.

7.23. Phenolphthalein indicator solution, 0.5 wt.% ($C_{20}H_{14}O_4$): Dissolve 0.5 g phenolphthalein in 100 mL ethanol (95%).

7.24. Sodium nitrite solution, 3.5M: Dissolve 6.0 g of $NaNO_2$ in 25 mL of water. Prepare fresh daily.

7.25. Sodium hydroxide pellets.

7.26. Sulfamic acid solution, 1.5M: Dissolve 72.8 g of H_3NSO_3 in 400 mL of water and dilute to 500 mL with water.

7.27. TEVA® resin – 2-mL cartridge, 50- to 100-µm mesh size, Eichrom Technologies, Inc., Lisle, IL part number TE-R50-S and TE-R200-S, or equivalent.

7.28. Titanium (III) chloride solution, 10 wt.% in 20-30 wt.% HCl.

Note: If 10 wt.% $TiCl_3$ is not available, other concentrations of $TiCl_3$ (e.g., 12-20%) may be used if the amount is adjusted based on the assay of the solution to deliver the same or slightly more titanium. For example, if 17 wt.% $TiCl_3$ is used, the volume added may be decreased to 3 mL.

8. Sample Collection, Preservation, and Storage

8.1. Water samples:
  8.1.1. No sample preservation is needed if sample analysis is initiated within three days of sample collection.
  8.1.2. If sample analysis is not started within three days of sample collection, add concentrated HNO_3 to achieve a pH<2 and then store for at least 16 hours prior to analysis.
  8.1.3. If the concentration of americium in the dissolved fraction is sought, the insoluble fraction must be removed by filtration before preserving with acid.
8.2. No sample preservation is needed for air particulate filters, swipes, or soil samples.

9. Quality Control
9.1. Batch QC 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 QC sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.
  9.1.1. One 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.
    9.1.1.1. Although the relative concentration of ^{252}Cf and ^{250}Cf is not known for samples, it should be known for standards. The expected value for the LCS should be calculated as the sum of the activity of ^{252}Cf and ^{250}Cf decay corrected to the reference date for the measurement (e.g., collection date) before comparison to the measured value.
  9.1.2. One method blank shall be run with each batch of samples. The laboratory blank should consist of demineralized water.
  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 is not required as a chemical yield tracer is used in each sample.
9.2. The source preparation method should produce a sample test source in which the full width-at-half-maximum (FWHM) for the tracer peak is less than 100 keV.[1]
  9.2.1. Each spectrum should be reviewed for evidence of peaks that overlap or evidence of interference with the tracer or analyte peaks.
  9.2.2. The sample test source may require reprocessing to remove interfering mass if the FWHM maximum cannot be achieved and there are any indications that degraded resolution may have impacted the quantification of ^{252}Cf.

10. Calibration and Standardization

[1] This helps minimize interference from other alpha-emitting isotopes.

10.1. Set up the alpha spectrometry system according to the manufacturer's recommendations consistent with ASTM Standard Practice D7282, Section 9.3, "Alpha Spectrometry Initial Instrument Set-up" (Reference 16.3). The energy range of the spectrometry system should at minimum include the range that encompasses 4.5 and 7.0 MeV.

10.2. Establish initial instrument QCs as described in ASTM Standard Practice D7282, Section 10-15, "Initial Instrument Quality Control Testing" (Reference 16.3)

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

10.4. Perform Continuing Instrument Quality Control Testing according to ASTM Standard Practice D7282, Sections 20, 21, and 24, "Continuing Instrument Quality Control Testing" and "Quality Control for Alpha Spectrometry Systems" (Reference 16.3).

11. Procedure

11.1. Preparation of Water Samples

NOTE: This section addresses the analysis of soluble californium only. Solid material, if present, must be removed from the sample prior to aliquanting by filtering the unpreserved sample aliquant through a 0.45-µm filter. The solid material may be screened for radioactivity or saved for potential future analysis.

NOTE: If a sample aliquant larger than 200 mL is needed, the aliquant may be added to a large beaker, heated on a hot plate to near boiling, reagents added with stirring, and then allowed to cool and settle. After pouring off enough of the supernate, the precipitate may be transferred to a 225-mL tube, rinsing the beaker well with water, and centrifuged.

11.1.1. Aliquant 200 mL of sample into a 225-mL centrifuge tube.

11.1.2. Set up an empty 225-mL centrifuge tube for use as a reagent blank sample.

11.1.3. Acidify each sample by adding enough concentrated (16M) HNO_3 to at least reach a pH of less than 2. This usually requires about 2 mL of HNO_3 per 1000 mL of sample.

11.1.4. Set up a laboratory control sample by adding a known amount of ^{252}Cf to a 225-mL centrifuge tube.

11.1.5. Add 10-40 dpm of ^{243}Am tracer to each sample, following laboratory protocol.

11.1.6. Add 1 mL of 1.25M $Ca(NO_3)_2$, 3 mL of 3.2M $(NH_4)_2HPO_4$ solution and 2–3 drops of phenolphthalein indicator to each beaker.

11.1.7. Slowly add concentrated (15M) NH_4OH with a squeeze bottle to centrifuge tube. Add enough NH_4OH to reach a dark pink phenolphthalein end point and form $Ca_3(PO_4)_2$ precipitate. Cap and mix tubes and centrifuge at 2000 rotations per minute (rpm) or more for ~5 minutes.

11.1.8. Decant supernatant solution and discard to waste.

11.1.9. Dissolve the calcium phosphate precipitate with 7 mL of 6M HNO_3 and 7 mL 2.0M $Al(NO_3)_3$. If the residue volume is large, or if residual solids remain, an additional 5 mL 3M HNO_3 may be needed to obtain complete dissolution.

11.1.10. Continue with Section 11.5, Rapid Californium Separation using TEVA® and DGA resins.

11.2. Sample Preparation for Furnace Ashing and Acid Digestion of Swipes or Organic-Polymer-Based Air Particulate Filters

NOTE: The sample and associated QC samples may be split after digestion to provide a back-up fraction.

11.2.1. Aliquant the entire sample into a 150-mL glass beaker.
11.2.2. Set up an empty 150-mL glass beaker for use as a reagent blank
11.2.3. Set up an LCS by adding a known amount of ^{252}Cf to a 150-mL glass beaker.
11.2.4. Add 10-40 dpm ^{243}Am tracer to the blank, LCS, and sample beakers following laboratory protocol.
11.2.5. Heat beaker with swipe on hot plate to dryness.
11.2.6. Place beaker in furnace at 200 ºC and ramp to 550 ºC. Hold for 30 to 60 minutes. Remove from oven and allow to cool.
11.2.7. Digest furnace-ashed sample as follows:
11.2.7.1. Add 5 mL concentrated (16M) HNO_3 to the glass beaker and 1 ml of 30 wt.% hydrogen peroxide (H_2O_2), warm on a hot plate with medium heat to dissolve residue and transfer to 250-mL Teflon beaker.
11.2.7.2. Add 5 mL concentrated HNO_3 to the glass beaker and 1 ml of 30 wt.% H_2O_2 , warm on hot plate and transfer the rinse the Teflon beaker.
11.2.7.3. If necessary to remove any sample residue, add 3 mL concentrated HNO_3 and 1 ml 30 wt.% H_2O_2 to the glass beaker, warm on hot plate with medium heat and add rinse to the Teflon beaker.
11.2.7.4. Add 2 ml concentrated (28M) HF to each beaker. Evaporate to dryness.
11.2.7.5. Add 3 mL concentrated HNO_3 and 2 ml 30 wt.% H_2O_2 and evaporate to dryness.
11.2.7.6. Add 3 mL concentrated HNO_3, 2 ml 30 wt.% H_2O_2 and 3 mL 3M HNO_3-0.25M boric acid and evaporate to dryness.
11.2.7.7. Dissolve the sample residue by adding 7 mL 6M HNO_3, to each beaker, warming on a hot plate.
11.2.7.8. Add 7 ml 2M $Al(NO_3)_3$. Swirl to mix well.
11.2.7.9. Continue with Section 11.5, Rapid Californium Separation using TEVA® and DGA resins.

11.3. Sample Preparation for Air Particulate Filter Samples

NOTE: This method is effective for cellulose-based or glass-fiber air filters. The sample and associated QC samples may be split after digestion to provide a back-up fraction.

11.3.1. Aliquant the entire 2" – 4" air filter into a 250-mL Teflon beaker.
11.3.2. Set up an empty 250-mL Teflon beaker for use as a reagent blank sample.
11.3.3. Set up a laboratory control sample by adding a known amount of ^{252}Cf to a 250-mL Teflon beaker.
11.3.4. Add 10-40 dpm ^{243}Am tracer to all samples following laboratory protocol.
11.3.5. Digest air filters as follows:

11.3.5.1. Add 5 mL concentrated HNO_3, 5 ml concentrated HF, and 2 ml of 30 wt.% H_2O_2. Evaporate to dryness on a hot plate with medium heat.
11.3.5.2. Add 3 mL concentrated HNO_3 and 2 ml of 30 wt.% H_2O_2 and take to dryness.
11.3.5.3. Repeat Step 11.3.5.2, two more times (or as needed to achieve complete digestion).

NOTE: Step 11.3.5.2 may be repeated as needed to effect complete digestion of the sample matrix.

11.3.5.4. Add 3 mL concentrated HNO_3, 2 ml 30 wt.% H_2O_2 and 3 mL 3M HNO_3-0.25M boric acid and evaporate to dryness.
11.3.5.5. Dissolve the sample residue by adding 7 mL 6M HNO_3, to each beaker, warming on a hot plate.
11.3.5.6. Add 7 ml 2M $Al(NO_3)_3$. Swirl to mix well.
11.3.5.7. Continue with Section 11.5, Rapid Californium Separation using TEVA® and DGA resins.

11.4. Fusion of soil samples
11.4.1. In accordance with the DQOs and sample processing requirements stated in the project plan documents, remove extraneous materials from the soil sample using clean forceps or tweezers.
11.4.2. Set up an empty crucible for use as a reagent blank sample.
11.4.3. Set up a laboratory control sample by adding a known amount of ^{252}Cf to an empty crucible.
11.4.4. Weigh out a representative, finely ground 1-g aliquant of dry sample into a crucible.
11.4.5. Add 10-40 dpm ^{243}Am tracer to all samples following laboratory protocol.
11.4.6. Place crucibles on a hot plate and take to dryness at medium heat.

NOTE: Heat on medium heat to dry quickly but not so high as to cause splattering

11.4.7. Remove crucibles from hot plate and allow to cool.
11.4.8. Add 15 g NaOH of sodium hydroxide to each crucible.
11.4.9. Place the crucibles with lids in the 600 °C furnace using tongs.
11.4.10. Fuse samples in the crucibles for ~15 minutes.

NOTE: Longer times may be needed for larger particles.

11.4.11. Remove hot crucibles from furnace very carefully using tongs, and transfer to hood.
11.4.12. Add ~25-50 mL of water to each crucible ~8 to 10 minutes (or longer) after removing crucibles from furnace, and heat on hotplate to loosen/dissolve solids.
11.4.13. Transfer each fused sample to a 225-mL centrifuge tube, rinse crucible well with water, and transfer rinses to each tube.
11.4.14. If necessary to obtain complete dissolution, add more water and warm as needed on a hotplate. Transfer the rinse to the 225-mL tube. If needed, repeat

this step until all solids have been dissolved and transferred to the centrifuge tube.

11.4.15. Add 10 mL 3M HNO_3 to each crucible and heat crucibles on a hot plate until hot. Transfer the 3M HNO_3 rinse to the 225-mL tube, followed by additional rinses of water.

NOTE: The iron (Fe) and La carriers may be added to the 225-mL centrifuge tube before adding the dissolved sample.

11.4.16. Pipet 2.5 mL of iron carrier (50 mg/mL) and 3 mL 1.0 mg La/mL into the 225-mL centrifuge tube.
11.4.17. Dilute each sample to approximately 180 mL with water.
11.4.18. Cool the 225-mL centrifuge tube in an ice water bath to approximately room temperature, as needed.
11.4.19. Pipet 2 mL 1.25M $Ca(NO_3)_2$ and 5 mL 3.2M $(NH_4)_2HPO_4$ into each tube. Cap tubes and mix well.
11.4.20. Add 5 mL of 10 wt.% $TiCl_3$ to each tube. Cap and mix immediately.

NOTE: If 10 wt.% $TiCl_3$ is not available, other concentrations of $TiCl_3$ (e.g., 12-20%) may be used if the amount is adjusted based on the assay of the solution to deliver the same or slightly more titanium. For example, if 17 wt.% $TiCl_3$ is used, the volume may be decreased to 3 mL.

11.4.21. Cool the 225-mL centrifuge tubes in an ice water bath for ~5 minutes.
11.4.22. Centrifuge tubes for 6 minutes at 3000 rpm.
11.4.23. Pour off the supernate and discard to waste.
11.4.24. Add 1.5M HCl to a total volume of ~80 mL to redissolve each sample.
11.4.25. Cap and shake each tube to dissolve solids as well as possible.

NOTE: There will typically be undissolved solids, which is acceptable.

11.4.26. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix well.
11.4.27. Pipet 1 mL of 1.0 mg La/mL and 0.5 mL 1.25M $Ca(NO_3)_2$ to each tube.
11.4.28. Add 3 mL of 10 wt.% $TiCl_3$ into each tube. Cap and mix immediately.

NOTE: If 10 wt.% $TiCl_3$ is not available, other concentrations of $TiCl_3$ (e.g., 12-20%) may be used if the amount is adjusted based on the assay of the solution to deliver the same or slightly more titanium. For example, if 17 wt.% $TiCl_3$ is used, the volume may be decreased to 2 mL.

11.4.29. Add 25 mL of concentrated (28M) HF into each tube. Cap and mix well.
11.4.30. Place tubes in an ice water bath for ~10 minutes to get the tubes very cold.
11.4.31. Remove the tubes from the ice water bath and wait 5 minutes, then centrifuge for ~10 minutes at 3000 rpm, or longer or as needed.
11.4.32. Pour off supernate and discard to waste.
11.4.33. Pipet 5 mL of 3M HNO_3 - 0.25M boric acid (H_3BO_3) into each tube.
11.4.34. Cap, mix and transfer contents of the tube into a labeled 50-mL centrifuge tube.
11.4.35. Pipet 6 mL of 7M HNO_3 and 7 mL of 2M aluminum nitrate ($Al(NO_3)_3$) into each tube, cap and mix (shake or use a vortex stirrer). Transfer rinse to 50-mL centrifuge tube.

11.4.36. Pipet 3 ml of 3M HNO_3 directly into the 50-mL centrifuge tube.
11.4.37. Warm each 50-mL centrifuge tube in a hot water bath for a few minutes, swirling to dissolve.
11.4.38. Remove each 50-mL centrifuge tube from the water bath and allow to cool to room temperature.
11.4.39. Centrifuge the tubes at 3000 rpm for 5 minutes to remove any traces of solids (may not be visible prior to centrifuging).
11.4.40. Transfer solutions to labeled beakers or tubes for further processing. Discard any solids.
11.4.41. Continue with Section 11.5, Rapid Californium Separation using TEVA® and DGA resins.

11.5. Rapid Californium Separation using TEVA® and DGA resins

NOTE: 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.

11.5.1. Add 0.2 mL of 1.5M sulfamic acid (H_3NSO_3) to each solution. Swirl to mix.

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.

NOTE: If Neptunium-237 (^{237}Np) is potentially present in the sample, also add 0.5 mL of 4 mg/mL iron carrier to enhance neptunium reduction to Np^{4+}. The addition of ascorbic acid in the next step will convert Fe^{3+} to Fe^{2+} and ensure removal of neptunium on TEVA® resin.

11.5.2. Add 1.25 mL of 1.5M ascorbic acid ($C_6H_8O_6$) to each solution. Swirl to mix. Wait 3 minutes.

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

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

NOTE: The load solution nitrate concentration is increased after valence adjustment to provide greater retention of californium and americium and more effective removal of calcium on the DGA resin.

11.5.4. Add 1.5 mL concentrated (16M) HNO_3 to each sample and swirl to mix.

NOTE: The steps in this section were optimized for a commercially available filtration system. Other vacuum systems may be substituted here. The cartridges may be set up and conditioned with nitric acid so that they are ready for column loading just prior to completion of the valence adjustment steps. More than one vacuum box may be used to increase throughput.

11.5.5. Set up TEVA® and DGA cartridges on the vacuum box system.
11.5.5.1. 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.

11.5.5.2. 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.
11.5.5.3. For each sample, assemble a TEVA® and a DGA cartridge and lock these onto the inner white tip (DGA cartridge below TEVA®).
11.5.5.4. Place reservoirs on the top end of the TEVA® cartridge.
11.5.5.5. Seal unused openings on the vacuum box by inserting yellow caps included with the vacuum box into unused white tips to achieve good seal during the separation. Alternately, plastic tape can be used to seal the unused lid holes.
11.5.5.6. Turn the vacuum on and ensure proper fitting of the lid.
11.5.5.7. Add 5 mL of 3M HNO_3 to the column reservoir to precondition the TEVA® cartridges.
11.5.5.8. Adjust the vacuum to achieve a flow rate of ~1 mL/min.

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

11.5.6. TEVA® and DGA resin Separation

11.5.6.1. Transfer the load solution from Step 11.5.4 into the appropriate reservoir. Allow solution to pass through the stacked TEVA® + DGA cartridge at a flow rate of ~1 mL/min.
11.5.6.2. Rinse each tube/beaker with 5 mL of 6M HNO_3 and transfer the solution to the appropriate reservoir (the flow rate can be adjusted to ~2 mL/min).
11.5.6.3. Rinse the columns with 5 mL of 6M HNO_3 (~2 mL/min).
11.5.6.4. Turn off vacuum, discard rinse solutions and remove TEVA® cartridges. Discard TEVA® cartridges and reservoirs and place new reservoirs on the DGA cartridges.
11.5.6.5. Rinse each DGA column with 10 mL of 3M HCl at ~2 mL/min.
11.5.6.6. Rinse each DGA column with 3 mL of 1M HNO_3 at ~2 mL/min.
11.5.6.7. Rinse each DGA column with 20 mL of 0.1M HNO_3 at ~1-2 mL/min.
11.5.6.8. If lanthanum was used in alkaline fusion preconcentration steps (i.e., soil matrix), add a 5 ml rinse of 0.075M HNO_3 to remove La from DGA resin at ~1-2 mL/min.

NOTE: The rinses with dilute nitric acid remove uranium while californium and americium are retained. Precipitation of uranium is also inhibited during microprecipitation by adding hydrogen peroxide to ensure uranium is present as UO_2^{2+}.

NOTE: If problems with peak resolution are encountered, the volume of the 0.075M HNO_3 rinse may need to be increased to 10 ml or 15 ml to more effectively remove lanthanum.

11.5.6.9. Rinse each column with 15 mL of 3M HNO_3–0.25M HF at ~1-2 mL/min to complex and remove thorium from the DGA resin.
11.5.6.10. Place a fresh reservoir onto each column to minimize residual fluoride.
11.5.6.11. Rinse residual fluoride from each DGA column with 5 mL of 4M HCl at ~2 mL/min.

11.5.6.12. Place clean, labeled plastic tubes in the tube rack under each cartridge. Also place clean connector tips on each column prior to Cf/Am elution.

NOTE: Traces of lanthanum used in the soil method can precipitate as an oxalate and lead to co-precipitation and loss of californium on the DGA cartridge. It is therefore very important to minimize residual lanthanum with the 0.25M HCl eluent step prior to adding ammonium bioxalate to fully elute californium from the DGA resin.

11.5.6.13. Elute californium and americium by adding 10 mL of 0.25M HCl solution to each cartridge and reducing the flow rate to ~1 mL/min (or slightly slower).

11.5.6.14. If lanthanum was used in alkaline fusion preconcentration steps (i.e., soil matrix), continue eluting californium and americium by adding 5 ml of 0.25M HCl.

11.5.6.15. After the 0.25 M HCl has passed through the column, add 15 mL 0.1M ammonium bioxalate at ~1 mL/min to complete elution of ^{252}Cf from the column.

11.5.6.16. Set the californium fraction in the plastic tube aside for cerium fluoride coprecipitation, Step 11.6.

11.5.6.17. Discard the DGA cartridge.

11.6. 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.

11.6.1. Pipet 100 µL of the 0.5 mg/mL cerium carrier solution into each tube.

11.6.2. Pipet 0.2 mL 30 wt.% H_2O_2 into each tube to prevent any residual uranium from precipitating.

11.6.3. Pipet 2 mL of concentrated (28M) HF into each tube.

11.6.4. Cap the tube and mix. Allow samples to sit for ~ 15 minutes before filtering.

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

Caution: Following deposition of the microprecipitate, there is no visible difference between the two sides of the filter.

11.6.6. If a hydrophobic filter is used, 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.

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

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

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

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

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

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

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

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

11.6.15. Discard the filtrate to waste for future disposal. If the filtrate is to be retained, it should be placed in a plastic container since glass will be attacked by HF.

NOTE: Other methods for STS preparation, such as electrodeposition 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.

12. Data Analysis and Calculations

12.1. Equation for determination of initial screening 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 collection (or other reference time), in picocuries per gram (pCi/ L, g, swipe, sample)

A_t = activity of the tracer added to the sample aliquant on the tracer solution its reference time (pCi)

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

R_t = net count rate of the tracer in the defined ROI, cps)

W_a = size of the sample aliquant (L, g, swipe, sample)

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

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, pCi/g, pCi/swipe, pCi/sample)
$u(A_t)$ = 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 size of the sample aliquant weight (L, g, swipe, sample)

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

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

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

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

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

and

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

where:

R_x = net count rate of analyte or tracer (cps)
C_x = sample counts in the analyte or the tracer ROI (cnt)
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, $(cps)^2$

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

[2] For methods with very low counts, MARLAP Section 19.5.2.2 (Reference 16.2) recommends adding one count each to the gross counts and the background counts when estimating the uncertainty of the respective net counts. This minimizes negative bias in the estimate of uncertainty and protects against calculating zero uncertainty when a total of zero counts are observed for the sample and background.

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

and

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

where:

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

12.1.3. If the critical level concentration (L_c) or the minimum detectable concentration (MDC) are requested (at an error rate of 5%), they can be calculated using the following equations: [3]

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

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

where:

R_{ba} = background count rate for the analyte in the defined ROI (cps)

[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 (Reference 16.2). The formulations presented here assume an error rate of $\alpha = 0.05$, $\beta = 0.05$ (with $z_{1-\alpha} = z_{1-\beta} = 1.645$) and $d = 0.4$. For methods with very low numbers of counts, these expressions provide better estimates than do the traditional formulas for the critical level and MDC.

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 and documented as required.

13.2. Expected turnaround time per batch of 10-20 samples plus QC, from aliquanting through microprecipitation and counting using a vacuum box system is:

13.2.1. For water samples, ~8 hours.

13.2.2. For swipe or organic-polymer-based air particulate filter samples, ~11 ¼ hours.

13.2.3. For air particulate filter samples, ~10 hours.

13.2.4. For soil samples, ~9 ¾ hours.

13.2.5. See Section 17.4 for detailed flow charts and estimates of time 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 californium fraction.

15. Waste Management

15.1. Types of waste generated per sample analyzed

15.1.1. Approximately 210 mL basic waste from the initial preconcentration of water samples.

15.1.2. Approximately 55-70 mL of acidic waste from loading and rinsing the two extraction columns will be generated.

15.1.3. Approximately 25-35 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.

15.1.4. TEVA® cartridge – ready for appropriate disposal.

15.1.5. DGA cartridge – ready for appropriate disposal.

15.1.6. The sample test source consisting of a polypropylene filter disk with ~100 micrograms of cerium fluoride.

15.1.7. These waste streams may contain low levels of ^{243}Am (added as tracer), $^{252/250}$Cf (added to LCS) and other radionuclides as may be present in samples.

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

16. References

Cited References

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

17.1 Tables

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

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance	α Emission Energy (keV)
^{252}Cf	2.645	8.304×10^{-11}	0.816	6118
			0.152	6076
			0.0023	5977
^{250}Cf	13.08	1.679×10^{-09}	0.8258	6030
			0.1711	5990
			0.00283	5891
$^{252/250}$Cf [2]	2.645	8.304×10^{-11}	0.970[3]	6118/6030/6076…
^{243}Am	7.370×10^{3}	2.98×10^{-12}	0.0016	5349
			0.0016	5321
			0.871	5275
			0.112	5233
			0.0136	5181
^{243}Am [2]	7.370×10^{3}	2.98×10^{-12}	0.9998 [3]	5275
^{251}Cf	898	2.45×10^{-11}	0.0260	6078
			0.125	6017
			0.0060	5946
			0.276	5854
			0.0400	5817
			0.0250	5798
			0.0360	5766
			0.354	5679
			0.0330	5651
			0.049	5635
			0.010	5569
			0.010	5567
^{249}Cf	351	6.258E-11	0.02460	6194
			0.0133	6139
			0.00346	6072
			0.0333	5946
			0.0321	5903
			0.0143	5849
			0.822	5813
			0.0469	5760

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance	α Emission Energy (MeV)
^{241}Am	432.6	5.077×10^{-11}	0.0037	5545
			0.00225	5512
			0.848	5486
			0.131	5443
			0.0166	5388
^{243}Cm	29.1	7.55×10^{-10}	0.0150	6066
			0.047	6058
			0.010968	6010
			0.0568	5992
			0.0069797	5876
			0.730	5785
			0.115	5742
			0.015954	5686
			0.0019942	5682
			0.0013959	5639
^{244}Cm	6614.6	3.321×10^{-12}	0.7690	5805
			0.2310	5763
^{246}Cm	4760	4.61×10^{-12}	0.822	5387
			0.178	5344
^{246}Cm	348,000	6.31E-14	0.750	5078
			0.1652	5035

[1] Only the particle energies for the most abundant alpha emission intensities have been noted here.

[2] This line shows the half –life, summed alpha emission intensity and the approximate peak centroid energy for the region of interest used to calculate results for the listed nuclide or nuclide combination based on alpha particles emitted by the radionuclide(s) that fall in the region of interest. The laboratory may need to adjust these values depending on the region of interest established for a given radionuclide.

[3] The region of interest used for the calculation of the $^{252/250}$Cf summed abundance includes the alpha emissions of ^{252}Cf (6118, 6076, 5977 keV) and ^{250}Cf (6030, 5990, 5891 keV).

Table 17.2 Alpha Emissions Sorted by Decreasing Energy

Isotope	Half-life (years)	λ (sec^{-1})	α-emission energy (keV)	Abundance	Uncertainty
^{249}Cf	351	6.258×10^{-11}	6194	0.02460	0.00020
^{249}Cf	351	6.258×10^{-11}	6139	0.0133	0.0010
^{252}Cf	2.645	8.304×10^{-09}	6118	0.816	0.003
^{251}Cf	898	2.45×10^{-11}	6078	0.0260	0.0010
^{252}Cf	2.645	8.304×10^{-09}	6076	0.152	0.003
^{243}Cm	29.1	7.55×10^{-10}	6066	0.0150	0.0020
^{243}Cm	29.1	7.55×10^{-10}	6058	0.047	0.003
^{250}Cf	13.08	1.679×10^{-09}	6030	0.8258	0.0011
^{251}Cf	898	2.45×10^{-11}	6017	0.125	0.003
^{243}Cm	29.1	7.55×10^{-10}	6010	0.010968	--
^{243}Cm	29.1	7.55×10^{-10}	5992	0.0568	0.0020
^{250}Cf	13.08	1.679×10^{-09}	5990	0.1711	0.0011
^{252}Cf	2.645	8.304×10^{-09}	5976	0.0023	0.0004
^{251}Cf	898	2.45×10^{-11}	5946	0.0060	0.0006
^{249}Cf	351	6.258×10^{-11}	5946	0.0333	0.0003
^{249}Cf	351	6.258×10^{-11}	5903	0.0321	0.0003
^{250}Cf	13.08	1.679×10^{-09}	5891	0.00283	0.00015
^{251}Cf	898	2.45×10^{-11}	5854	0.276	0.005
^{243}Cm	29.1	7.55×10^{-10}	5876	0.0069797	--
^{249}Cf	351	6.258×10^{-11}	5849	0.0143	0.0020
^{254}Cf	0.1656	1.33×10^{-07}	5833	0.00257	0.00018
^{244}Cm	18.11	3.321×10^{-12}	5805	0.7690	0.0010
^{251}Cf	898	2.45×10^{-11}	5817	0.0400	0.0020
^{249}Cf	351	6.258×10^{-11}	5813	0.822	0.005
^{251}Cf	898	2.45E-11	5798	0.0250	0.0020
^{243}Cm	29.1	7.55×10^{-10}	5785	0.730	0.023
^{251}Cf	898	2.45×10^{-11}	5766	0.0360	0.0020
^{244}Cm	18.11	3.321×10^{-12}	5763	0.2310	0.0010
^{249}Cf	351	6.258×10^{-11}	5760	0.0469	0.0005
^{243}Cm	29.1	7.55×10^{-10}	5742	0.115	0.005
^{243}Cm	29.1	7.55×10^{-10}	5686	0.015954	--
^{243}Cm	29.1	7.55×10^{-10}	5682	0.0019942	--
^{251}Cf	898	2.45×10^{-11}	5679	0.354	0.005
^{251}Cf	898	2.45×10^{-11}	5651	0.0330	0.0020
^{243}Cm	29.1	7.55×10^{-10}	5639	0.0013959	--
^{251}Cf	898	2.45×10^{-11}	5635	0.049	0.0020
^{251}Cf	898	2.45×10^{-11}	5569	0.010	0.010
^{251}Cf	898	2.45×10^{-11}	5567	0.010	0.010
^{241}Am	432.6	5.077×10^{-11}	5545	0.0037	0.0003
^{241}Am	432.6	5.077×10^{-11}	5512	0.00225	0.0005

Isotope	Half-life (years)	λ (sec^{-1})	α-emission energy (keV)	Abundance	Uncertainty
^{241}Am	432.6	5.077×10^{-11}	5486	0.848	0.005
^{241}Am	432.6	5.077×10^{-11}	5443	0.131	0.003
^{241}Am	432.6	5.077×10^{-11}	5388	0.01660	0.00020
^{246}Cm	4760	4.61×10^{-12}	5387	0.822	0.012
^{243}Am	7,370	2.980×10^{-12}	5349	0.0016	0.0007
^{246}Cm	4760	4.61×10^{-12}	5343	0.178	0.012
^{243}Am	7,370	2.980×10^{-12}	5321	0.0016	0.0003
^{243}Am	7,370	2.980×10^{-12}	5275	0.871	0.003
^{243}Am	7,370	2.980×10^{-12}	5233	0.112	0.003
^{243}Am	7,370	2.980×10^{-12}	5181	0.0136	0.0010

17.2 Ingrowth Curves and Ingrowth Factors

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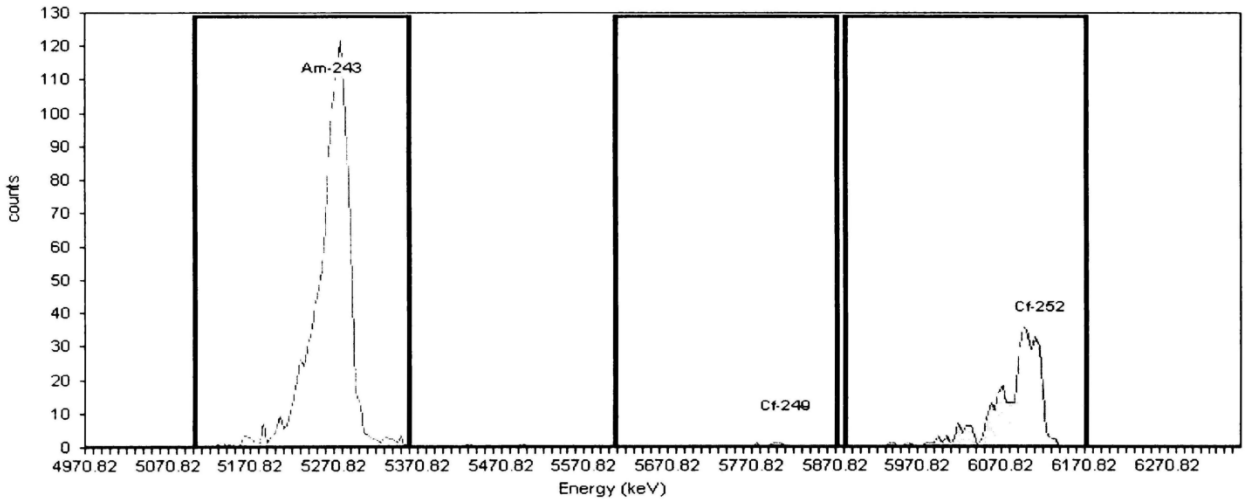
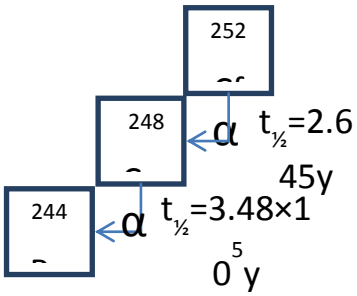
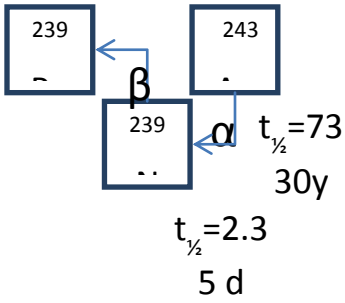
17.3 Spectrum from a Processed Sample

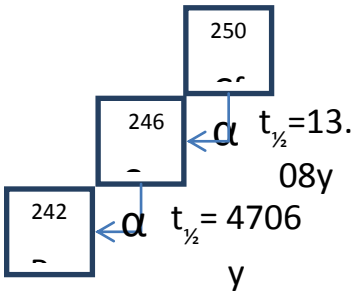


Californium Spectrum

17.4 Decay Schemes

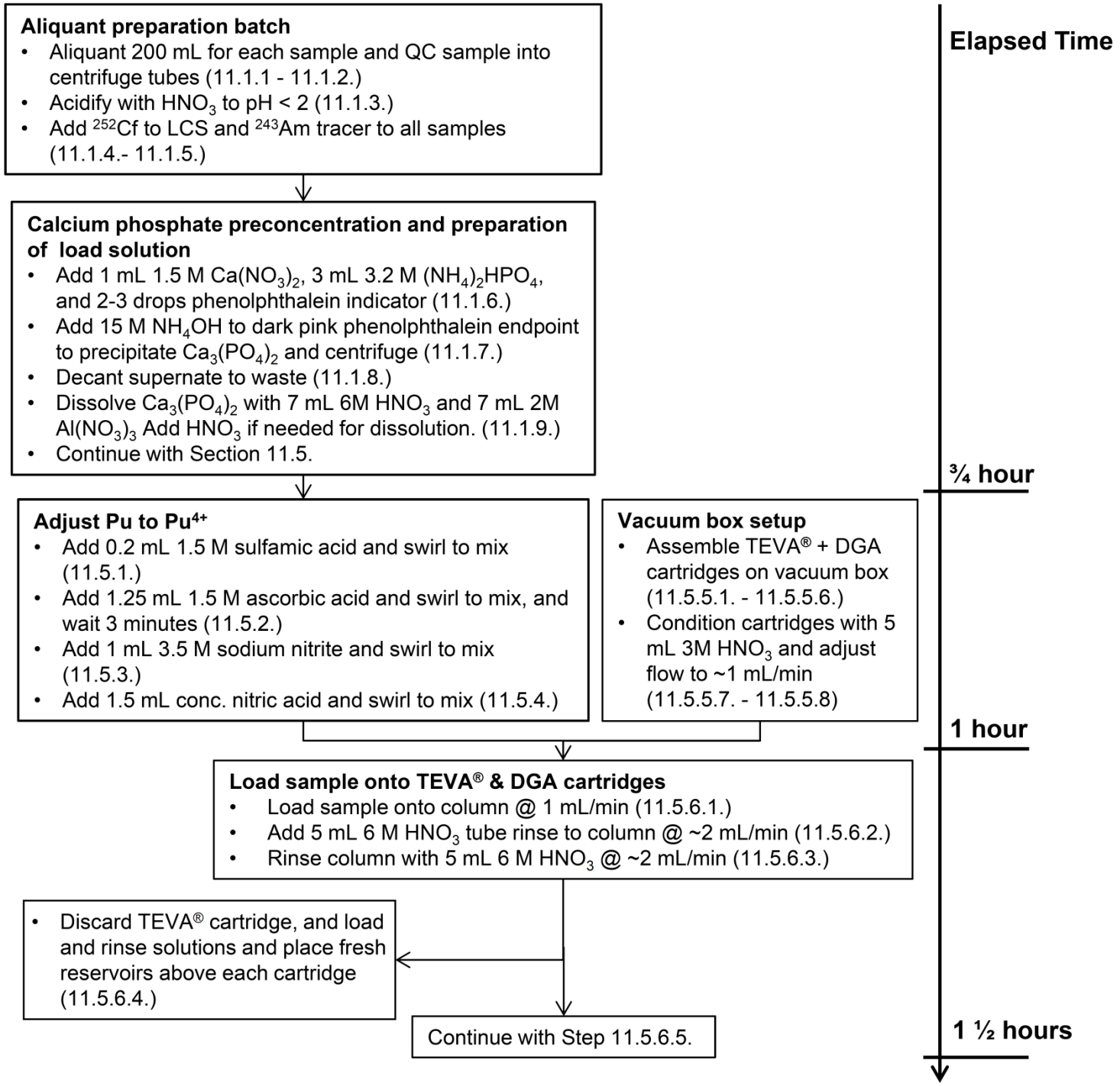




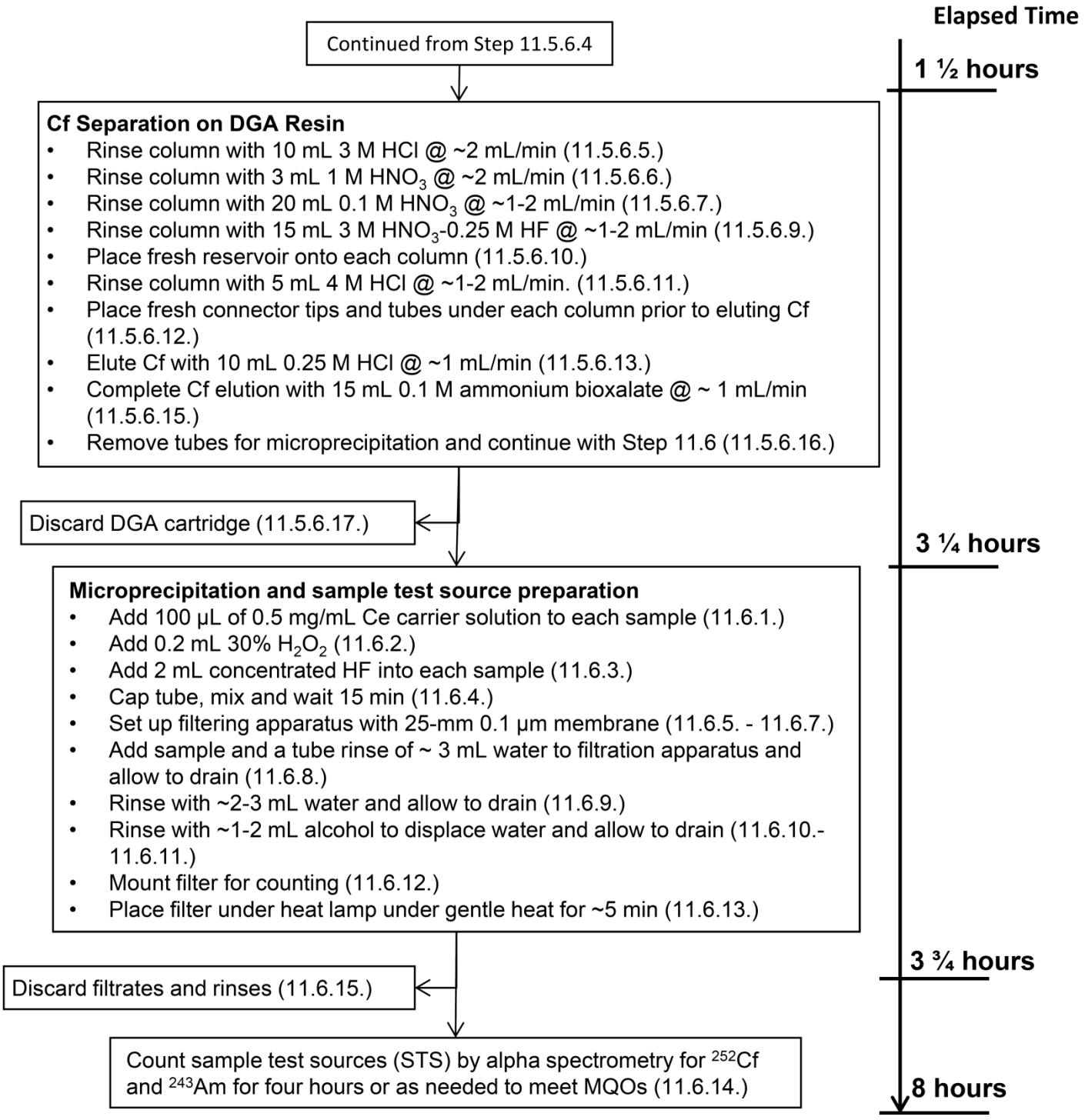


17.5 Flow Chart and Timeline

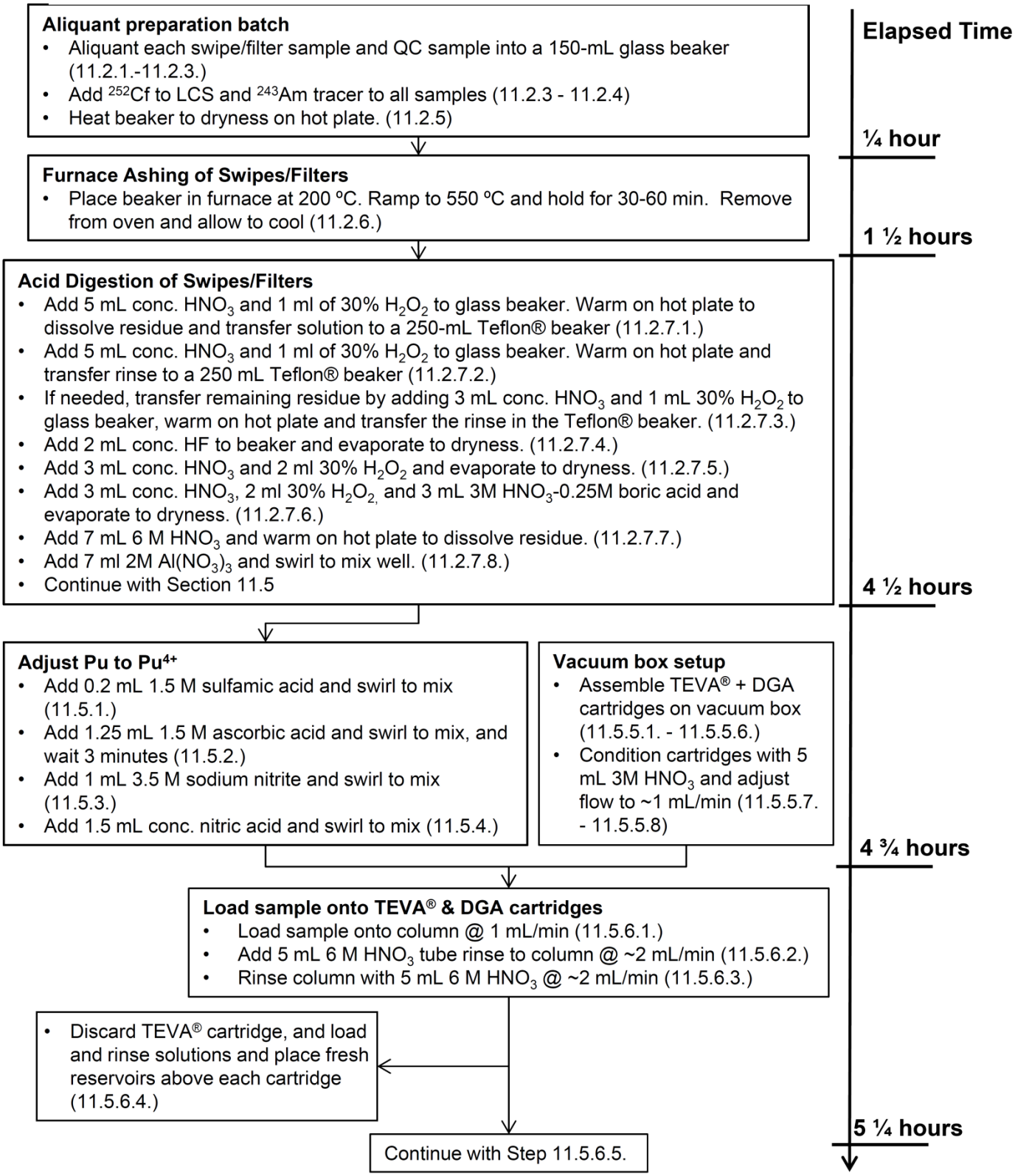
Sample Preparation Scheme and Timeline for the Determination of ^{252}Cf in Water Samples



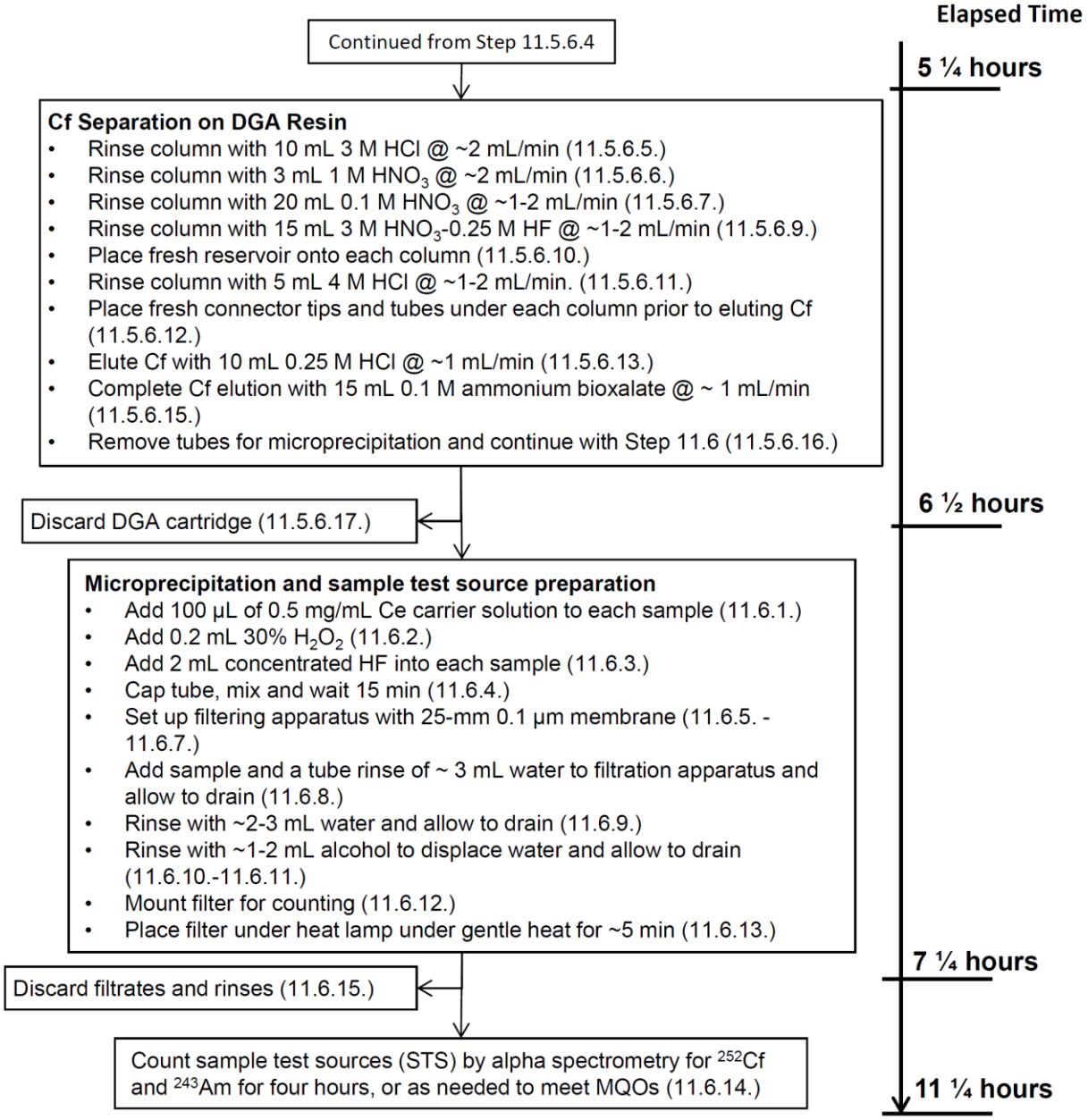
Sample Preparation Scheme and Timeline for the Determination of ^{252}Cf in Water Samples (cont.)



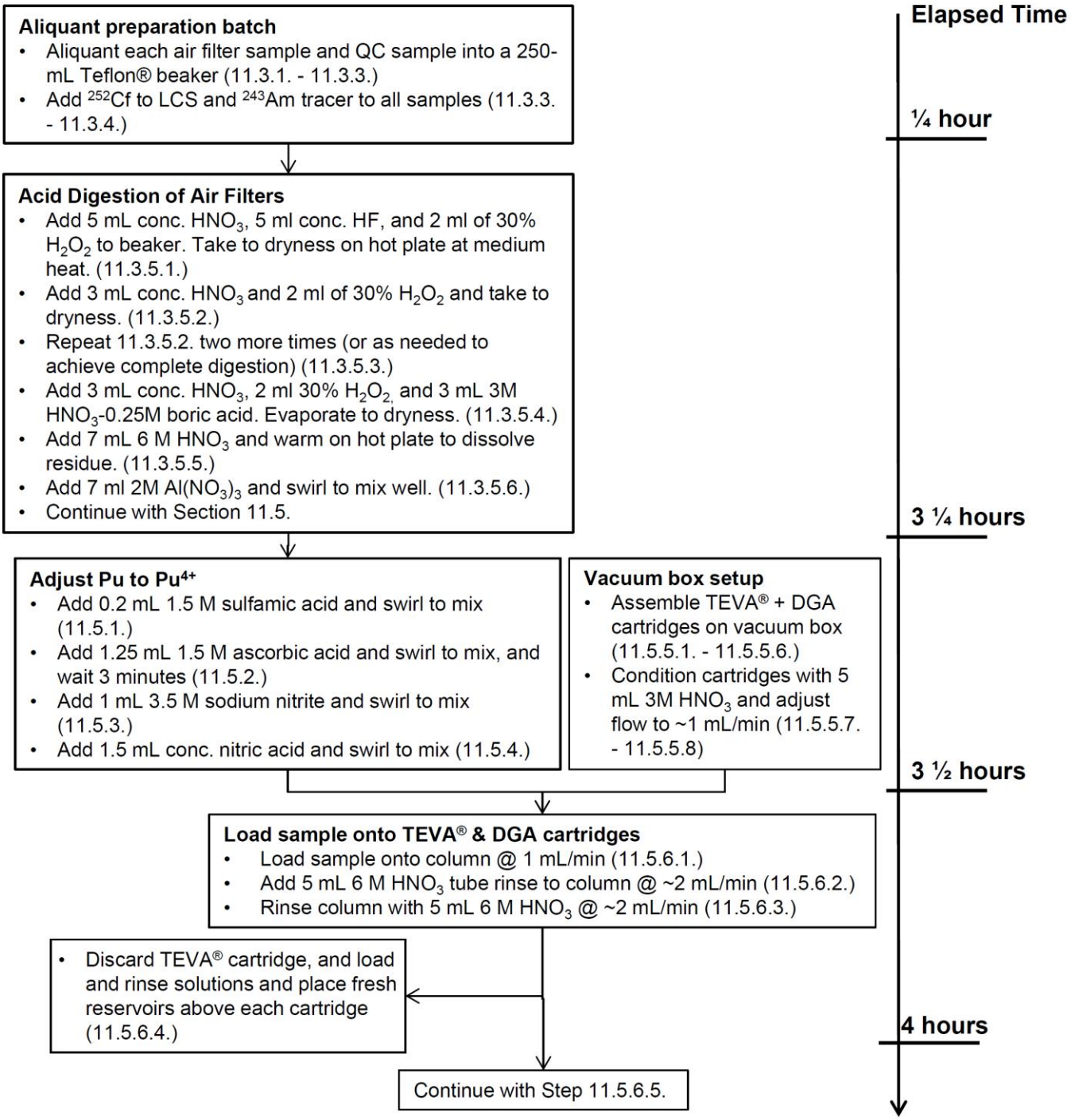
Separation Scheme and Timeline for the Determination of ^{252}Cf in Swipes and Organic-Polymer-Based Air Particulate Filters



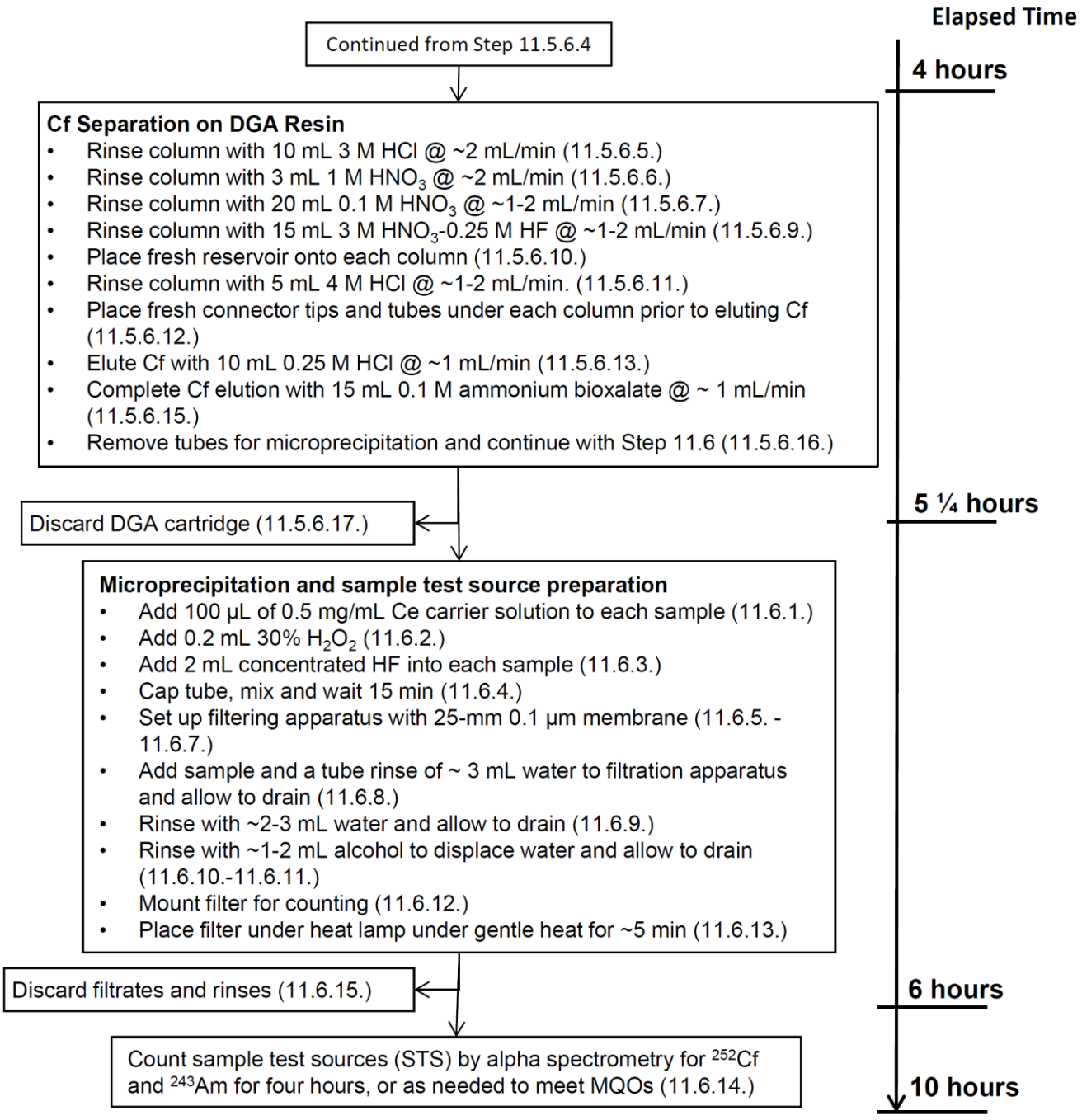
Separation Scheme and Timeline for the Determination of ^{252}Cf in Swipes and Organic-Polymer-Based Air Particulate Filters (cont.)



Separation Scheme and Timeline for the Determination of ^{252}Cf in Air Particulate Filter Samples



Separation Scheme and Timeline for the Determination of ^{252}Cf in Air Particulate Filter Samples (cont.)



Separation Scheme and Timeline for the Determination of ^{252}Cf in Soil

Aliquant preparation batch
- Set up QC samples and aliquant a representative, finely ground 1 gram aliquant of dry sample into a crucible. (11.4.1. – 11.4.4.)
- Add ^{243}Am tracer to all samples (11.4.5.)
- Place crucibles on hot plate and take to dryness. (11.4.6.)

Sodium Hydroxide Fusion
- Remove crucibles from hot plate and allow to cool. (11.4.7.)
- Add 15 g NaOH to each crucible and place the crucibles with lids in the 600 °C furnace using tongs. Fuse samples in the crucibles for ~15 minutes. (11.4.8. - 11.4.10.)
- Remove hot crucibles from furnace and transfer to hood. Allow to cool for 8-10 minutes (or longer). Add ~25-50 mL of water to each crucible, and heat on hotplate to loosen/dissolve solids. (11.4.11.-11.4.12.)
- Transfer fused sample to 225-mL centrifuge tube. Rinse crucible well with water and transfer rinses to tube. (11.4.13.)
- If necessary, add more water and warm on hotplate. Transfer rinse to 225-mL tube. (repeat until all solids are dissolved and transferred to the centrifuge tube). (11.4.14.)
- Add 10 mL 3 M HNO3 to each crucible and heat crucibles on a hot plate until hot. Transfer nitric acid rinse to the tube, followed by additional rinses of water. (11.4.15.)

Fusion Matrix Removal and Preparation of Load Solution
- Add 2.5 mL 50 mg/mL Fe carrier and 3 mL 1 mg/mL La carrier to tube. (11.4.16.)
- Dilute to ~180 mL with H_2O. Cool in ice bath to room temperature. (11.4.17.-11.4.18.)
- Add 2 mL 1.25 M $Ca(NO_3)_2$ and 5 mL 3.2 M $(NH_4)_2HPO_4$, cap, mix well. (11.4.19.)
- Add 5 mL of 10% $TiCl_3$. Cap and mix immediately. Cool 225-mL tube in an ice bath for ~5 minutes. (11.4.20.-11.4.21.)
- Centrifuge at 3000 rpm for 6 minutes. Pour off supernate to waste. (11.4.22.-11.4.23.)
- Add 1.5 M HCl to total volume of ~80 mL to dissolve precipitate. Cap and shake each tube to dissolve solids. (some undissolved solids are acceptable). (11.4.24.-11.4.25.)
- Dilute to ~170 mL with 0.01 M HCl. Cap and mix well. (11.4.26.)
- Add 1 mL 1.0 mg/mL La carrier and 0.5 mL 1.25 M $Ca(NO_3)_2$. (11.4.27.)
- Add 3 mL 10% $TiCl_3$ to each tube. Cap and mix immediately. (11.4.28.)
- Add 25 mL of conc. HF to each tube, cap and mix well. (11.4.29.)
- Place tubes in ice bath for ~10 minutes until tubes are very cold. (11.4.30.)
- Wait 5 min., then centrifuge ~10 minutes at 3000 rpm (or longer as needed). (11.4.31.)
- Pour off supernate and discard to waste. (11.4.32)
- Add 5 mL of 3 M HNO_3-0.25 M boric acid into each tube. (11.4.33.)
- Cap, mix and then transfer contents to a 50-mL centrifuge tube. (11.4.34.)
- Pipet 6 mL of 7 M HNO_3 and 7 mL of 2 M aluminum nitrate into the tube. Cap and mix (shake or use a vortex stirrer). Transfer rinse to 50-mL centrifuge tube. (11.4.35.)
- Pipet 3 ml 3 M HNO_3 into 50-mL tube. Warm in water bath, swirl to dissolve. (11.4.36.-11.4.37.)
- Remove tube from water bath. Allow to cool to room temperature. (11.4.38.)
- Centrifuge at 3000 rpm for 5 minutes to remove solids (11.4.39.)
- Transfer solution to beakers or tubes. Discard any solids. 11.4.40.)

Continue with Section 11.5

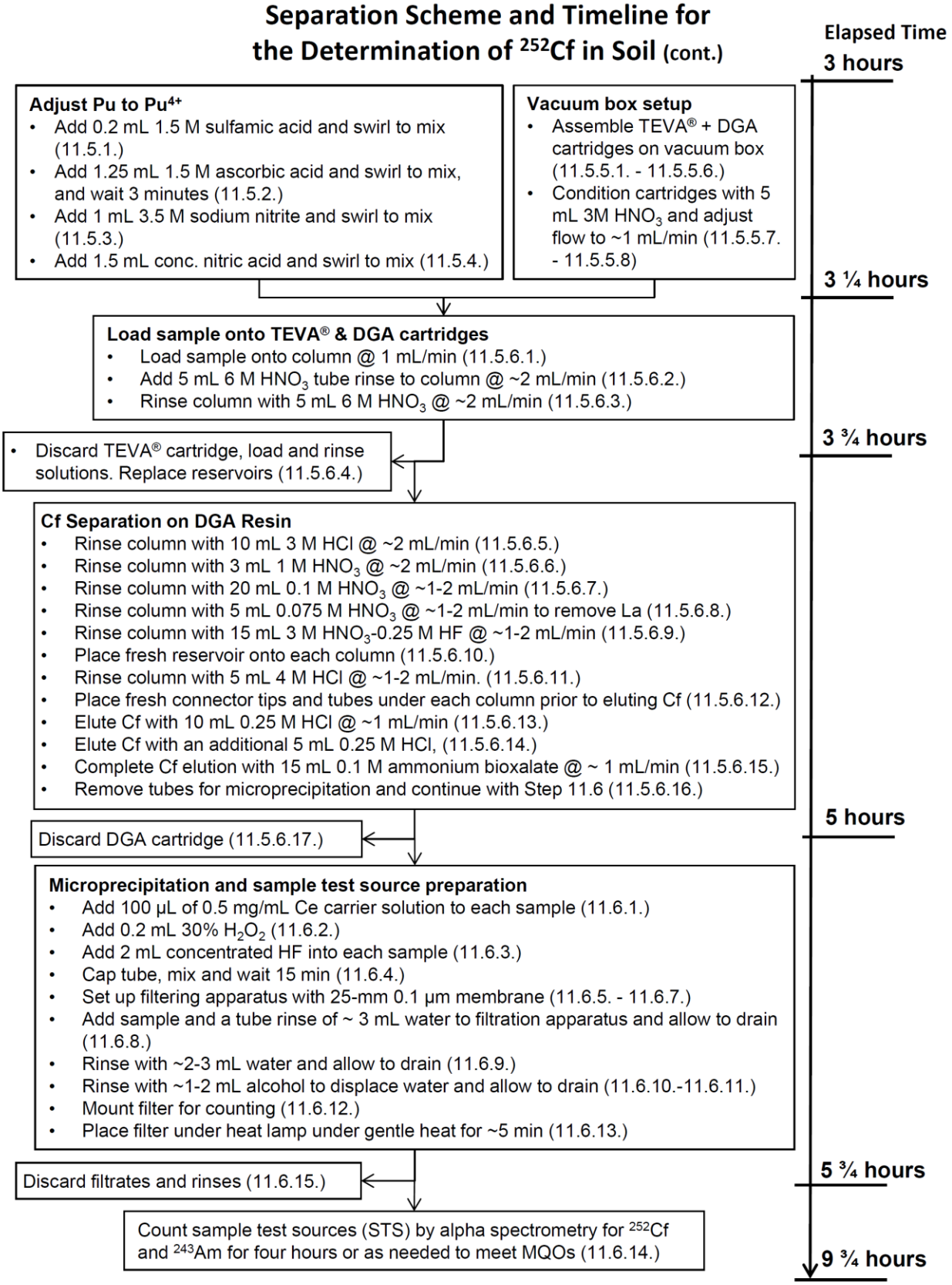
Elapsed Time

¼ hour

1 ¾ hour

3 hours

Separation Scheme and Timeline for the Determination of ^{252}Cf in Soil (cont.)



Appendix A: Rapid Technique for Milling and Homogenizing Soil Samples

A1. Scope and Application

A1.1. The method describes one approach for the rapid, gross preparation of soil samples to yield dried, representative 1–2-g aliquant for radiochemical analysis of non-volatile radionuclides. The method addresses steps for splitting, drying, and milling of 50–2,000-g soil samples.

A1.2. This rapid milling method is designed to be used as a preparatory step for the fusion of soils for Am, Pu, U, ^{90}Sr, and ^{226}Ra. It may also be applied to other matrices whose physical form is amenable to pulverization in the ball mill. It is not amenable to radionuclides that are volatile at 110 ºC or below.

A1.3. The use of the term soil is not intended to be limiting or prescriptive. The method described applies to soil-related materials such as sand, humic/fulvic soils, peat, loam, sediment, etc.

A1.4. If the levels of activity in the sample are low enough to permit safe radiological operations, up to 2 kg of soil can be processed.

A2. Summary of Method

A2.1. This method uses only disposable equipment to contact the sample minimizing the risk of contamination and cross-contamination and eliminating concerns about adequate cleaning of equipment.

A2.2. Extraneous material, such as vegetation, biota, or rocks or debris may be removed prior to processing the sample unless the project requires that they be processed as part of the sample.

NOTE: The sample mass is generally used for measuring the size of solid samples. The initial process of acquiring a representative aliquant uses the volume of the sample, as the total sample size is generally based on a certain volume of soil (e.g., 500 mL).

A2.3. The entire sample as received is split by coning and quartering until ~75-150 mL of soil are available for subsequent processing. If less than ~450 mL of soil are received, the entire sample is processed.

A2.4. The soil is transferred to a paint can and dried. Percent solids are determined, if required.

A2.5. Grinding media (stainless-steel or ceramic balls or rods) are added, and the sample is milled to produce a finely-ground, well-homogenized, powder with predominant particle size less than 300 μm.

A2.6. If the sample may contain discreet radioactive particles (DRPs), particles larger than a nominal size of 150 μm are screened for radioactivity, and further milled, or processed with another appropriate method to ensure that they will be chemically available for subsequent processing.

A2.7. The resulting milled sample is stored in, and aliquanted directly from, the container used for drying and pulverization.

A3. Definitions, Abbreviations, and Acronyms

A3.1. 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).

A3.2. *Multi-Agency Radiological Analytical Laboratory Protocol* (MARLAP) Manual (see Reference 16.2).

A4. Interferences

A4.1. Radiological Interferences

A4.1.1. Coning and quartering provides a mechanism for rapidly decreasing the overall size of the sample that must be processed while optimizing the representativeness of the subsampling process. By decreasing the time and effort needed to prepare the sample for subsequent processing, sample throughput can be significantly improved. Openly handling large amounts of highly contaminated materials, however, even within the containment provided by a fume hood, may pose an unacceptable risk of inhalation of airborne contamination and exposure to laboratory personnel from radioactive or other hazardous materials. Similarly, it may unacceptably increase the risk of contamination of the laboratory.

A4.1.2. In such cases, coning and quartering process may be eliminated in lieu of processing the entire sample. The time needed to dry the sample will increase significantly, and the container size and the number and size of grinding media used will need to be adjusted to optimize the milling process. See ASTM C999 (see Reference A16.33) for an approach for homogenization and milling of larger soil samples.

A4.2. The precise particle size of the milled sample is not critical to subsequent processes. However, milling the sample to smaller particle sizes, and thorough mixing, both facilitate representative sub-sampling by minimizing the amount of sample that is not pulverized to fine mesh and must be discarded. Additionally, subsequent fusion and digestion processes are more effective when performed on more finely milled samples.

A4.3. This method assumes that radioactivity in the sample is primarily adsorbed onto the surface of particles, as opposed to being present as a hot particle (see discussion of DRPs below). Thus, nearly all of the activity in a sample will be associated with sample fines. By visually comparing the sample to a qualitative standard of ~50–100 mesh size particles, it is possible to rapidly determine whether the sample is fine enough to facilitate the subsequent fusion or digestion. This method assumes that when greater than 95% of the sample is as fine or finer than the 50–100 mesh sample, bias imparted from losses of larger particles will be minimal.

A4.4. If the sample was collected near the epicenter of an radiological dispersal device (RDD) or improvised nuclear device (IND) explosion, it may contain millimeter- to micrometer-sized particles of contaminant referred to as "discrete radioactive particles," or DRPs. DRPs may consist of small pieces of the original radioactive source and thus may have very high specific activity. They may also consist of

chemically intractable material and present special challenges in the analytical process. Even when size reduced to less than 50–100 mesh, these particles may resist fusion or digestion of the solids into ionic form which can be subjected to chemical separations.

A4.5. When DRPs may be present, this method isolates larger particles by passing the sample through a disposable 50 mesh screen after which they can be reliably checked for radioactivity. DRPs may reliably be identified by their very high specific activity which is readily detectable since they show high count rates using hand-held survey equipment such as a thin-window Geiger-Muller (G-M) probe.

A4.6. When present, DRPs may be further milled and then recombined with the original sample. Alternatively, the particles, or the entire sample may need to be processed using a different method capable of completely solubilizing the contaminants such that the radionuclides they contain are available for subsequent chemical separation.

A5. Safety

A5.1. General

A5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.

A5.1.2. Refer to the laboratory chemical hygiene plan for general chemical safety rules

A5.2. Radiological

A5.2.1. Refer to your radiation safety manual for direct on working with known or suspected radioactive materials.

A5.2.2. This method has the potential to generate airborne radioactive contamination. The process should be carefully evaluated to ensure that airborne contamination is maintained at acceptable levels. This should take into account the activity level, and physical and chemical form of contaminants possibly present, as well as other engineering and administrative controls available.

A5.2.3. Hot Particles (DRPs)

A5.2.3.1. Hot particles will usually 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). Filtration using a 0.45-µm filter or smaller may be needed following subsequent fusion to identify the presence of smaller DRPs.

A5.2.3.2. Care should be taken to provide suitable containment for filter media used in the pretreatment of samples that may have DRPs, because the particles become highly statically charged as they dry out and will “jump” to other surfaces potentially creating contamination-control issues.

A5.3. Method-Specific Non-Radiological Hazards

A5.3.1. This method employs a mechanical shaker and should be evaluated for personnel hazards associated with the high kinetic energy associated with the milling process.

A5.3.2. This method employs a mechanical shaker and involves vigorous agitation of steel or ceramic balls inside steel cans. The process should be evaluated to determine whether hearing protection is needed to protect the hearing of personnel present in the area in which the apparatus is operated.

A6. Equipment and supplies

A6.1. Balance, top-loading, range to accommodate sample size encountered, readability to ±1%.

A6.2. Drying oven, at 110±10 ºC.

A6.3. Steel paint cans and lids (pint, quart, 2-quart, 1-gallon, as needed).

A6.4. Steel or ceramic grinding balls or rods for ball milling, ~15-mm diameter. The size and number of grinding media used should be optimized to suit the types of sand or soil, the size of the can, and the volume of soil processed.

A6.5. Wire cloth – nominal 48 mesh size (~300 µm).

A6.6. Sieves, U.S. Series No. 50 (300-µm or 48 mesh) and U.S. Series No. 100 (150-µm or 100 mesh).

A6.7. Red Devil 5400 mechanical paint shaker, or equivalent mechanical.

A6.8. Disposable scoop, scraper, tongue depressor or equivalent.

A7. Reagents and Standards

No reagents needed.

A8. Sample Collection, Preservation and Storage

A8.1. Samples should be collected in appropriately sized plastic, metal or glass containers.

A8.2. No sample preservation is required. If samples are to be held for an extended period of time, refrigeration may help minimize bacterial growth in the sample.

A8.3. Default sample collection protocols generally provide solid sample volumes equivalent to approximately 500 mL of sample. Such samples will require two splits to obtain a ~100 mL sample.

A9. Quality Control

A9.1. Batch quality control results shall be evaluated and meet applicable Analytical Project 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.

A9.2. Quality control samples should be initiated as early in the process as possible. Since the risk of cross-contamination using this process is relatively low, initiating blanks and laboratory control samples at the start of the chemical separation process is acceptable. If sufficient sample is available, a duplicate sample should be prepared from the two discarded quarters of the final split of the coning and quartering procedure.

A10. Procedure

NOTE: This method ensures that only disposable equipment comes in contact with sample materials to greatly minimize the risk sample cross-contamination and concerns about adequate cleaning of equipment.

A10.1. Estimate the total volume of sample, as received.

NOTES: If the sample is dry, the risk of resuspension and inhalation of the solids may be determined to be unacceptable. In such cases, the entire sample may be processed in a larger can. The drying and milling time will be increased, and more grinding media will be required to obtain a satisfactory result

The next step uses absorbent paper in the reverse fashion for the normal use of this type of paper; it allows for a smooth division of the sample and control of contamination.

A10.1.1. Spread a large piece of plastic backed absorbent paper, plastic side *up* in a hood.

A10.1.2. If the sample volume is less than ~450 mL, there is no benefit to coning and quartering.[4]

A10.1.2.1. Carefully pour the sample onto the paper.

A10.1.2.2. Remove extraneous material, such as vegetation, biota, or rocks or debris unless the project requires that such material be processed as part of the sample. Continue with Step A10.1.6.

A10.1.2.3. If the sample volume is greater than ~450 mL, carefully pour the entire sample into a cone onto the paper.

Remove extraneous material, such as vegetation, biota, or rocks or debris unless the project requires that such material be processed as part of the sample.

A10.1.3. If levels of gross activity in the sample permit, the sample is split at least twice using the coning and quartering steps that follow.

NOTE: Unused quarters are considered representative of the original sample and may be reserved for additional testing. The process should be carried out expediently to minimize loss of volatile components in the sample, especially volatile components or percent solids are to be determined.

A10.1.4. Spread the material into a flat circular cake of soil using a tongue depressor or other suitable disposable implement. Divide the cake

[4] See IUPAC Gold Book, *Coning and Quartering in Analytical Chemistry*, available at: goldbook.iupac.org/C01265.html

radially and return two opposing quarters to the original sample container.

A10.1.5. Reshape the remaining two quarters into a smaller cone, and repeat Step A10.1.3 until the total volume of the remaining material is approximately 100-150 mL.

NOTE: Tare the can and lid together. Do not apply an adhesive label rather label the can with permanent marker since the can will be placed in a drying oven. The lid should be labeled separately since it will be removed from the can during drying

A10.1.6. Transfer the coned and quartered sample to a tared and labeled 1-pint paint can. If the total volume was less than ~450 mL, transfer the entire sample to a tared and labeled 1-quart paint can.

NOTE: Constant mass may be determined by removing the container from the oven and weighing repeatedly until the mass remains constant with within 1% of the starting mass of the sample. This may also be achieved operationally by observing the time needed to ensure that 99% of all samples will obtain constant mass.

A10.2. Place the can (without lid) in an oven at 110 ± 10 ºC and dry the soil to constant mass.

A10.3. Weigh the combined mass of the can, sample, and lid. If the percent solids are required see Step A12.1 calculations.

A10.4. Add five 1.5-cm stainless-steel or ceramic balls or rods to the can. Replace the lid and seal well.

A10.5. Shake the can and contents for 5–15 minutes, or longer, as needed to produce a finely-milled, well-homogenized, sample.

NOTE: Although the precise particle size of the milled sample is not critical, complete pulverization and fine particle size facilitates representative sub-sampling and subsequent fusion or digestion processes. A qualitative standard can be prepared by passing quartz sand or other milled material through a 50-mesh and then a 100-mesh screen. The portion of the sample retained in the 100 mesh screen can be used as a qualitative visual standard to determine if samples have been adequately pulverized.

A10.6. Visually compare the resulting milled sample to a qualitative 50–100 mesh pulverized sample (~150–300-µm or 50–100 mesh using the Tyler screen scale). The process is complete once 95% of the sample (or greater) is as fine, or finer, than the qualitative standard. If, by visual estimation, more than ~5% of total volume of the particles in the sample appear to be larger than the particle size in the standard, return the sample to the shaker and continue milling until the process is complete.

A10.7. Following milling, a small fraction of residual larger particles may remain in the sample.

A10.7.1. If the sample was collected close to the epicenter of an RDD or IND explosion, it may also contain particles of contaminant referred to as “discrete radioactive particles” or DRPs. In such a case, the larger

particles should be isolated by passing through a disposable 48 mesh screen and checked for radioactivity. DRPs are readily identified by their very high specific activity which is detectable using hand-held survey equipment such as a thin-window G-M probe held within an inch of the particles.

A10.7.1.1. If radioactivity is clearly detected, the sieved material is returned to the can and ball milled until the desired mesh is obtained. In some cases, these materials may be resistant to further pulverization and may need to be processed according to a method specially designed to address highly intractable solids.

A10.7.1.2. If the presence of DRPs is of no concern, the larger particles need not be included in subsequent subsamples taken for analysis. It may be possible to easily avoid including them during aliquanting with a disposable scoop. If not, however, they should be removed by sieving through a nominal 50 mesh screen (disposable) prior to further subsampling for subsequent analyses.

A10.8. Sample fines may be stored in, and aliquanted directly from, the container used for drying and pulverization.

A11. Calibration and Standardization

Balances used shall be calibrated using National Institute of Standards and Technology (NIST)-traceable weight according to the process defined by the laboratory's quality manual.

A12. Data Analysis and Calculations

A12.1. The percent solids (dry-to-as-received mass ratio) for each sample is calculated from data obtained during the preparation of the sample as follows:

$$\%\,\text{Solids} = \frac{M_{dry} - M_{tare}}{M_{as\,rec} - M_{tare}} \times 100$$

Where:

M_{dry} = mass of dry sample + labeled can + lid (g)
M_{tare} = tare mass of labeled can + lid (g)
$M_{as\,rec,}$ = mass of sample as received + labeled can + lid (g)

A12.2. If requested, convert the equivalent mass of sample, as received, to dry mass as follows:

$$\text{Dry Sample Equivalent} = M_{total\text{-}as\,rec.} \times \frac{\%\,\text{Solids}}{100}$$

Where:
$M_{total\text{-}as\,rec.}$ = total mass of sample, as received (g)

A12.3. Results Reporting

The result for percent solids and the approximate total mass of sample as received should generally be reported for each result.

A13. Method Performance

A13.1. Results of method validation performance are to be archived and available for reporting purposes.

A13.2. Expected turnaround time is about 3 hours for an individual sample and about 4 hours per batch.

A14. Pollution Prevention.

Not applicable.

A15. Waste Management.

All radioactive and other regulated wastes shall be handled according to prevailing regulations.

A16. References

A16.1. A. D. McNaught and A. Wilkinson, Coning and Quartering in Analytical Chemistry, *IUPAC Compendium of Chemical Terminology, The Gold Book*, Second Edition, Blackwell Science, 1997 (online edition).

A16.2. ALS Environmental, Fort Collins, SOP 736.

A16.3. ASTM C 999-05, Standard Practice for Soil Sample Preparation for the Determination of Radionuclides, Volume 12.01, ASTM, 2005.

A17. Tables, Diagrams, and Flow Charts

A17.1. Homogenization