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Rapid Method for Sodium Carbonate Fusion of Soil and Soil-Related Matrices Prior to Strontium-90 Analyses for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

Office of Air and Radiation
Office of Radiation and Indoor Air
National Air and Radiation Environmental Laboratory
Montgomery, AL 36115

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

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RAPID METHOD FOR SODIUM CARBONATE FUSION OF SOIL AND SOIL RELATED MATRICES PRIOR TO STRONTIUM-90 ANALYSIS

1. Scope and Application

   1.1. The method is applicable to the fusion digestion of soil and soil related matrices (e.g., sediments, dry deposition samples, loam, etc.).

   1.2. This is a general method for soil samples, dry particulate deposition samples, and sediments collected following a radiological or nuclear incident.

   1.3. Alternative rapid methods exist for sodium carbonate fusion of americium, plutonium, or isotopic uranium (see Reference 16.2), and radium-226 (see Reference 16.3) in soil matrices. These fusion methods lead into analyses using the published rapid methods for radionuclides in water (see Reference 16.5).

   1.4. The dissolution by fusion of soils, or related matrices, by this method is expected to take approximately 2–3 hours per batch of 20 samples. This assumes the laboratory starts with a representative, finely ground, 1-g aliquant of dried sample.[1] An initial sample combustion at 600 °C is necessary for removal of any organic matter prior to fusion, unless it has been established that the amount of organic matter present will not interfere with the analytical separations.

   1.5. Soil samples must be dried and ground to at least 50–100 mesh size prior to fusion. A *Rapid Technique for Milling and Homogenizing Soil Samples* is included as Appendix A to this method.

   1.6. This method combines the sample preparation by fusion, strontium separation, and sample test source preparation in one method. The method differs from the previously published method for strontium in water, "Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Water for Environmental Restoration Following Homeland Security Events (see Reference 16.5)," due to unique separation issues that arose during method validation. However, Step 11.25 of this method merges into and proceeds with Step 11.11 of the water method.

   1.7. Application of this method by any laboratory should be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (see Reference 16.1), or the protocols published by a recognized standards organization for method validation.

      1.7.1. In the absence of project-specific guidance, measurement quality objectives (MQOs) for soil 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 Incident Response — Radionuclides in Soil*, (see Reference 16.4).

[1] The laboratory should have a separate method for achieving sub-sampling of the sample based on grinding, mixing and sizing the sample to achieve aliquant uniformity.

2. Summary of Method

2.1. The method is based on the complete fusion of a representative, finely ground 1-g aliquant of dried sample with no insoluble residue remaining after dissolution of the fused melt in acid.

2.2. For media composed of organic soil matrices, the sample is dry-ashed at 600 ^{o}C in an appropriate vessel prior to fusion.

3. Definitions, Abbreviations and Acronyms

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

3.2. *Multi-Agency Radiological Analytical Laboratory Protocol* (MARLAP) Manual (see Reference 16.5).

3.3. The use of the term soil throughout this method is not intended to be limiting or prescriptive, and the method described herein refers to all soil related materials such as sand, humic/fulvic soils, peat, loam, sediment, etc. In cases where the distinction is important, the specific issues related to a particular sample type will be discussed.

4. Interferences and Limitations

NOTE: Large amounts of extraneous debris (pebbles larger than ¼", non-soil related debris, plant roots, etc.) are not generally considered to be part of a soil matrix. When consistent with DQOs, these should be removed from the sample prior to drying. It is recommended, that this be verified with incident command before discarding any materials.

4.1. Soils with high silica content may require either additional fusing reagent and boric acid or a longer fusion melt during Step 11.11.

4.2. Soil and soil-related matrices contain a wide variety of elements in the ppm and higher concentration range. As much information regarding the elemental composition of the sample should be obtained as possible. For example some soils may have native concentrations of uranium, thorium, strontium or barium, all of which may have an effect on the chemical separations used following the fusion of the sample. It is recommended that elemental analysis of the digest for strontium prior to chemical separations be performed to determine native concentrations of strontium present in the sample.

4.3. Matrix blanks for these soil and soil-related matrices may not be practical to obtain. Efforts should be made to obtain independent, analyte-free materials that have similar composition as the samples to be analyzed. These will serve as process monitors for the fusion, and as potential monitors for cross contamination during batch processing.

4.4. Samples with elevated activity or samples that require multiple analyses from a single soil sample may need to be split after dissolution. In these cases the initial digestate and the split fractions should be carefully measured to ensure that the sample aliquant for analysis is accurately determined.

4.4.1. Tracer or carrier amounts (added for yield determination) may be increased where the split allows for the normal added amount to be present in the subsequent aliquant. For very high activity samples, the addition of the tracer or carrier may need to be postponed until following the split, in which case special care must be taken to ensure that the process is quantitative until isotopic exchange with the yield monitor is achieved. This deviation from the method should be thoroughly documented and reported in the case narrative.

4.5. The analytical results for this method are reported directly in units of pCi/g.

4.6. In the preparation of blank samples, LCSs and duplicates, care should be taken to create these QC samples as early in the process as possible, and to follow the same tracer/carrier additions, digestion process, and sample splitting used for the field samples. In the case of this method, QC samples should be initiated at the point samples are aliquanted into crucibles for the fusion.

4.7. Platinum crucibles are required to withstand the harsh conditions of the digestion and fusion processes used in this method.

4.7.1. The laboratory must develop effective processes for cleaning crucibles. The effectiveness of the cleaning process should be demonstrated through measures such as measurements of fusion blanks.

4.7.2. 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. See *Rapid Method for Sodium Hydroxide Fusion of Concrete Matrices prior to Am, Pu, Sr, Ra, and U Analyses* (see Reference 16.6) and *Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents* (see Reference 16.7).

5. Safety

5.1. General

5.1.1. Refer to your 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).

5.2.1.2. Soil media should be individually surveyed using a thickness of the solid sample that is appropriate for detection of the radionuclide decay particles.

5.2.2. The sample size initially dried and homogenized should be of adequate size to conduct all required measurements but not too large as to cause a potential for generating airborne contamination.

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

5.3. Procedure-Specific Non-Radiological Hazards:

5.3.1. This procedure employs molten salts generated at high temperatures (≈ 1,000 °C) in an open flame. The operator should exercise extreme care when using the burners and when handling the hot crucibles. Thermal protection gloves and a face shield are recommended when performing this part of the procedure. The entire fusion process should be carried out in a laboratory fume hood.

6. Equipment and Supplies

NOTE: For samples with elevated activity concentrations of these radionuclides, labware should be used only once due to potential for cross contamination unless the cleaning process is demonstrated to be effective in removing residual contamination. The laboratory quality manual should provide guidance for making these decisions.

6.1. Adjustable temperature laboratory hotplates.

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

6.3. Beakers, 250 mL capacity.

6.4. Crucibles, minimum capacity, 50 mL, platinum.

6.5. Dispensing pipette, 10 mL delivery volume. Alternately, a bottle-top dispenser, small volume graduated cylinder, or any other device for delivering nominal 10 mL volumes of reagent into a beaker or disposable cup.

6.6. Fisher blast burner or Meeker burner.

NOTE: Ordinary Bunsen burners will not achieve the high temperatures needed for fusion.

6.7. Ring stand with ceramic triangle (optional).

6.8. Drying oven.

6.9. Programmable muffle furnace capable of reaching at least 600 ^{o}C

6.10. Teflon spatula or glass rod.

6.11. Tongs for handling crucibles, platinum tipped.

6.12. Ten (10) mL transfer pipette.

6.13. Tweezers or forceps.

NOTE: See appendix for a method for ball-milling and homogenization of soils.

6.14. Sample size reduction equipment (ball mill, paint shaker, etc) and screens. The necessary equipment will be based on a laboratory's specific method for the process of producing a dry uniformly ground sample from which to procure an aliquant.

6.15. Filters, 0.45 micron, Environmental Express Flipmate filters or equivalent.

6.16. Plastic backed absorbent paper.

7. Reagents and Standards

NOTE: Unless otherwise indicated, all references to water should be understood to mean Type I Reagent water (ASTM D1193; see Reference 16.9).

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

7.1. Sodium Carbonate, Na_2CO_3, anhydrous. Note that anhydrous sodium carbonate is to be stored in a desiccator.

7.2. Potassium Carbonate, K_2CO_3, anhydrous. Note that anhydrous potassium carbonate is to be stored in a desiccator.

7.3. Boric Acid, H_3BO_3. Stored in a desiccator to eliminate any moisture uptake.

7.4. Nitric Acid (8 M), HNO_3. Carefully add 500 mL of concentrated nitric acid to about 500 mL of water.

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

7.6. Dry flux mix. Dry each reagent separately at 105 ^oC to remove moisture. Mix equal weights of sodium carbonate, potassium carbonate and boric acid and store in a desiccator.

7.7. Calcium carrier solution,100 mg/mL Ca: Dissolve 37.8 g of $CaCl_2 \cdot 2H_2O$ in 100 mL of water

7.8. Na_2CO_3 solution, 2 M: Dissolve 212 g of dry Na_2CO_3 in 200 mL of water and dilute to 1 liter

7.9. Na_2CO_3 solution, 0.05 M: Dissolve 5.3 g of Na_2CO_3 in 1 L of water

7.10. NaOH solution, 10 M: 40 g of NaOH in 100 mL of water

7.11. Phenolphthalein

7.12. Radioactive tracers/carriers (used as yield monitors) and spiking solutions. Refer to the strontium in water method (see Reference 16.5)

NOTE: In those samples where native constituents are present that could interfere with the determination of the chemical yield (e.g., strontium for ^{90}Sr analysis) it may be necessary to determine the concentration of these native constituents in advance of chemical separation (using a separate aliquant of fused material) and make appropriate adjustments to the yield calculations or amount of carrier added.

8. Sample Collection, Preservation, and Storage

Not Applicable.

9. Quality Control

9.1. Where the subsequent chemical separation technique requires the addition of carriers and radioactive tracers for chemical yield determinations, these are to be added prior to

beginning the fusion procedure (or prior to charring of organic matter when applicable), unless there is good technical justification for doing otherwise.

9.2. 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's Quality Manual and procedures shall be used to determine acceptable performance for this method.

9.2.1. An exception to this may need to be taken for samples of exceptionally high activity where human safety may be involved.

9.3. Quality Control samples are generally specified in the laboratory's Quality Manual or in a project's analytical protocol specifications. At the very minimum the following are suggested:

9.3.1. A laboratory control sample (LCS), which consists solely of the reagents used in this procedure and a known quantity of radionuclide spiking solution, 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.

9.3.2. One reagent blank shall be run with each batch of samples. The reagent blank should consist solely of the reagents used in this procedure (including tracer or carrier from the analytical method added prior to the fusion process).

9.3.3. A sample duplicate that is equal in size to the original aliquant should be analyzed with each batch of samples. This provides assurance that the laboratory's sample size reduction and sub-sampling processes are reproducible.

10. Calibration and Standardization.

10.1. Refer to the individual chemical separation and analysis methods for calibration and standardization protocols.

11. Procedure

11.1. In accordance with the DQOs and sample processing requirements stated in the project plan documents remove extraneous materials from the soil using clean forceps or tweezers.

11.2. Samples should be heated in an oven at 105 ^{o}C until dry (i.e., constant weight).

11.3. Homogenize the sample so that a representative finely ground sample aliquant can be removed.

11.4. Weigh 2-g aliquants into separate crucibles. Add 5.0 mg of strontium carrier being used to each of the sample aliquants in the batch.

11.5. For samples containing sufficient organic matter to cause concerns with the subsequent fusion process, the samples should be further heated in a muffle furnace with temperature programming (using temperature hold points to ensure sample ignition does not occur) up to 600 ^{o}C to ensure combustion of all organic matter.

NOTE: Combustion of the organic matter in the sample can usually be accomplished over the course of 1–2 hours for 1-g samples of soil where the material is spread into a thin layer (up to about 0.4 cm thick).

11.6. Add 30 mL of concentrated hydrofluoric acid and evaporate to dryness on a hotplate at medium to high heat (~300 °C). The evaporation should be complete in approximately 90 minutes.

11.7. Add 6 g of dry flux mix (Step 7.6).

11.8. Warm the crucible slowly over the low flame of a Meeker or Fisher blast burner. The initial heating may produce a vigorous reaction, which may last approximately 5 minutes. The crucible may be held over the flame with tongs or supported on a ring stand with a ceramic triangle.

11.9. After the initial reaction has subsided, increase the heat gradually over 5 minutes until the burner is at full flame.

11.10. Heat until the crucible glows bright red.

11.11. Continue heating over full flame for 5 minutes until no visible reaction is observed and the melt is completely liquid and homogeneous.

11.12. Remove the crucible from the flame and swirl the contents so that the melt solidifies on the sides of the crucible, approximately half-way up the sides. This will facilitate the rapid dissolution of the cooled melt.

11.13. The crucible should be allowed to cool to the point so that addition of 8 M HNO_3 will not create a violent reaction. Usually this is cool enough to touch.

11.14. When the crucible is moderately cool carefully add approximately 10 mL 8 M HNO_3 by using a clean transfer pipette to wash the solid fusion cake down the inside walls of the crucible. The reaction of the acid with the fused carbonate material may be vigorous and care must be taken to avoid frothing the sample over the top of the crucible. It may be necessary to place a lid on the crucible during the acid reaction to avoid sample cross-contamination.

11.15. If necessary, heat the crucible gently on a hotplate and occasionally swirl the sample to facilitate the dissolution of the fusion cake. Ensure that the entire fusion cake is dissolved and that no solid material remains on the sides of the crucible.

11.16. If necessary, add additional 8 M HNO_3 in small (≈1 mL) increments to facilitate the complete dissolution of the fusion cake.

11.17. Transfer the dissolved sample to an appropriately sized beaker, rinsing the crucible with 8 M HNO_3 to ensure a quantitative transfer of material.

11.18. Add 1 mL of 100 mg/mL calcium to the diluted, dissolved fusion cake

11.19. Add ~ 0.5 mL of 0.1% phenolphthalein indicator and adjust pH to > 8.3 by adding 10 M NaOH while stirring continuously. The sample will become pinkish-orange due to the indicator color change and the formation of hydroxide precipitate.

11.20. Add 30 mL of 2 M Na_2CO_3. Heat and stir for ~ 30 minutes.

11.21. Remove from heat and allow precipitate to settle for at least 30 minutes.

11.22. Decant supernatant and transfer precipitate to 50 mL centrifuge tube.

11.23. Rinse precipitate with 40 mL of 0.05 M Na_2CO_3. Re-suspend the precipitate in the 0.05 M Na_2CO_3 then centrifuge and decant.

11.24. Dissolve precipitate with 4 mL of concentrated HNO_3. Add water to bring volume to 8 mL. This is the column load solution (nitrate concentration is ~ 8 M). If more concentrated HNO_3 is needed to dissolve a larger precipitate add water to bring the volume to twice the volume of the added acid.

11.25. Perform strontium resin separation as described in "Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Water for Environmental Restoration Following Homeland Security Events" (see Reference 16.5) beginning at Step 11.11 (the load solution is the solution produced in Step 17 above).

NOTE: Step 11.19.3 of the rapid water method for strontium-90 (see Reference 16.5) describes evaporation of the strontium eluate on a hotplate or under a heat lamp. Evaporation of the eluate should be done on a hotplate set at ~ 300 °C (digital display) in order to determine gravimetric chemical yields accurately. Initial drying is done at ~ 180 °C to avoid spattering and then the temperature is increased to ~ 300 °C for about 15 minutes.

11.26. Continue following the rapid water method for strontium-90 (Reference 16.5) to prepare sample test source, count, and perform data analysis and calculations.

12. Data Analysis and Calculations

12.1. Equations for determination of final result, combined standard uncertainty and radiochemical yield (if required) are found in the corresponding chemical separation and analysis methods, with the exception that the sample size is calculated as described below, with the units being provided by the incident command, rather than liters of water.

12.2. In cases where samples have elevated activity, aliquants should be removed carefully, first measuring the mass or volume of the entire final digestate. The mass or volume of the aliquants removed must also be carefully measured to ensure that the sample aliquant size used for analysis is accurately determined. The creation of multiple aliquants of a sample should be thoroughly documented and reported in the case narrative.

For a single split the effective size of sample is calculated:

$$V_a = V_s \frac{D_a}{D_s} \qquad \text{Equation 1}$$

Where:

V_s = original sample size, in the units designated by the incident command (e.g., 1 g, etc.)

D_s = mass or volume of the entire final digestate, created in Step 11.13 of this procedure (e.g., 100 g, 50 mL, etc.).

D_a = mass or volume of the aliquant of digestate used for the individual analyses, as described in the various parts of Step 11.14-11.17 of this procedure (e.g., 25 g, 5.0 mL, etc.). Note that the values for D_a must be in the same units used in D_s.

V_a = sample aliquant size, used for analysis, in the units designated by the incident command (e.g., kg, g, etc.).

NOTE: For higher activity samples, additional dilution may be needed. In such cases, Equation 1 should be modified to reflect the number of splits and dilutions performed. It is also important to measure the masses or volumes, used for aliquanting or dilution, to enough significant figures so that their uncertainties have an insignificant impact on the final uncertainty budget.

12.2.1. In cases where the sample will not be split prior to analysis, the sample aliquant size is simply equal to the original sample size, in the same units requested by the incident commander.

13. Method Performance

13.1. Method validation results should be archived by the laboratory.

13.2. Expected turnaround time per sample.

13.2.1. For representative, finely ground, 1-g aliquant of dried sample where combustion to remove organi*cs is required*, combustion of the sample and the subsequent fusion should add approximately 5 hours per batch to the time specified in the individual chemical separation methods.

13.2.2. In some cases, it may not be necessary to perform combustion to remove organic matter. For representative, finely ground, 1-g aliquant of dried sample where combustion to remove organics *is not required*, the fusion should add approximately 2 hours per batch to the time specified in the individual chemical separation methods.

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

14. Pollution Prevention

With the exception of minute quantities of combustion products, 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

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

16.2. U.S. Environmental Protection Agency (EPA). 2012. *Rapid Method for Sodium Carbonate Fusion of Soil and Soil-Related Matrices Prior to Americium, Plutonium, and Uranium Analyses for Environmental Remediation Following Radiological*. Revision 0. Office of Air and Radiation, National Air and Radiation Environmental Laboratory. Available at: www.epa.gov/narel/incident_guides.html.

16.3. U.S. Environmental Protection Agency (EPA). 2012. *Rapid Method for Radium in Soil Incorporating the Fusion of Soil and Soil-Related Matrices with the Radioanalytical Counting Method for Environmental Remediation Following Radiological Incidents*. Revision 0. Office of Air and Radiation, National Air and Radiation Environmental Laboratory. Available at: www.epa.gov/narel/incident_guides.html.

16.4. U.S. Environmental Protection Agency (EPA). 2012. *Radiological Sample Analysis Guide for Incident Response — Radionuclides in Soil*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-12-006, September. Available at: www.epa.gov/narel/incident_guides.html.

16.5. MARLAP. 2004. *Multi-Agency Radiological Laboratory Analytical Protocols Manual*. Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421. July. Available at: www.epa.gov/radiation/marlap/.

16.6. U.S. Environmental Protection Agency (EPA). 2010. *"Radiostrontium (Sr-90) in Water: Rapid Method for High-Activity Samples."* Revision 0. In, *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, EPA 402-R-10-001, February. Office of Air and Radiation, National Air and Radiation Environmental Laboratory. Revision 0.1 of rapid methods issued October 2011. Available at: www.epa.gov/narel/incident_guides.html.

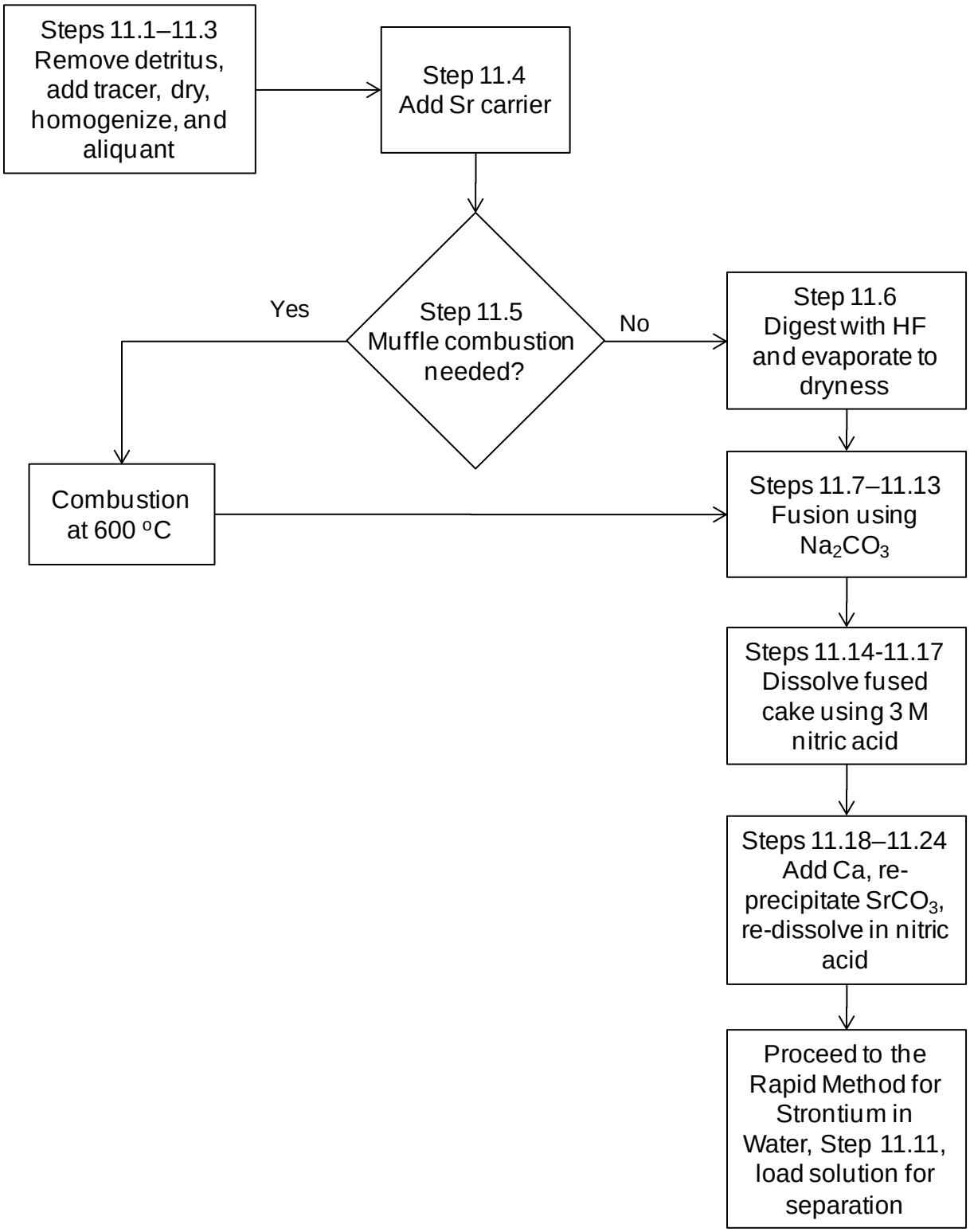
16.7. U.S. Environmental Protection Agency (EPA). 2012. *"Rapid Method for Sodium Hydroxide Fusion of Concrete Matrices Prior to Am, Pu, Sr, Ra, and U Analyses."* Revision 0. Office of Air and Radiation, National Air and Radiation Environmental Laboratory. Available at: www.epa.gov/narel/incident_guides.html.

16.8. U.S. Environmental Protection Agency (EPA). 2012. *"Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents."* Revision 0. Office of Air and Radiation, National Air and Radiation Environmental Laboratory. Available at: www.epa.gov/narel/incident_guides.html.

16.9. ASTM D1193, "Standard Specification for Reagent Water" ASTM Book of Standards 11.01, current version, ASTM International, West Conshohocken, PA.

17. Flow Chart

17.1. Flow Chart for Separation



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 16.8).

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 A16.3) 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.

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.[2]

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.

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

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 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:

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

Where:
$M_{\text{total-as rec.}}$ = 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