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Rapid Method for Sodium Carbonate Fusion of Glass-Fiber and Organic/Polymeric Composition Filters and Swipes Prior to Isotopic Uranium, Plutonium, Americium, Strontium, and Radium Analyses for Environmental Remediation Following Homeland Security Events

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RAPID METHOD FOR SODIUM CARBONATE FUSION OF GLASS-FIBER AND ORGANIC/POLYMERIC COMPOSITION FILTERS AND SWIPES PRIOR TO ISOTOPIC URANIUM, PLUTONIUM, AMERICIUM, STRONTIUM, AND RADIUM ANALYSES

1. Scope and Application

1.1. The method will be applicable to the fusion digestion of air particulate filters, removable contamination swipes and smears, and other similar sample matrices, prior to the chemical separation procedures described in the following procedures (see Reference 16.3[1]):

1.1.1. Rapid Radiochemical Method for Americium-241 in Water for Environmental Remediation Following Homeland Security Events.

1.1.2. Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Water for Environmental Remediation Following Homeland Security Events.

1.1.3. Rapid Radiochemical Method for Isotopic Uranium in Water for Environmental Remediation Following Homeland Security Events.

1.1.4. Rapid Radiochemical Method for Radium-226 in Water for Environmental Remediation Following Homeland Security Events

1.1.5. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Water for Environmental Remediation Following Homeland Security Events.

1.2. The method is specific for the fusion of glass-fiber and organic/polymeric composition filters, swipes, and smears, and the associated particulate deposition collected during air sampling events and removable contamination surveys following a radiological or nuclear incident. **An alternate method using inorganic acids is presented separately in the document*, Rapid Method for Acid Digestion of Glass-Fiber and Organic/ Polymeric Composition Filters and Swipes Prior to Isotopic Uranium, Plutonium, Americium, Strontium, and Radium Analyses.*** Generally, the sodium carbonate fusion technique should be chosen when refractory constituents are suspected in the sampled particulates or when the acidic digestion procedure is otherwise deemed to be ineffective. The Incident Commander (or designee, IC) should be involved in the selection of the appropriate digestion technique.

1.3. 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.

1.3.1. In the absence of project-specific guidance, measurement quality objectives (MQOs) for air particulate samples may be based on the Analytical Action Levels (AALs) and Required Method Uncertainties (u_{MR}) found in the

[1] Revision 0.1 for all five rapid methods in water were released in October 2011 and are available at www.epa.gov/erln/radiation.html and www.epa.gov/narel/incident_guides.html. These revisions addressed typographical errors, improved wording consistency with other methods, and clarified some examples. There were no substantive changes to any of the methods.

Radiological Sample Analysis Guide for Incidents of National Significance — Radionuclides in Air, Appendix I (see Reference 16.2).

1.3.2. In the absence of project-specific guidance, measurement quality objectives (MQOs) for swipe samples may be based on the Analytical Action Levels (AALs) derived from the Removable Contamination Values found in 10 CFR 835, Appendix D, with a default Required Method Uncertainty (u_{MR}) of not more than 13% at the AAL.

1.4. As this method is a gross pre-treatment technique, to be used prior to other separation and analysis methods, the user should refer to those individual methods and any project-specific requirements for the determination of applicable measurement quality objectives.

1.5. The dissolution of glass-fiber filters, or similar swipes, by this method is expected to take approximately one hour. This is based on a sample consisting of one 47-mm diameter filter, loaded with approximately 10 mg of particulate material. For organic filter or swipe matrices, an additional fifteen minutes is expected for charring the sample prior to fusion. For the dissolution of larger filters, or filters loaded with significantly more particulate material, additional time and proportionately larger volumes of reagents may be required.

2. Summary of Method

2.1. The method is based on the complete dissolution of both the filter or swipe material and the deposited particulates.

2.2. In the case of glass-fiber media, the media and the deposited particulates are destroyed by fusion with molten sodium carbonate in a nickel or platinum crucible. The resulting fusion cake is dissolved in hydrochloric acid in preparation for the ensuing chemical separation techniques.

2.3. For media composed of organic matrices, such as cellulose or polypropylene, the sample is charred in a crucible 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 contained in a tiny particle (μm range).

3.2. *Multi-Agency Radiological Analytical Laboratory Protocol* (MARLAP) Manual (see Reference 16.4).

3.3. The use of specific terminology, such as “filter,” “swipe,” “smear,” etc., throughout this method is not intended to be limiting or prescriptive, and the terms may be used interchangeably. In cases where the distinction is important, the specific issues related to a particular sample type will be discussed.

4. Interferences and Limitations

4.1. Samples that contain large amounts of particulate material may result in persistent undissolved particulates in the fusion melt during Step 11.7. These samples may require

additional time in the hot fusion process to cause a complete dissolution of the particulates.

4.2. In some cases particulate material may become dislodged during shipping or handling and may be found loose in the shipping envelope or container. For these samples, care should be taken to ensure a quantitative transfer of the sample to the digestion vessel. In some cases, it may become necessary to include the envelope for ashing and digestion, to ensure a quantitative transfer of material. Irregularities in sample processing such as these should be thoroughly documented and reported in the case narrative.

4.3. Most glass-fiber filters and swipes contain significant amounts of barium, which may ultimately interfere with the separation and analysis of radium, where that analyte is required. Initial characterization of the filter matrix to determine the content of elemental barium may help the laboratory make decisions about the optimum sample aliquant that the separation method will successfully process.

4.4. Some media, particularly glass-fiber filters and swipes, contain measurable quantities of naturally occurring radionuclides, such as uranium. The radionuclides native to the filter matrix should be measured and this activity should be considered in the assessment of the particulate results.

Matrix blanks, prepared with new, uncontaminated filters or swipes should be requested by the incident commander to assess the concentration of radionuclides native to the filter material. This may be done outside the scope of the initial background determination for the project, especially if the manufacture or lot number changes during the project.

4.4.1. In the preparation and analysis of matrix blanks the laboratory should verify with the incident commander that a sufficient number of blank samples are provided for analysis, and that those samples are of the same manufacture and lot (if practicable) as those used in the incident sampling.

4.4.2. In the absence of specific direction from the incident commander or in the project specifications, at least three uncontaminated blank samples should be processed at the beginning of each project and the results of these analyses should be properly identified and reported to the incident commander.

4.5. In the analysis of air filters, where the available sample is limited and irreplaceable, the laboratory is strongly encouraged to reserve an aliquant of the sample digestate to allow for unforeseen analysis requirements, and to guard against the loss of sample through failure of the method or laboratory error. It is acknowledged that the creation of a reserve aliquant may not be possible in all cases, particularly where very low detection limits are required and the entire sample must be used.

4.6. Samples for which the creation of a reserve aliquant is appropriate, as well as samples with elevated activity and samples that require multiple analyses from a single filter, may need to be split after dissolution. In these cases care should be taken to carefully measure the initial digestate and the split fractions to ensure that the sample aliquant for analysis is accurately determined. The creation of multiple aliquants of a sample should be thoroughly documented and reported in the case narrative.

4.7. Samples that require the creation of multiple aliquants, or samples that require analyses for which the addition of tracers and carriers necessary for other tests may be an interferent (e.g., gross alpha/beta analyses), may necessitate the addition of those tracers and carriers to the individual split fractions of the sample, after dissolution. This necessary addition of tracers or carriers after the sample dissolution should be thoroughly documented and reported in the case narrative.

4.8. The subsequent chemical separation methods for water samples, which are referenced in Section 1.1 above, specify a sample size (in liters), which is used in the associated calculation of activity, uncertainty, etc.

4.8.1. When this method is employed and the entire volume of digestate is processed in the subsequent chemical separation method, a sample size of "1 filter" is used in lieu of the water volume in all calculations, with the final result reported in units of activity per filter, rather than activity per liter.

4.8.2. In cases where the filter digestate is split prior to analysis the fractional aliquant of the filter is used for the sample size. The calculation of the appropriate sample size used for analysis is described in Section 12, below.

4.9. In some cases, the IC may provide air volumes or areal sample sizes to be assigned to each filter or swipe and may request that the results are reported in units of activity per volume of air or activity per area.

4.9.1. In cases where the entire filter sample is used for analysis, the volume of air, generally in liters or cubic meters, is used in place of the "1 filter" sample size described above.

4.9.2. In cases where the entire swipe is used for analysis, the areal sample size, generally in square centimeters or square meters, is used in place of the "1 filter" sample size described above.

4.9.3. When the sample is split prior to analysis, the sample size used for analysis must reflect the product of the total sample size times the fractional aliquant of the filter used for analysis.

4.10. Where volumetric or areal sample sizes are provided by the IC and used in the calculation of sample activity concentrations, the laboratory should note in the case narrative whether the uncertainties associated with these volumetric or areal measurements are included in the calculated combined standard uncertainty using this method.

4.11. As with any analytical method, QC requirements may be superseded by the IC and the project specifications. Nonetheless, this method attempts to address QC requirements and considerations, particularly those associated with the unique nature of air filters and swipes.

4.12. Duplicate analyses are not generally possible in air filters. Consequently, this procedure does not address the preparation of duplicate samples for analysis.

4.13. Similarly, matrix spikes are not generally possible, nor are they required in this procedure. At the direction of the incident commander, a specific sample may be requested for spiking and analysis. While the IC may use these results to evaluate

potential matrix effects in the sample, this is not considered a matrix spike by the laboratory, and the laboratory will not correct or control a batch of samples based on the results.

4.14. In the preparation of blank samples and LCSs, 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.

4.15. Although this method is applicable to a variety of subsequent chemical separation procedures, it is not appropriate where the analysis of volatile constituents such as iodine or polonium is required. The user of this method must ensure that analysis is not required for any radionuclide that may be volatile under these sample preparation conditions, prior to performing this procedure.

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. Hot particles (DRPs)

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

5.2.1.2. Filter media should be individually surveyed for the presence of these particles, and this information should accompany the samples during processing.

5.3. Procedure-Specific Non-Radiological Hazards:

This procedure employs molten salts generated under 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

6.1. Adjustable temperature laboratory hotplates.

6.2. Balance, top loading or analytical, readout display of ± 0.1 g or less.

6.3. Beakers, 250 mL capacity.

6.4. Crucibles, minimum 50 mL capacity, nickel or 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. pH paper.

6.8. Ring stand with ceramic triangle (optional).

6.9. Teflon spatula or glass rod.

6.10. Tongs for handling crucibles. Should be tipped with platinum if platinum crucibles are used.

6.11. Transfer pipette.

6.12. Tweezers or forceps.

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 16.5).

Note: All reagents are ACS grade or equivalent unless otherwise specified.

7.1. Sodium Carbonate, anhydrous. *Note that anhydrous sodium carbonate should be stored in a desiccator.*

7.2. Hydrochloric acid (6 M). Carefully add 500 mL of concentrated HCl to 400 mL of water and dilute to 1 L with water.

7.3. Radioactive tracers/carriers (used as yield monitors) and spiking solutions. Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Any tracers/carriers that are used to monitor radiochemical/ chemical yield should be added at the beginning of this procedure. This allows for the monitoring of chemical losses in the digestion process, as well as in the chemical separation method. Carriers used to prepare sample test sources but not used for chemical yield determination (e.g., neodymium added for uranium fluoride precipitation), should be added where indicated.

8. Sample Collection, Preservation, and Storage

There are no special collection, preservation, or storage considerations for this method.

9. Quality Control

9.1. In all cases, 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, 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 quality manual and procedures shall be used to determine acceptable performance for this method.

9.3. 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

9.4. One reagent blank shall be run with each batch of samples. The reagent blank should consist solely of the reagents used in this procedure. The reagent blank should not include a blank filter or swipe.

9.5. The purpose and use of matrix blanks is described in Section 4.4. At the discretion of the IC, when matrix blanks are analyzed with each batch and the native filter constituents are sufficiently well characterized so that incidents of laboratory contamination may be differentiated from native blank filter activity, the use of reagent blanks described in this section may be omitted.

9.6. This method does not define quality control parameters or acceptance criteria. Those quality control factors are defined in the individual separation methods that follow this technique.

10. Calibration and Standardization.

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

11. Procedure

11.1. For glass-fiber sampling media, proceed to Step 11.3.

11.2. For organic sampling media, the sample should first be charred in the crucible to minimize violent reaction during the fusion process.

11.2.1. Remove the filter from its container or sleeve, using clean forceps if necessary, and transfer the filter into a nickel or platinum crucible.

11.2.2. If any loose particulate material is present transfer that material to the crucible as well.

11.2.3. Add any necessary tracers or carriers, as prescribed in the subsequent chemical separation methods, adding the solution directly onto the sample material. The tracer solution should be absorbed into the sample material, if possible.

11.2.4. Gradually warm the uncovered crucible over the low flame of a Meeker or Fisher blast burner to dry the tracer and carrier solutions. The crucible may be held over the flame with tongs or supported on a ring stand with a ceramic triangle.

11.2.5. Increase the flame, heating the crucible gradually until the sample begins to char. Care should be taken to avoid open combustion (flaming) of the sample, which could result in the loss of analyte in the escaping ash and fume. Rather, the sample should be slowly charred. In addition, the crucible lid should be readily available and the crucible should be covered and removed from the heat if open combustion appears to be imminent.

11.2.6. Maintain this heat and continue until the sample appears to be completely charred.

11.2.7. Remove the crucible from the heat and allow it to cool for approximately two minutes.

11.2.8. Add 2 g anhydrous Na_2CO_3 to the crucible.

11.2.9. Thoroughly mix the sample with the added Na_2CO_3 using a Teflon spatula to avoid damage to the crucible.

11.2.10. Cover the mixed sample with another 2 g Na_2CO_3.

11.2.11. Proceed to Step 11.4.

11.3. For glass-fiber media, the sample can be fused whole, without pretreatment.

11.3.1. Add 2 g anhydrous Na_2CO_3 to the bottom of a nickel or platinum crucible.

11.3.2. Remove the filter from its container or sleeve, using forceps if necessary, and transfer the filter into the crucible.

11.3.3. If any loose particulate material is present transfer that material to the crucible as well.

11.3.4. Carefully and slowly add any necessary tracers or carriers, as prescribed in the subsequent chemical separation methods, adding the solution directly onto the sample material. The tracer solution should be absorbed into the sample material, if possible.

11.3.5. Cover the sample with another 2 g Na_2CO_3.

11.3.6. Proceed to Step 11.4.

11.4. 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. It is important to perform this step very carefully to avoid losses due to sample sputtering or boiling over the rim of the crucible.

11.5. After the initial reaction has subsided, increase the heat gradually over 5 minutes until the Meeker or Fisher blast burner is at full flame.

11.6. Continue heating until the crucible glows bright red.

11.7. Continue heating over full flame for 5 minutes. The sample should be fully fused, with a completely liquid and homogenous melt, and there should be no visible reaction occurring in the melt. If this is not the case, continue heating over full flame until the fusion process is complete.

11.8. 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.

11.9. Allow the crucible and contents to cool approximately five minutes. The crucible should be cool enough to handle and to allow for the addition of hydrochloric acid without violent reaction.

11.10. When the crucible is moderately cool carefully add approximately 10 mL of 6 M HCl by using a clean transfer pipette to wash the solid fusion cake down the inside walls

of the crucible. The reaction may be vigorous and care should be taken to avoid frothing the sample over the top of the crucible.

11.11. 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.

11.12. If necessary, add additional 6 M HCl in small (≈1 mL) increments to facilitate the complete dissolution of the fusion cake.

11.13. Transfer the dissolved sample to an appropriately sized beaker, rinsing the crucible with 6 M HCl to ensure a quantitative transfer of material.

11.14. Proceed to the chemical separation methods. In all cases omit the addition of tracers and carriers, as those reagents were added at the beginning of the fusion process:

Note: The counting time stated in Section 1.4 of the applicable rapid water method must be reevaluated for the required air filter or swipe MQOs as well as the expected chemical yield, aliquanting of the sample, and for air filters a nominal sample volume.

11.14.1. For actinide analyses, proceed directly to any of those methods listed in Sections 1.1.1, 1.1.2, or 1.1.3, proceeding directly to Step 11.1.4, *"Calcium phosphate coprecipitation option,"* and following the calcium phosphate coprecipitation to remove the excess sodium added during the fusion process.

11.14.2. For radium analysis, proceed directly to the method listed in Section 1.1.4, proceeding directly to Step 11.2, *"Water Sample Preparation and Pre-concentration of Radium on MnO_2 Resin."*

11.14.3. For strontium analysis, dilute the sample to 0.2 L with water and proceed directly to the method listed in Section 1.1.5, proceeding directly to Step 11.1, "*For each sample in the batch….*" Note that if the sample is already at a pH less than 2, no additional nitric acid will be added.

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 IC, rather than liters of water.

12.2. In cases where the creation of a reserve aliquant is appropriate, as well as samples with elevated activity and samples that require multiple analyses from a single filter, the sample should be split after dissolution. In these cases care should be taken to carefully measure the mass or volume of the entire final digestate, and the mass or volume of the subsequent split fractions to ensure that the sample aliquant for analysis is accurately determined. The creation of multiple aliquants of a sample should be thoroughly documented and reported in the case narrative.

12.3. The sample aliquant size for analysis is calculated:

$$V_a = V_s \times (D_a/D_s)$$

Where:

V_s = the original sample size, in the units designated by the IC (e.g., 100 cm^2, 68.5 m^3, etc.)

D_s = the 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 = the mass or volume of the aliquant of digestate used for the individual analyses, as described in the various parts of Step 11.14 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 = the sample aliquant size, used for analysis, in the units designated by the IC (e.g., 25 cm^2, 6.85 m^3, etc.).

12.4. 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 IC.

13. Method Performance

13.1. Method validation results are to be reported.

13.2. Expected turnaround time per sample;

13.2.1. For 47-mm diameter glass-fiber filters, the fusion should add approximately 45 minutes to the time specified in the individual chemical separation methods.

13.2.2. For 47-mm organic matrix filters, charring the sample and the subsequent fusion should add approximately one hour to the time specified in the individual chemical separation methods.

These expected turnaround times are for a single sample preparation, without regard to batching efficiencies, if any. This process is generally not amenable to simultaneous preparation of multiple samples. 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). 2009a. *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 and www.epa.gov/erln/radiation.html.

16.2. U.S. Environmental Protection Agency (EPA). 2009b. *Radiological Laboratory Sample Analysis Guide for Incidents of National Significance–Radionuclides in Air*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-007, June. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.3. U.S. Environmental Protection Agency (EPA). 2010. *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, Office of Air and Radiation, National Air and Radiation Environmental Laboratory. EPA 402-R-10-001, February. Revision 0.1 of rapid methods issued October 2011. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.4. 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/.

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

17. Flow Chart