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Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

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Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

1. Scope and Application

1.1. The method is applicable to the sodium hydroxide fusion of concrete and brick samples, prior to the chemical separation procedures described in the following procedures:

1.1.1. Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.1).

1.1.2. Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.2).

1.1.3. Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.3).

1.1.4. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.4).

1.1.5. Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.5).

1.2. This general method for concrete and brick building material applies to samples collected following a radiological or nuclear incident. The concrete and brick samples may be received as core samples, pieces of various sizes, dust or particles (wet or dry) from scabbling, or powder samples.

1.3. The fusion method is rapid and rigorous, effectively digesting refractory radionuclide particles that may be present.

1.4. Concrete or brick samples should be ground to at least 50–100 mesh size prior to fusion, if possible.

1.5. After a homogeneous, finely ground sample is obtained, the dissolution of concrete or brick matrices by this fusion method is expected to take approximately 1 hour per batch of 20 samples. This method assumes the laboratory starts with a representative, finely ground, 1–1.5-g aliquant of sample and employs simultaneous heating in multiple furnaces. The preconcentration steps to eliminate the alkaline fusion matrix and collect the radionuclides are expected to take approximately 1 hour.

1.6. As this method is a sample digestion and pretreatment 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 (MQOs).

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 (Reference 16.6), or the protocols published by a recognized standards organization for method validation.

1.7.1. In the absence of project-specific guidance, MQOs for concrete or brick samples may be based on the Analytical Action Levels (AALs), the Required Method Uncertainty (u_{MR}) and the Required Relative Method Uncertainty (φ_{MR}) found in the *Radiological Laboratory Sample Analysis Guide for Incident Response — Radionuclides in Soil* (Reference 16.7).

2. Summary of Method

2.1. The method is based on the rapid fusion of a representative, finely ground 1–1.5 g aliquant using rapid sodium hydroxide fusion at 600 °C.

2.2. Pu, U, and Am are separated from the alkaline matrix using an iron/titanium hydroxide precipitation (enhanced with calcium phosphate precipitation) followed by a lanthanum fluoride matrix removal step.

2.3. Sr is separated from the alkaline matrix using a carbonate precipitation, followed by a calcium fluoride precipitation to remove silicates.

2.4. Ra is separated from the alkaline matrix using a carbonate precipitation.

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 Protocols (MARLAP) Manual* (Reference 16.8).

3.3. The use of the term concrete or brick throughout this method is not intended to be limiting or prescriptive, and the method described herein refers to all concrete or masonry related materials. 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) are not generally considered to be part of a concrete or brick matrix. When consistent with data quality objectives (DQOs), materials should be removed from the sample prior to drying. It is recommended this step be verified with Incident Command before discarding any materials.

4.1. Concrete or brick samples with larger particle size may require a longer fusion time during Step 11.1.8.

4.2. As much information regarding the elemental composition of the sample should be obtained as possible. For example some concrete or brick may have native concentrations of uranium, radium, thorium, strontium or barium, all of which may have

an effect on the chemical separations used following the fusion of the sample. In some cases (e.g., radium or strontium analysis), elemental analysis of the digest prior to chemical separations may be necessary to determine native concentrations of carrier elements present in the sample.

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) or with the creation of a sample test source (e.g., Ba for ^{226}Ra analysis by alpha spectrometry), 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.

4.3. Matrix blanks for these 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 blanks will serve as process monitors for the fusion, and as potential monitors for cross contamination during batch processing.

4.4. Uncontaminated concrete or brick material may be acceptable blank material for Pu, Am, and Sr analyses, but these materials will typically contain background levels of U and Ra isotopes.

4.4.1. If analyte-free blank material is not available and an empty crucible is used to generate a reagent blank sample, it is recommended that 100–125 milligram (mg) calcium (Ca) per gram of samples be added as calcium nitrate to the empty crucible as blank simulant. This step facilitates Sr/Ra carbonate precipitations from the alkaline fusion matrix.

4.4.2. Tracer yields may be slightly lower for reagent blank matrices, since the concrete and brick matrix components typically enhance recoveries across the precipitation steps.

4.5. Samples with elevated activity or samples that require multiple analyses from a single concrete or brick 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.

4.5.1. 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.

4.5.2. When this method is employed and the entire volume of fused sample is processed in the subsequent chemical separation method, the original sample size and units are used in all calculations, with the final results reported in the units requested by the project manager.

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

4.6. In the preparation of blank samples, laboratory control samples (LCSs) and duplicates, care should be taken to create these quality control (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. 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.

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

4.8.1. It is very important that the laboratory have a process for cleaning and residual contamination assessment of the reused zirconium crucibles. The crucibles should be cleaned very well using soap and water, followed by warm nitric acid and then water. Blank measurements should be monitored to ensure effective cleaning.

4.8.2. 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.

4.9. Centrifuge speed of 3500 rpm is prescribed but lower rpm speeds (>2500 rpm) may be used if 3500 rpm is not available.

4.10. Titanium chloride ($TiCl_3$) reductant is used during the co-precipitation step with iron hydroxide for actinides to ensure tracer equilibrium and reduce uranium from U^{+6} to U^{+4} to enhance chemical yields. This method adds 5 mL of 10 percent by mass (wt%) $TiCl_3$ along with the Fe. Adding up to 10 mL of 10 wt% $TiCl_3$ may increase uranium chemical yields, but this will need to be validated by the laboratory.

4.11. Trace levels of ^{226}Ra may be present in Na_2CO_3 used in the ^{226}Ra pre-concentration step used in this method. Adding less 2M Na_2CO_3 (<25 mL used in this method) may reduce ^{226}Ra reagent blank levels, while still effectively pre-concentrating ^{226}Ra from the fusion matrix. This will need to be validated by the laboratory.

4.12. La is used to pre-concentrate actinides along with LaF_3 in this method to eliminate matrix interferences, including silica, which can cause column flow problems. La follows Am in subsequent column separations and must be removed. Less La (2 mg) was used for brick samples to minimize the chance of La interference on alpha spectrometry peaks. While this may also be effective for concrete samples, this will have to be validated by the laboratory.

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 your laboratory's 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 millimeter (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. Concrete/brick media should be individually surveyed using a thickness of the solid sample that is appropriate for detection of the radionuclide decay particles.

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. The sodium hydroxide fusion is performed in a furnace at 600 °C. The operator should exercise extreme care when using the furnace and when handling the hot crucibles. Long tongs are recommended. Thermal protection gloves are also recommended when performing this part of the procedure. The fusion furnace should be used in a ventilated area (hood, trunk exhaust, etc.).

5.3.2. 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. Adjustable temperature laboratory hotplates.

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

6.3. Beakers, 100 mL, 150 mL capacity.

6.4. Centrifuge able to accommodate 225 mL tubes.

6.5. Centrifuge tubes, 50 mL and 225 mL capacity.

6.6. Crucibles, 250 mL, zirconium, with lids.

6.7. 100 µL, 200 µL, 500 µL, and 1 mL pipets or equivalent and appropriate plastic tips.

6.8. 1-10 mL electronic/manual pipet(s).

6.9. Drill with masonry bit (¼-inch carbide bit recommended).

6.10. Hot water bath or dry bath equivalent.

6.11. Muffle furnace capable of reaching at least 600 °C.

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

6.13. Tweezers or forceps.

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 uniformly ground sample from which to procure an aliquant.

NOTE: See appendix for a method for ball-milling and homogenization of concrete or brick.

6.15. Vortex stirrer.

7. Reagents and Standards

NOTES:

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

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

7.1. Type I reagent water as defined in ASTM Standard D1193 (Reference 16.9).

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

7.2.1. Aluminum nitrate solution (2M): Add 750 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) to ~700 mL of water and dilute to 1 L with water. Low-levels of uranium are typically present in $Al(NO_3)_3$ solution.

NOTE: Aluminum nitrate reagent typically contains trace levels of uranium concentration. To achieve the lowest possible blanks for isotopic uranium measurements, some labs have removed the trace uranium by passing ~250 mL of the 2M aluminum nitrate reagent through ~7 mL TRU® Resin or UTEVA® Resin (Eichrom Technologies), but this will have to be tested and validated by the laboratory.

7.3. Ammonium hydrogen phosphate (3.2M): Dissolve 106 g of $(NH_4)_2HPO_4$ in 200 mL of water, heat on low to medium heat on a hot plate to dissolve and dilute to 250 mL with water.

7.4. Boric Acid, H_3BO_3.

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

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

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

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

7.6.2. Hydrochloric acid (1.5M): Add 125 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.

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

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

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

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

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

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

7.10.4. Nitric acid (8M): Add 506 mL of concentrated HNO_3 to 400 mL of water and dilute to 1 L with water.

7.11. Sodium carbonate (2M): Dissolve 212 g anhydrous Na_2CO_3 in 800 mL of water, then dilute to 1 L with water.

7.12. Sodium hydroxide pellets.

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

7.14. Radioactive tracers/carriers (used as yield monitors) and spiking solutions. A radiotracer is a radioactive isotope of the analyte that is added to the sample to measure any losses of the analyte. A carrier is a stable isotope form of a radionuclide (usually the analyte) added to increase the total amount of that element so that a measureable mass of the element is present. A carrier can be used to determine the yield of the chemical process and/or to carry the analyte or radiotracer through the chemical process. Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Tracers/carriers that are used to monitor radiochemical/chemical yield should be added at the beginning of this procedure. This timing allows for monitoring and correction of chemical losses in the combined 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., cerium added for microprecipitation of plutonium or uranium), should be added where indicated.

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, unless there is good technical justification for doing otherwise.

9.2. Batch quality control results shall be evaluated and meet applicable analytical protocol specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality

control sample acceptance criteria defined in the laboratory's Quality Manual and procedures shall be used to determine acceptable performance for this method.

9.2.1. An exception to this approach 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 APS. 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 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 approach 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. Fusion

11.1.1. In accordance with the DQOs and sample processing requirements stated in the project plan documents, remove extraneous materials from the concrete or brick sample using a clean forceps or tweezers.

11.1.2. Weigh out a representative, finely ground 1-g aliquant of sample into a crucible (1.5-g aliquants for ^{90}Sr analysis).

NOTES:

It is anticipated that concrete or brick powder sample material will be dry enough to aliquant without a preliminary drying step. In the event samples are received that contain moisture, the samples may be dried in a drying oven at 105 °C prior to taking the aliquant.

For Sr and Ra analyses, a reagent blank of 100–150 mg calcium per gram of sample (prepared by evaporating 2.5 mL of 1.25M calcium nitrate, $Ca(NO_3)_2$, for radium and 3 mL of 1.25M $Ca(NO_3)_2$ for strontium) should be added to the crucible as a blank simulant to ensure the blank behaves like the concrete or brick samples during the precipitation steps.

11.1.3. Add the proper amount of tracer or carrier appropriate for the method being used and the number of aliquants needed.

11.1.4. Place crucibles on a hot plate and heat to dryness on medium heat.
NOTE: Heat on medium heat to dry quickly but not so high as to cause splattering.

11.1.5. Remove crucibles from hot plate and allow to cool.

11.1.6. Add the following amounts of sodium hydroxide based on the aliquant size/analysis required.

1 g for Pu, Am, U:	15 g NaOH
1.5 g for Sr:	15 g NaOH
1 g for Ra:	10 g NaOH

11.1.7. Place the crucibles with lids in the 600 °C furnace using tongs.

11.1.8. Fuse samples in the crucibles for ~15 minutes.

NOTE: Longer times may be needed for larger particles.

11.1.9. Remove hot crucibles from furnace very carefully using tongs, and transfer to hood.

11.1.10. 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.

11.1.11. If necessary for dissolution, add more water, and warm as needed on a hotplate.

11.1.12. Proceed to Section 11.2 for the actinide preconcentration procedure, 11.4 for Sr preconcentration, or 11.5 for Ra preconcentration steps.

11.2. Preconcentration of Actinides (Pu, U, or Am) from Hydroxide Matrix

11.2.1. Pipet 2.5 mL of iron carrier (50 mg/mL) into a labeled 225-mL centrifuge tube for each sample.

11.2.2. Add La carrier to each 225-mL tube as follows:

Concrete: 5 mL 1 mg La/mL for Pu, Am, U

Brick: 5 mL 1 mg La/mL for Pu, and U; 2 mL 1 mg La/mL for Am

11.2.3. Transfer each fused sample to a 225 mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.2.4. Dilute each sample to approximately 180 mL with water.

11.2.5. Cool the 225 mL centrifuge tubes in an ice bath to approximately room temperature as needed.

11.2.6. Pipet 1.25M $Ca(NO_3)_2$ and 3.2M $(NH_4)_2HPO_4$ into each tube as follows:

Pu, Am: 2 mL 1.25M $Ca(NO_3)_2$ and 3 mL 3.2M $(NH_4)_2HPO_4$

U: 3 mL 1.25M $Ca(NO_3)_2$ and 5 mL 3.2M $(NH_4)_2HPO_4$

11.2.7. Cap tubes and mix well.

11.2.8. Pipet 5 mL of 10 wt% $TiCl_3$ into each tube, and cap and mix immediately.

11.2.9. Cool 225 mL centrifuge tubes in an ice bath for ~ 10 minutes.

11.2.10. Centrifuge tubes for 6 minutes at 3500 rpm.

11.2.11. Pour off the supernate, and discard to waste.

11.2.12. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~60 mL.

11.2.13. Cap and shake each tube to dissolve solids as well as possible.

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

11.2.14. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.2.15. Pipet 1 mL of 1.0 mg La/mL into each tube.

11.2.16. Pipet 3 mL of 10 wt% $TiCl_3$ into each tube. Cap and mix.

11.2.17. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.2.18. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.2.19. Centrifuge for ~10 minutes at 3000 rpm or more or as needed.

11.2.20. Pour off supernate, and discard to waste.

11.2.21. Pipet 5 mL of 3M HNO_3 - 0.25M boric acid into each tube.

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

11.2.23. Pipet 6 mL of 7M HNO_3 and 7 mL of 2M aluminum nitrate into each tube, cap and mix (shake or use a vortex stirrer), and transfer rinse to 50-mL centrifuge tube.

11.2.24. Pipet 3 ml of 3M HNO_3 directly into the 50 mL centrifuge tube.

11.2.25. Warm each 50 mL centrifuge tube in a hot water bath for a few minutes, swirling to dissolve.

11.2.26. Remove each 50 mL centrifuge tube from the water bath and allow to cool to room temperature

11.2.27. Centrifuge the 50 ml tubes at 3500 rpm for 5 minutes to remove any traces of solids (may not be visible prior to centrifuging), and transfer solutions to labeled beakers or tubes for further processing. Discard any solids.

11.2.28. Proceed directly to any of those methods listed in Sections 1.1.1, 1.1.2, or 1.1.5 (for Pu, U, or Am).

11.3. Preconcentration of ^{90}Sr from Hydroxide Matrix (Concrete)

NOTE: The preconcentration steps for ^{90}Sr in this section can also be applied to brick samples, but this will have to be validated by the laboratory. See Section 11.4 for steps validated for ^{90}Sr in brick samples.

11.3.1. Transfer each fused sample to a 225-mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.3.2. Dilute to approximately 150 mL with water.

11.3.3. Add 15-mL concentrated HCl to each tube.

11.3.4. Cap and mix solution in each tube.

11.3.5. Pipet 1-mL 1.25M $Ca(NO_3)_2$ into each tube.

11.3.6. Add 2-mL 50-mg/mL iron carrier into each tube.

11.3.7. Add 25-mL 2M Na_2CO_3 to each tube.

11.3.8. Cap tubes and mix well.

11.3.9. Cool 225-mL centrifuge tubes in an ice bath for ~10 minutes.

11.3.10. Centrifuge tubes for 5 minutes at 3500 rpm.

11.3.11. Pour off the supernate, and discard to waste.

11.3.12. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~50 mL.

11.3.13. Cap and shake each tube to dissolve solids as well as possible.

11.3.14. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.3.15. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.3.16. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.3.17. Centrifuge for ~6 minutes at 3500 rpm.

11.3.18. Pour off supernate, and discard to waste.

11.3.19. Pipet 5 mL of concentrated HNO_3 and 5 mL of 3M HNO_3 - 0.25M boric acid into each 225 mL tube to dissolve precipitate.

11.3.20. Cap and mix well. Transfer contents of the tube into a labeled 50-mL centrifuge tube.

11.3.21. Pipet 5 mL of 3M HNO_3 and 5 mL of 2M aluminum nitrate into each tube, cap tube and mix.

11.3.22. Transfer rinse solutions to 50-mL centrifuge tubes and mix well (shake or use vortex stirrer).

11.3.23. Centrifuge the 50 mL tubes at 3500 rpm for 5 minutes to remove any traces of solids.

11.3.24. Transfer solutions to labeled beakers or new 50 mL tubes for further processing.

11.3.25. If solids remain, add 5 mL 3M HNO_3 to each tube, cap, and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.

11.3.26. Set aside for ^{90}Sr analysis using *Rapid Radiochemical Method for Total Radiostrontium (Sr-90) In Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.4).

11.4. Preconcentration of ^{90}Sr from Hydroxide Matrix (Brick)

NOTE: The preconcentration steps for ^{90}Sr in this section, using calcium phosphate instead of calcium carbonate, can also be applied to concrete samples but this will have to be validated by the laboratory. See Section 11.3 for steps validated for ^{90}Sr in concrete samples.

11.4.1. Transfer each fused sample to a 225-mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.4.2. Dilute to approximately 150 mL with water.

11.4.3. Pipet 2 mL 1.25M $Ca(NO_3)_2$ into each tube.

11.4.4. Add 1 mL 50-mg/mL iron carrier into each tube.

11.4.5. Add 5 mL 3.2M $(NH_4)_2HPO_4$ to each tube.

11.4.6. Cap tubes and mix well.

11.4.7. Centrifuge tubes for 5 minutes at 3500 rpm.

11.4.8. Pour off the supernate and discard to waste.

11.4.9. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~60 mL.

11.4.10. Cap and shake each tube to dissolve solids as well as possible.

11.4.11. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.4.12. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.4.13. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.4.14. Centrifuge for ~6 minutes at 3500 rpm.

11.4.15. Pour off supernate and discard to waste.

11.4.16. Pipet 5 mL of concentrated HNO_3 and 5 mL of 3M HNO_3 – 0.25M boric acid into each 225 mL tube to dissolve precipitate.

11.4.17. Cap and mix well. Transfer contents of the tube into a labeled 50-mL centrifuge tube.

11.4.18. Pipet 5 mL of 3M HNO_3 and 5 mL of 2M aluminum nitrate into each tube, cap tube and mix.

11.4.19. Transfer rinse solutions to 50 mL centrifuge tubes and mix well (shake or use vortex stirrer).

11.4.20. Centrifuge the 50 mL tubes at 3500 rpm for 5 minutes to remove any traces of solids.

11.4.21. Transfer solutions to labeled beakers or new 50 mL tubes for further processing.

11.4.22. If solids remain, add 5 mL 3M HNO_3 to each tube, cap and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.

11.4.23. Set aside for ^{90}Sr analysis using *Rapid Radiochemical Method for Total Radiostrontium (Sr-90) In Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.4).

11.5. Preconcentration of ^{226}Ra from Hydroxide Matrix

11.5.1. Transfer each sample to a 225 mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.5.2. Dilute to approximately 150 mL with water.

11.5.3. Add 10 mL of concentrated HCl to each tube.

11.5.4. Cap and mix each tube well.

11.5.5. Pipet 0.5 mL of 1.25M $Ca(NO_3)_2$ into each tube.

11.5.6. Add 25 mL of 2M Na_2CO_3 to each tube.

11.5.7. Cap tubes and mix.

11.5.8. Cool 225-mL centrifuge tubes in an ice bath for ~ 5–10 minutes.

11.5.9. Centrifuge tubes for 6 minutes at 3500 rpm.

11.5.10. Pour off the supernate, and discard to waste.

11.5.11. Pipet 10 mL 1.5M HCl into each tube to dissolve precipitate. Cap and mix.

11.5.12. Transfer sample solution to a 50-mL centrifuge tube.

11.5.13. Pipet 10 mL 1.5M HCl into each 225-mL tube to rinse. Cap and rinse well.

11.5.14. Transfer rinse solution to 50 mL-tube and mix well.

NOTE: Typically the HCl added to dissolve the carbonate precipitate is sufficient to acidify the sample. If the precipitate was unusually large and milky suspended solids remain, indicating additional acid is needed, the pH can be checked to verify it is pH 1 or less. To acidify the pH <1, 1 or 2 mL of concentrated hydrochloric acid may be added to acidify the solution further and get it to clear. Undissolved solids may be more likely to occur with brick samples. Tubes may be warmed in a water bath to help dissolve samples.

11.5.15. If solids remain, add 5 mL 1.5M HCl to each tube, cap and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.

11.5.16. Set aside for ^{226}Ra analysis using *Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.3).

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 units being provided by the project manager.

12.2. In cases where samples have elevated activity, smaller initial sample aliquants may be taken from the original sample. Alternately, smaller aliquant volumes may be taken from the final sample volume containing the dissolved precipitate (digestate). Aliquants should be removed carefully and accurately from this final sample volume.

NOTE: Small aliquants taken from the final sample digestate for Sr and Ra analysis may be used in the respective analytical procedures as is. Smaller aliquants for actinide analysis should be diluted to a 15 mL total volume with 3M HNO_3 so that load solution acidity is maintained when valence adjustment reagents are added.

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

$$W_a = W_s \frac{D_a}{D_s} \quad (1)$$

Where:

- W_s = original sample size, in the units designated by the project manager (e.g., 1 g, etc.)
- D_s = mass or volume of the entire final digestate, (e.g., 20 mL, etc.).
- D_a = mass or volume of the aliquant of digestate used for the individual analyses, (e.g., 5.0 mL, etc.). Note that the values for D_a must be in the same units used in D_s.
- W_a = sample aliquant size, used for analysis, in the units designated by the project manager (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. 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 project manager.

13. Method Performance

13.1. Method validation results are to be reported.

13.2. The method performance data for the analysis of concrete and brick by this dissolution method may be found in the attached appendices.

13.3. Expected turnaround time per sample

13.3.1. For a representative, finely ground 1-g aliquant of sample, the fusion should add approximately 2 hours per batch to the time specified in the individual chemical separation methods.

13.3.2. The preconcentration steps should add approximately 2 to 2.5 hours per batch.

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

14. Pollution Prevention

This method inherently produces no significant pollutants. The sample and fusion reagents are retained in the final product and are carried into the ensuing chemical separation techniques, which marginally increases the salt content of the effluent waste. It is noted that if the sampled particulates include radionuclides which may be volatile under the fusion conditions, these constituents will be exhausted through the fume hood system.

15. Waste Management

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

16. References

Cited References

16.1. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-007. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.2. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Pu-238 and Pu-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-006. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.3. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-002. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.4. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-001. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.5. U.S. Environmental Protection Agency (EPA). 2014. Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents. Revision 0, EPA 402-R14-005. Office of Air and Radiation, Washington, DC. Available at: www.epa.gov/narel.

16.6. 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.

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

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

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

Other References

16.10. Maxwell, S., Culligan, B. and Noyes, G. 2010. Rapid method for actinides in emergency soil samples, *Radiochimica Acta*. 98(12): 793-800.

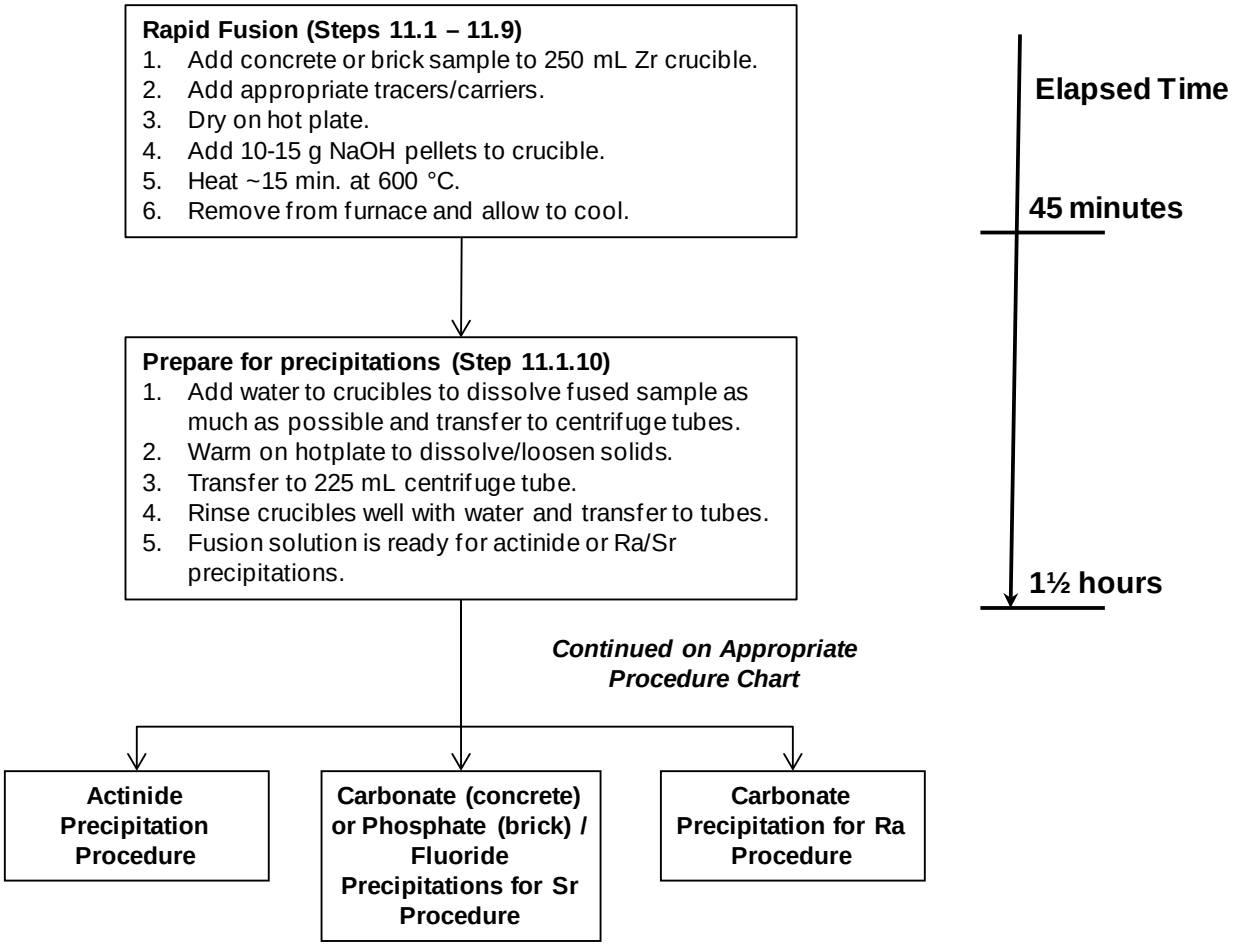
16.11. Maxwell, S., Culligan, B., Kelsey-Wall, A. and Shaw, P. 2011. "Rapid Radiochemical Method for Actinides in Emergency Concrete and Brick Samples," *Analytica Chimica Acta*. 701(1): 112-8.

16.12. 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. EPA 402-R-10-001, February. Revision 0.1 of rapid methods issued October 2011. Available at: www.epa.gov/narel/.

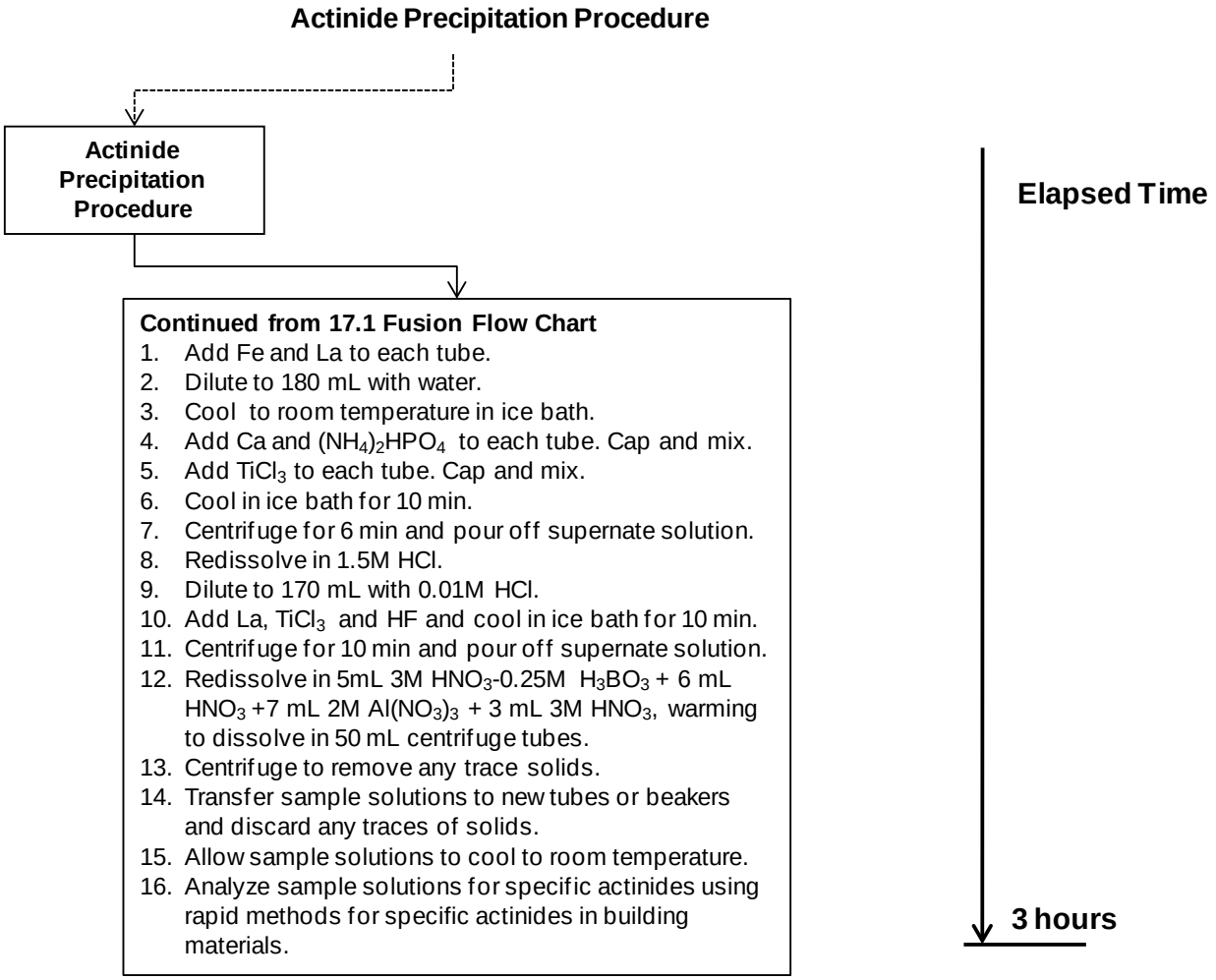
17. Tables, Diagrams, and Flow Charts

17.1. Fusion Flow Chart

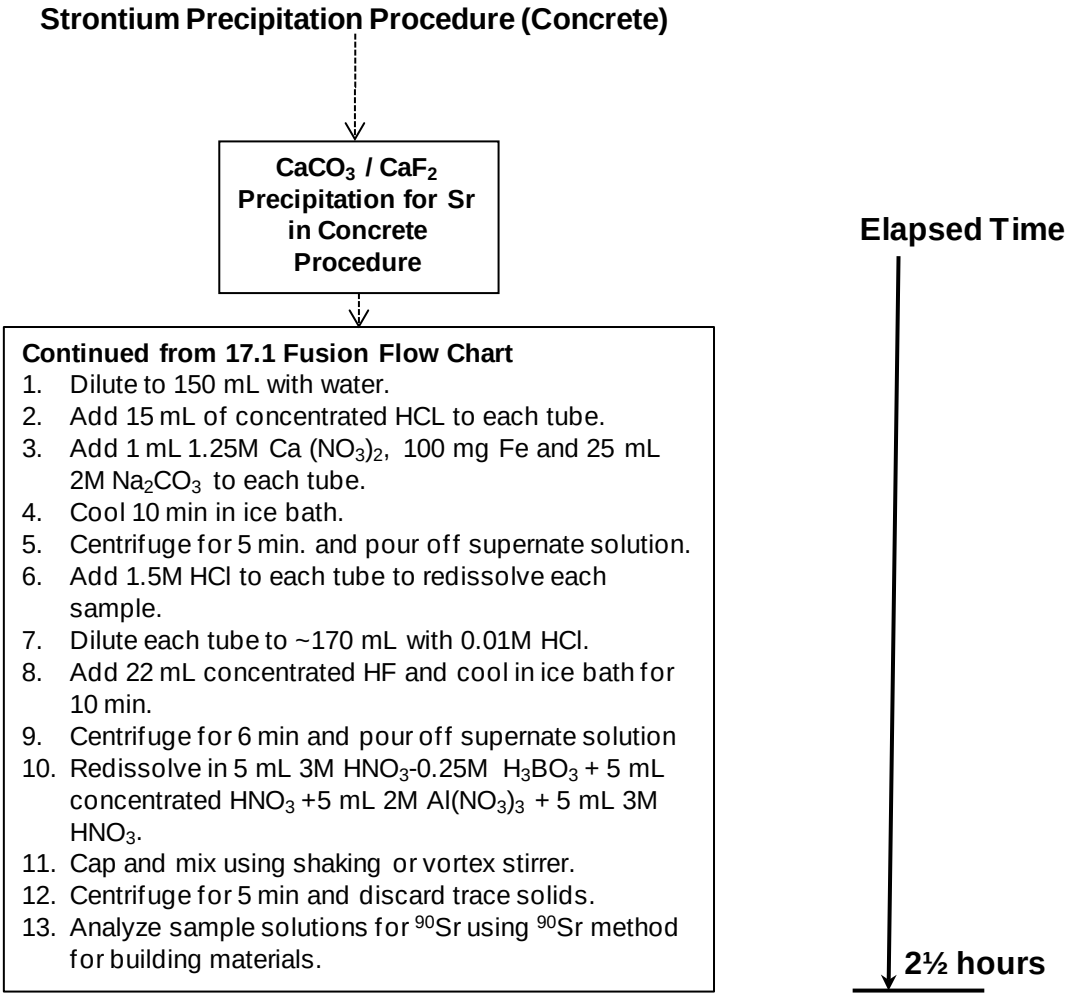
Timeline for Rapid Fusion and Preparation of Building Materials Samples for Precipitation and Analysis

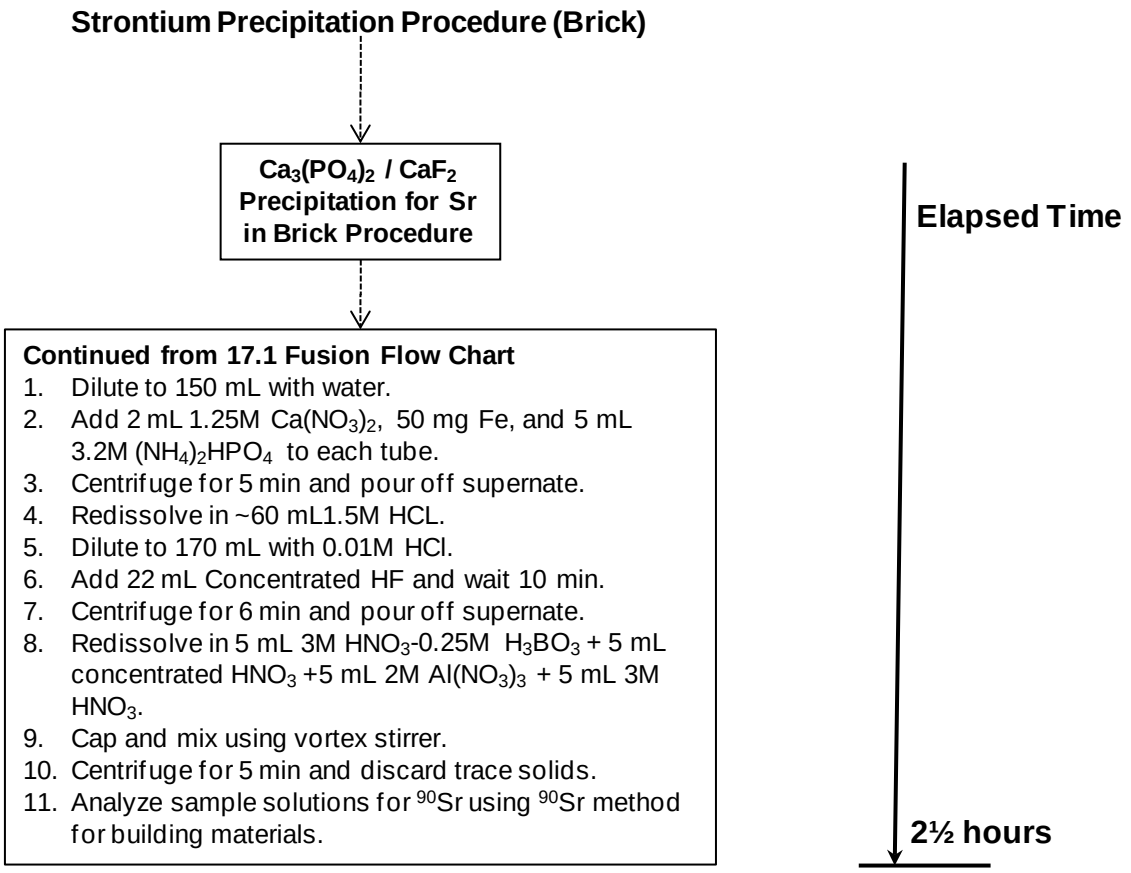


17.2. Actinide Precipitation Flow Chart

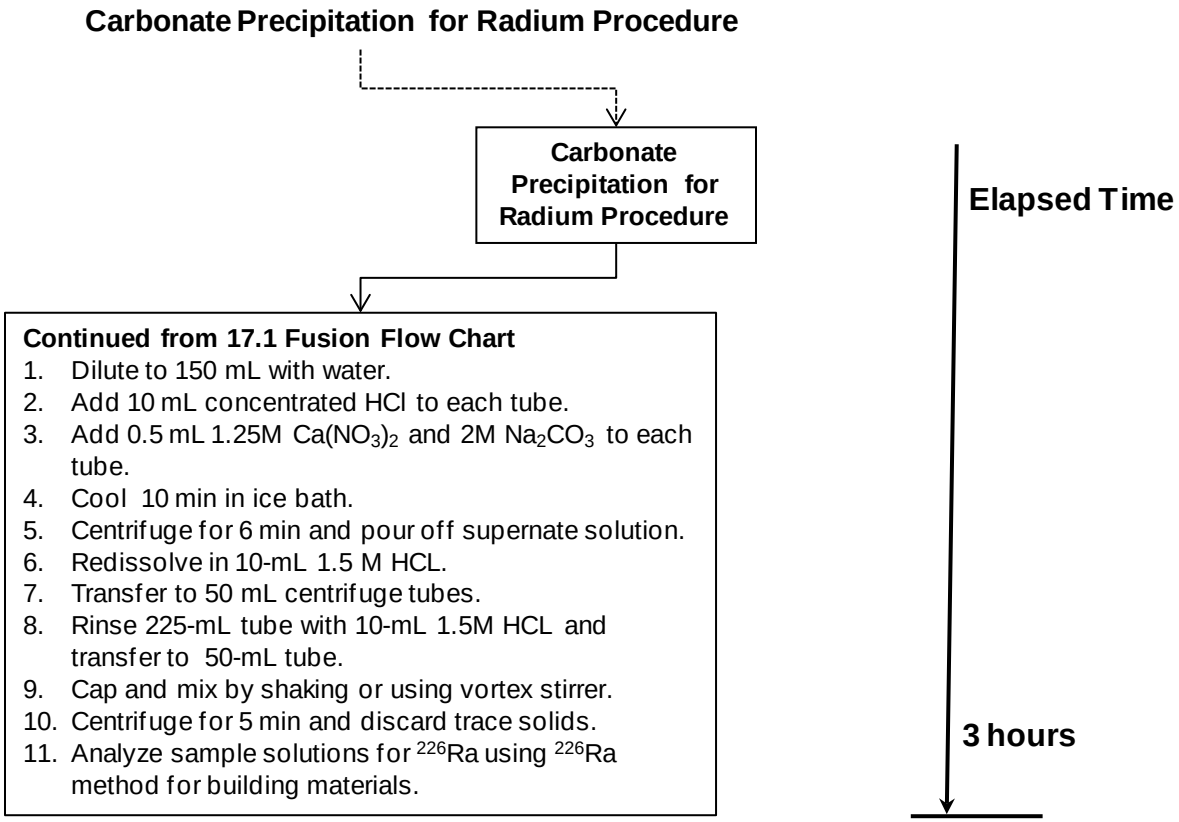


17.3. Strontium Precipitation Flow Chart




Strontium Precipitation Procedure (Brick)
$Ca_3(PO_4)_2$ / CaF_2 Precipitation for Sr in Brick Procedure
Continued from 17.1 Fusion Flow Chart
1. Dilute to 150 mL with water.
2. Add 2 mL 1.25M $Ca(NO_3)_2$, 50 mg Fe, and 5 mL 3.2M $(NH_4)_2HPO_4$ to each tube.
3. Centrifuge for 5 min and pour off supernate.
4. Redissolve in ~60 mL1.5M HCL.
5. Dilute to 170 mL with 0.01M HCl.
6. Add 22 mL Concentrated HF and wait 10 min.
7. Centrifuge for 6 min and pour off supernate.
8. Redissolve in 5 mL 3M HNO_3-0.25M H_3BO_3 + 5 mL concentrated HNO_3 +5 mL 2M $Al(NO_3)_3$ + 5 mL 3M HNO_3.
9. Cap and mix using vortex stirrer.
10. Centrifuge for 5 min and discard trace solids.
11. Analyze sample solutions for ^{90}Sr using ^{90}Sr method for building materials.
Elapsed Time
2½ hours

17.4. Radium Precipitation Flow Chart



Appendix:

Rapid Technique for Milling and Homogenizing Concrete and Brick Samples

A1. Scope and Application

A1.1. Concrete or brick samples may be received as powder, core samples or other size pieces or chunks. The goal is to obtain representative sample aliquants from homogeneous amounts of sample.

A1.2. The ball mill method describes one approach for the rapid, gross preparation of concrete or brick samples to yield 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 concrete or brick samples. The concrete or brick sample must be reduced to pieces or fragments less than ~ 25 mm in diameter prior to using the ball mill. This can be done with a hydraulic press or mallet.

A1.3. The method is designed to be used as a preparatory step for the attached methods for fusion of concrete or brick for ^{241}Am, $^{239/240}$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.

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

A1.5. For smaller amounts of concrete or brick samples, a drill with masonry bit can be used in a lab hood inside a plastic bag to collect the powder that results.

A2. Summary of Methods

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 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 concrete or brick (e.g., 500 mL).

A2.3. The entire sample as received (after reducing fragment size to less than ~25 mm diameter) is split by coning and quartering until 75-150 mL of concrete or brick are available for subsequent processing. If less than 450 mL of concrete or brick is received, the entire sample is processed.

A2.4. The concrete or brick is transferred to a paint can or equivalent. Percent solids are determined, if required, by drying in a drying oven. A mallet and plastic bag or hydraulic press may be needed to break up larger pieces.

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 250 micrometers (μm).

NOTE: A mortar and pestle may also be used as needed to grind the sample further.

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 pulverization.

A2.8. The drill bit method involves drilling into the sample using a drill bit. The operation is performed inside a disposable plastic bag in a hood so that the drilled out sample is caught within the plastic bag (this also minimizes the spread of contamination). A drill bit such as a ¼-inch carbide bit is recommended. The holes should be drilled in such a way as to obtain representative powdered samples. The drill bit should be cleaned between uses on different samples using soap and water.

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 Protocols (MARLAP) Manual* (Reference A16.3).

A3.3. *ASTM C999 Standard Practice for Soil Sample Preparation for the Determination of Radionuclides* (Reference A16.4).

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* for an approach for homogenization and milling of larger soil samples.

A4.1.3. 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.

A4.1.4. 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.

A4.1.5. If the sample was collected near the epicenter of a 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 the size is reduced to less than 50-100 mesh, these particles may resist fusion or digestion of the solids into ionic form that can be subjected to chemical separations.

A4.1.6. 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.

A4.1.7. 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 your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

A5.2. Radiological

A5.2.1. Refer to your radiation safety manual for direction 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 or smaller filter 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, ~15-25 mm diameter. The size and number of grinding media used should be optimized to suit the types of concrete or brick, the size of the can, and the volume of soil processed.

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

A6.6. Disposable 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.

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 Protocol Specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.

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 of sample cross-contamination and concerns about adequate cleaning of equipment. Under certain circumstances (disposable sieves are not available, for example), careful, thorough cleaning of the sieves with water and the ethanol may be an option.

A10.1. If necessary, reduce the concrete or brick particle diameter to less than ~25 mm using a hydraulic press, mallet, or alternate equipment capable or reducing the fragment size.

A10.2. Estimate the total volume of sample, as received.

NOTE: 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.

NOTE: 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.

A10.2.1. Spread a large piece of plastic backed absorbent paper, plastic side *up* in a hood.

A10.2.2. If the sample volume is less than 450 mL, there is no benefit to coning and quartering.[1]

A10.2.2.1. Carefully pour the sample onto the paper.

A10.2.2.2. Remove extraneous material, such as rocks or debris, unless the project requires that such material be processed as part of the sample. Continue with Step A10.2.5.

A10.2.3. 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 rocks or debris unless the project requires that such material be processed as part of the sample.

A10.2.4. 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 if volatile components or percent solids are to be determined.

A10.2.4.1. 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.

A10.2.4.2. Reshape the remaining two quarters into a smaller cone, and repeat Step A10.2.2.1 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, la bel 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.

A10.2.5. Transfer the coned and quartered sample to a tared, labeled 1-pint paint can. If the total volume was less than ~450 mL, transfer the entire sample to a tared, 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 determination may also be achieved operationally by observing the time needed to ensure that 99% of all samples will obtain constant mass.

[1] International Union of Pure and Applied Chemistry (IUPAC). 1997. Compendium 1675 of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. (Reference A16.1).

A10.3. Place the can (without lid) in an oven at 110±10 ºC and dry the concrete or brick to constant mass.

NOTE: Concrete or brick samples may be dry enough such that heating prior to homogenizing the sample is not required.

A10.4. Weigh the combined mass of the can, sample, and lid. If the percent solids are required see Section A12.1 calculations. Remove can from oven and allow to cool.

A10.5. Add five 1.5 cm stainless steel or ceramic balls or rods to the can. Replace the lid and seal well.

A10.6. Shake the can and contents for 5 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.

A10.7. 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.

A10.8. Following milling, a small fraction of residual larger particles may remain in the sample.

A10.8.1. 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.

A10.8.1.1. 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.

A10.8.1.2. 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.

A10.9. Sample fines may be stored in, and aliquanted directly from, the container used for drying and pulverization.

A11. Calibration and Standardization

A11.1. Balances used shall be calibrated using National Institute of Standards and Technology (NIST)-traceable weights 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. Dry mass is calculated from a measurement of the total as received mass of the sample received 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

A12.3.1. 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

A15.1. All radioactive and other regulated wastes shall be handled according to prevailing regulations.

A16. References

A16.1. International Union of Pure and Applied Chemistry (IUPAC). 1997. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford. XML on-line corrected version: http://goldbook.iupac.org/C01265.html. (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. Last update: 2010-12-22.

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

A16.3. MARLAP. *Multi-Agency Radiological Laboratory Analytical Protocols Manual.* 2004. Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421, July. Available at: www.epa.gov/radiation/marlap.

A16.4. ASTM C 999-05, "Standard Practice for Soil Sample Preparation for the Determination of Radionuclides," Volume 12.01, ASTM, 2005.