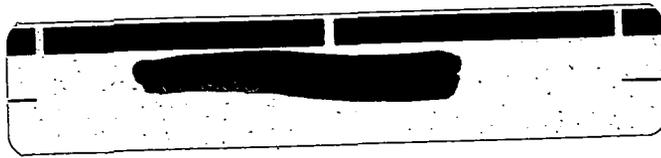


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**SITEWIDE CERCLA QUALITY ASSURANCE
PROJECT PLAN VOLUME V ATTACHMENT I
FEMP LABORATORY ANALYTICAL METHODS
MANUAL (CONTINUED) 4 MARCH 1992**

03/04/92

**228
ENCLOSURE**



VOLUME V

3204

Fernald Environmental Management Project

**SITEWIDE
CERCLA QUALITY ASSURANCE
PROJECT PLAN**

**Attachment I
FEMP Laboratory Analytical Methods Manual
(continued)**

Prepared by

Westinghouse Environmental Management Company of Ohio

for the

**United States Department of Energy
Fernald Office**

4 March 1992

VOLUME V
Methods for Radiometric and Geotechnical Parameters

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| Method | Method No. |
|--|-------------------|
| Isotopic Plutonium in Water by Alpha Spectrometry | FM-RAD-0010 |
| Radium-228 in Water and Air Filters by Beta Counting | FM-RAD-0040 |
| Radium-226 in Water by Emanation/Scintillation Counting | FM-RAD-0050 |
| Radium-226 in Soil/Sediment, Milk, and Air Filters by Emanation/Scintillation Counting | FM-RAD-0060 |
| Lead-210 in Water by Beta Counting | FM-RAD-0070 |
| Isotopic Thorium in Milk, Vegetation, Soil/Sediment, Water and Air Filters by Alpha Spectrometry | FM-RAD-0080 |
| Isotopic Uranium in Vegetation, Milk, Water and by Air Filters by Alpha Spectrometry | FM-RAD-0100 |
| Isotopic Uranium in Soil/Sediment by Alpha Spectrometry | FM-RAD-0110 |
| Uranium in Water, Soil/Sediment, and Air Filters by Pulsed-Laser Phosphorimetry | FM-RAD-0120 |
| Gross Alpha and Gross Beta Radioactivity in Water and Gross Beta Radioactivity in Air Filters by Proportional Counting | FM-RAD-0130 |
| Radioanalysis of Soil/Sediment, Air Filters, Milk and Water by Gamma Spectrometry | FM-RAD-0140 |
| Soil Classification (Lab) | FM-GTT-0011 |
| Soil Classification (Visual) | FM-GTT-0012 |
| Transporting Samples | FM-GTT-0013 |
| Wet Preparation of Samples | FM-GTT-0014 |
| Dry Preparation of Samples | FM-GTT-0015 |
| Moisture Content | FM-GTT-0021 |
| Moisture Content (Microwave) | FM-GTT-0022 |
| Moisture Correction (Oversize) | FM-GTT-0023 |
| Specific Gravity | FM-GTT-0024 |
| Volume-Weight Relationships | FM-GTT-0025 |
| Grain Size Analysis | FM-GTT-0031 |
| Atterberg Limits | FM-GTT-0032 |
| Shrinkage Limit | FM-GTT-0033 |
| Standard Proctor | FM-GTT-0041 |

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| Method | Method No. |
|---|-------------------|
| Modified Proctor | FM-GTT-0042 |
| Maximum (Relative) Density | FM-GTT-0043 |
| Minimum (Relative) Density | FM-GTT-0044 |
| Consolidation | FM-GTT-0051 |
| Unconfined Compression | FM-GTT-0061 |
| | |
| Direct Shear (Controlled-Displacement Method) | FM-GTT-0062 |
| Direct Shear (Controlled-Stress Method) | FM-GTT-0063 |
| Triaxial Compression (UU) | FM-GTT-0064 |
| Triaxial Compression (CU) | FM-GTT-0065 |
| California Bearing Ratio | FM-GTT-0066 |
| | |
| Permeability (Constant Head) | FM-GTT-0071 |
| Permeability (Triaxial) | FM-GTT-0072 |
| Btu Content (Solids) | FM-GTT-0082 |
| Ash Content | FM-GTT-0083 |
| Organic Content | FM-GTT-0084 |

Isotopic Plutonium in Water by Alpha Spectrometry

| | |
|------------------------------|---|
| Working Linear Range: | Greater than 0.02 pCi/L, infinite with dilution |
| Reporting Limit: | ~0.02 pCi/L |
| Reporting Units: | pCi/L |
| Matrix: | Water |

1.0 Scope and Application

- 1.1 This test method covers the determination of plutonium isotopes $^{239/240}\text{Pu}$ and ^{238}Pu in water by means of chemical separations and alpha spectrometry. The test method applies to soluble plutonium and to suspended particulate matter containing plutonium. In the latter situation, an acid dissolution step is required to assure that all of the plutonium dissolves. The nominal sensitivity may vary with each analysis but is approximately 0.02 pCi/L.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 Plutonium-242 is added as a tracer before any chemical separations are performed. Iron is added to the water sample as iron (III), and the plutonium is coprecipitated with the iron as ferric hydroxide. After decantation and centrifugation, the ferric hydroxide precipitate containing the coprecipitated plutonium is dissolved, and the solution is adjusted to 8 M in HNO_3 for anion exchange separation. When the sample fails to dissolve because of the presence of insoluble residue, the residue is treated by a rigorous acid dissolution using concentrated nitric and hydrofluoric acids.
- 2.2 After an anion exchange separation, the plutonium is electrodeposited onto a stainless steel disk for counting by alpha pulse height analysis using a silicon surface barrier detector. From the recovery of the ^{242}Pu tracer, the absolute activities of ^{238}Pu and $^{239/240}\text{Pu}$ can be calculated.

3.0 Interferences

- 3.1 Thorium-228 when present at concentrations 100 times or greater than ^{238}Pu has been found to interfere with the determination of the ^{238}Pu . Some ^{228}Th comes through the chemical separation procedure and is electrodeposited with the plutonium. If the disk is poorly plated and if the alpha energy resolution of the sample is not better than 60 keV, the ^{238}Pu and the ^{228}Th may appear as one peak; the principal alpha energy of ^{238}Pu is 5.50 MeV while that of ^{228}Th is 5.42 MeV.

- 3.2 If a sample contains both ^{239}Pu and ^{240}Pu , it is not possible to resolve the two isotopes since their principal alpha energies differ by only 0.01 MeV. Combined ^{239}Pu and ^{240}Pu should be reported.
- 3.3 Samples that have excess iron or other material deposited with the sample will undergo self-absorption. Self-absorption is indicated by poor resolution and low-energy tailing (peak straggling) in the sample spectrum.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA Regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous materials are used during the method, procedures for handling low level radioactive materials, acids and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Funnels, beakers, pipettes, centrifuge bottles, volumetric flasks. Class A volumetric glassware is used for tracer and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 6.2 Teflon beakers.
- 6.3 pH paper covering at least pH 9 to 10.
- 6.4 Electric hot plate/magnetic stirrer. This piece of apparatus should have a built-in stirrer demand.

- 6.5 Centrifuge, capable of handling a 250-mL centrifuge bottle.
- 6.6 Glass fiber filters, Gelman type A/E, or equivalent.
- 6.7 Ion exchange column, approximately 13-mm ID and 150-mm long with a 100 mL reservoir.
- 6.8 Electrodeposition apparatus, direct current, 0 to 12 V and 0 to 2 A, using disposable deposition cells. Cathode is stainless steel disk with mirror finish and anode is platinum wire loop. See reference 15.4 for example apparatus. All electroplating disks shall be cleaned with nitric acid before use.
- 6.9 Alpha spectrometry system: Consisting of solid state alpha detector, multichannel analyzer (or PC or minicomputer), electronics, printer, and vacuum chamber. System must be capable of providing a spectral resolution of 60 keV or better on a plated source.
- 7.0 Routine Preventive Maintenance**
- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks and replace as necessary.
- 8.0 Reagents**
- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. In all cases acids or bases are added to water.
- 8.2 Water: all references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Plutonium-242 Standard Solution, from NIST, or NIST traceable, or from another nationally recognized agency.

- 8.4 Plutonium-236 Standard Solution, from NIST, or NIST traceable, or from another nationally recognized agency.
- 8.5 Ferric chloride carrier solution (50 mg Fe/mL): Dissolve 24 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a mixture of 4.4 mL of concentrated hydrochloric acid and 95.6 mL of water.
- 8.6 Ammonium hydroxide (NH_4OH), 15 M: Concentrated reagent.
- 8.7 Nitric acid (HNO_3), 16 M: Concentrated reagent.
- 8.8 Hydrogen peroxide (H_2O_2), 30%: Reagent.
- 8.9 Nitric acid (HNO_3) 8 M: Dilute 500 mL of concentrated nitric acid to 1 L with water.
- 8.10 Hydrofluoric acid (HF), 29 M: Concentrated (48%) reagent.
- 8.11 Hydrochloric acid (HCl), 12 M: Concentrated reagent.
- 8.12 Boric acid (H_3BO_3), Powdered or crystalline reagent.
- 8.13 Anion exchange resin-strongly basic, styrene, quaternary ammonium salt, 4% crosslinked, 100 to 200 mesh, chloride form.
- 8.14 Sodium nitrite (NaNO_2): Reagent grade.
- 8.15 Hydrochloric acid (HCl), 9M: Dilute 800 mL of concentrated HCl to 1 L with water.
- 8.16 Ammonium iodide solution (NH_4I), 145 g/L: Dissolve 14.5 g of NH_4I in water and dilute to 100 mL. This solution must be prepared fresh weekly.
- 8.17 Sodium hydrogen sulfate-sulfuric acid solution ($\text{NaHSO}_4\text{-H}_2\text{SO}_4$): Dissolve 10 g of sodium hydrogen sulfate in 100 mL of water and then carefully add 100 mL of concentrated H_2SO_4 while mixing. This solution contains about 5% NaHSO_4 in 9 M H_2SO_4 .
- 8.18 Sulfuric acid (H_2SO_4), 18 M: Concentrated reagent.
- 8.19 Preadjusted ammonium sulfate electrolyte ($[(\text{NH}_4)_2\text{SO}_4]$): 1 M ammonium sulfate adjusted to pH 3.5 with 15 M NH_4OH and 18 M H_2SO_4 .
- 8.20 Thymol blue indicator, 0.04% solution: Dissolve 0.1 gram thymolsulfonephthalein in 21.5 mL 0.01 M NaOH and 228.5 mL water.

- 8.21 Sulfuric acid (H_2SO_4), 1.8 M: Dilute 100 mL of 18 M H_2SO_4 to 1 L with water.
- 8.22 Ammonium hydroxide (NH_4OH), 1.5 M: Dilute 100 mL of 15 M NH_4OH to 1 L with water.
- 8.23 Ammonium hydroxide (NH_4OH), 0.15 M: Dilute 10 mL of 15 M NH_4OH to 1 L with water.
- 8.24 Ethanol ($\text{C}_2\text{H}_5\text{OH}$), 98% reagent, made slightly basic with 3 to 5 drops of 15 M NH_4OH per 100 mL of alcohol.

9.0 Calibration Procedure

- 9.1 The alpha counting system is calibrated, i.e., operating voltages, etc., according to the manufacturers instructions at least annually and after every significant change to the counting system.
- 9.2 Use a mixed alpha emitting standard (e.g., ^{238}Pu , ^{239}Pu , ^{242}Pu , traceable to NIST or another nationally recognized agency) to calibrate each detector in counting system. Refer to the manufacturer's instructions for specific calibration procedure. Reference 15.3 may be consulted in regard to energy calibration and counting efficiency determination of the counting system.
- 9.3 Using an alpha check source verify the detector efficiency, detector resolution, and energy calibration daily or before use. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.4 A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed weekly. The results must be within established limits, e.g., ± 3 sigma before commencing analyses.

10.0 Sample Preparation

- 10.1 Measure a volume of water sample appropriate to meet the required sensitivity into an appropriate size beaker. Record volume of water used. Record comment if presence of any undissolved material is noted.
- 10.2 Add an accurately known amount of the ^{242}Pu standard solution to give about 5 pCi of activity or sufficient to provide less than or equal to 5% uncertainty at the 1 sigma level. Record activity and amount of tracer added. Mix the sample completely.

Note: The standard solution must have sufficient activity concentration such that volume added does not exceed 20% of the sample volume.

Note: If the ^{238}Pu or ^{239}Pu content of the sample is known to be high, ^{236}Pu tracer is recommended.

11.0 Sample Analysis

11.1 Coprecipitation

- 11.1.1 Heat the sample to $60^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and stir at this temperature for 1 hour.
- 11.1.2 Add 1 mL of ferric chloride carrier solution and stir for 10 minutes.
- 11.1.3 Add concentrated NH_4OH while stirring to precipitate the iron. Add a slight excess of the concentrated NH_4OH to raise the pH to 9 to 10 as indicated with pH paper.
- 11.1.4 Continue to stir the sample for about 30 min before allowing the precipitate to settle. (If the analyst wishes to continue immediately the iron hydroxide may be filtered out at this time.)
- 11.1.5 After the sample has settled sufficiently decant the supernate, being careful not to remove any precipitate.
- 11.1.6 Slurry the precipitate and remaining supernate and transfer to a centrifuge bottle.
- 11.1.7 Centrifuge the sample and discard the supernate.
- 11.1.8 Dissolve the ferric hydroxide with a minimum of concentrated HNO_3 . If solution is not clear and colorless, organic matter may be present. Add 30% H_2O_2 dropwise with heating until organic matter is oxidized. Additional concentrated HNO_3 acid may be required for complete oxidation.
- 11.1.9 If the precipitate dissolves completely, add a volume of concentrated HNO_3 equal to the volume of the sample solution, dilute to 100 to 150 mL with 8 M HNO_3 , and then proceed to Section 11.3, Column Preparation. If the precipitate does not dissolve in HNO_3 , proceed to Section 11.2, Acid Dissolution of Insoluble Residue.

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11.2 Acid Dissolution of Insoluble Residue.

- 11.2.1 If the precipitate fails to dissolve in HNO_3 , add more concentrated HNO_3 to a total volume of about 75 mL, transfer the entire sample to a Teflon beaker, and add 75 mL of concentrated HF. (Caution-Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
- 11.2.2 Stir and heat on a magnetic/stirrer hot plate for about 4 hours at a temperature near boiling. Add equal amounts of concentrated HNO_3 and concentrated HF to keep the volume at about 150 mL.
- 11.2.3 Allow the mixture to cool, and decant the solution into another Teflon beaker.
- 11.2.4 Evaporate solution in a second beaker to dryness.
- 11.2.5 While solution in second beaker is drying, add 75 mL of concentrated HCl and 2 g of H_3BO_3 to the undissolved residue in the first beaker. Stir and then let stand until the solution in the second beaker has evaporated to dryness.
- 11.2.6 Transfer the HCl- H_3BO_3 mixture from the first beaker to the dried sample in the second beaker, leaving any residue behind. Rinse the residue once with water and transfer this water to the second beaker.
- 11.2.7 Evaporate the sample in the second beaker to about 10 mL.
- 11.2.8 Add 100 mL of concentrated HNO_3 and boil to remove the HCl.
- 11.2.9 Evaporate the sample to a volume of about 50 mL.
- 11.2.10 Remove from the hot plate, and add a volume of water equal to the volume of the sample.
- 11.2.11 Add 8 M HNO_3 to a volume of 150 mL, add 1 g of H_3BO_3 , and allow the solution to cool.
- 11.2.12 Filter the solution through a glass fiber filter and wash the filter a few times with 8 M HNO_3 . Discard filter and residue.
- 11.2.13 Proceed with the analysis of the filtrate in accordance with Section 11.3, Column Preparation.

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11.3 Column Preparation

- 11.3.1 Slurry about 10 mL of the anion exchange resin with 8 M HNO₃.
- 11.3.2 Pour it onto a column of about 13-mm inside diameter to a resin depth of about 80 mm. Use more resin when analyzing samples containing suspended matter.
- 11.3.3 Wash the resin with 10 column volumes of 8 M HNO₃ to convert the resin to the nitrate form.

11.4 Anion Exchange Separation

- 11.4.1 To the solution from the coprecipitation procedure or from the acid dissolution treatment add 1 g of NaNO₂, heat to boiling and cool.
- 11.4.2 Pass the sample solution through the prepared anion exchange resin column at a flow rate no greater than 5 mL/minute.
- 11.4.3 After the sample has passed through the column, rinse the column with six column volumes of 8 M HNO₃ at a flow rate no greater than 5 mL/minute.
- 11.4.4 Rinse the ion exchange resin column with six column volumes of 9 M HCl at a flow rate no greater than 2 mL/min.

Note -The purpose of this step is to remove any thorium present in the sample. Experience with soil and other samples containing relatively large amounts of thorium has shown that additional rinsing of the column with 9 M HCl at low-flow rates is required to remove the thorium. Normally water samples will not contain large amounts of thorium, but if they do, additional rinsings at this step may, be required.

- 11.4.5 Elute the plutonium at a flow rate no greater than 2 mL/min with four column volumes of a freshly prepared NH₄I-HCl mixture containing 1 mL of 1 M NH₄I per 30 mL of concentrated HCl.
- 11.4.6 Rinse the column at maximum flow rate with two portions of concentrated HCl equal to the volume of the column of resin. Allow this rinse to flow into the eluant from step 11.4.5.
- 11.4.7 Evaporate the eluant containing the plutonium to about 20 mL and add 5 mL of concentrated HNO₃.

- 11.4.8 Evaporate the sample to near dryness.
- 11.4.9 Add 20 mL of concentrated HNO_3 and evaporate to near dryness.
- 11.5 Electrodeposition
- 11.5.1 Add 2 mL of a 5% solution of NaHSO_4 in 9 M H_2SO_4 to sample.
- 11.5.2 Add 5 mL of 16 M HNO_3 , mix well, and evaporate to dryness but do not bake.
- 11.5.3 Dissolve sample in 5 mL of preadjusted ammonium sulfate electrolyte, warming to hasten dissolution.
- 11.5.4 Transfer solution to electrodeposition cell using an additional 5 to 10 mL of electrolyte in small increments to rinse sample container.
- 11.5.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H_2SO_4 (or 1.5 M NH_4OH) until color is obtained.
- 11.5.6 Place platinum anode into solution so that it is about 1 cm above stainless steel disk that serves as cathode.
- 11.5.7 Connect electrodes to source of current, turn power on, and adjust power supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustments during the electrodeposition.)
- 11.5.8 Continue electrodeposition for 1.5 to 2.0 hours.
- 11.5.9 When electrodeposition is to be terminated, add 1 mL of 15 M NH_4OH and continue electrodeposition for 1 minute.
- 11.5.10 Turn off the power and remove the anode from the cell.
- 11.5.11 Discard the solution in the cell, and rinse cell 2 or 3 times with 0.15 M NH_4OH .
- 11.5.12 Disassemble cell, and wash disk with ethanol made basic with NH_4OH .
- 11.5.13 Touch edge of disk to tissue to absorb ethanol.

- 11.5.14 Dry disk, label it for counting, and place it in a designated holding/staging area before counting. If disk is not completely dry, moisture may adversely affect spectral resolution.

11.6 Alpha Spectrometry

- 11.6.1 Using the manufacturer's suggested operating procedure count samples as long as necessary to meet the Minimum Detectable Concentration requirements specified in the analytical laboratory service contract(s) or Sampling and Analysis Plan. Counting times may have to be further adjusted if sample counting efficiency is low, if the tracer recovery is less than expected, or if the anticipated activity is less than 1 dpm/sample.
- 11.6.2 Check the alpha spectrum for peaks at $^{239/240}\text{Pu}$, ^{242}Pu , and ^{238}Pu alpha energies (as listed below) and determine total counts in each peak. The ^{239}Pu and ^{240}Pu isotopes emit alpha particles that are too close in energy for resolution and the reported value is a sum of the two.
- 11.6.3 Samples with poorly resolved tracer or analyte peaks may indicate excessive self-absorption and the need to replat or repurify the sample.

| Plutonium Isotope | Primary Alpha Energies (MeV) | Probability per Decay |
|-------------------|------------------------------|-----------------------|
| 242 | 4.90 | 0.79 |
| | 4.86 | 0.21 |
| 240 | 5.17 | 0.73 |
| | 5.12 | 0.27 |
| 239 | 5.16 | 0.73 |
| | 5.14 | 0.15 |
| | 5.10 | 0.12 |
| 238 | 5.50 | 0.72 |
| | 5.46 | 0.28 |
| 236 | 5.77 | 0.69 |
| | 5.72 | 0.31 |

12. Calculation

12.1 Calculate the concentrations of $^{239/240}\text{Pu}$ and ^{238}Pu in pCi/L as follows:

$$\text{Pu}_g = \frac{(A - A_1)(F)(Y_t)}{2.22(B - B_1)(V)(Y_s)}$$

where:

Pu_g = gross concentration of plutonium-239/240 or plutonium-238 in the water sample, pCi/L.

A = gross sample counts per minute in the $^{239/240}\text{Pu}$ or ^{238}Pu energy region of the alpha spectrum.

A_1 = detector background counts per minute in same α peak as A above.

F = activity of ^{242}Pu tracer added in dpm.

B = gross counts per minute in the ^{242}Pu tracer energy region of the alpha spectrum.

B_1 = detector background counts per minute in the same α peak as B above.

V = liters of the water sample taken for analysis. (This does not include the volume of acid added for preservation.)

Y_t = probability of α emission per decay for α of interest (in tracer) in B above.

Y_s = probability of α emission per decay for α of interest in A above.

2.22 = dpm per pCi.

Note: pCi may be converted to Bq by using the following multiplicative factor: 3.667E-02 Bq/pCi. The overall recovery for the tracer is included in the above equation as $[(F)(Y_t)]/(B - B_1)$.

12.2 Final sample results shall be corrected for reagent blank contribution. Using above equation calculate the reagent blank activity (Pu_b) and subtract from gross sample activity (Pu_g) to obtain final sample activity (Pu_s); $\text{Pu}_s = \text{Pu}_g - \text{Pu}_b$.

- 12.3 The minimum detectable concentration (MDC) in pCi/L shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s). The total propagated uncertainty and MDC shall be determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical services contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project specific Sampling and Analysis Plan, or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|---------------|-----------|------------------|-------------------|
| Reagent Blank | 1/20* | To Be Determined | Qualify Data |
| Pu Tracer | 1/1 | To Be Determined | Qualify Data |
| LCS | 1/20* | To Be Determined | Qualify Data |
| Duplicate | 1/20* | To Be Determined | Qualify Data |

* or per batch or fraction thereof

15.0 References

- 15.1 *Standard Test Method for Plutonium in Water*, ASTM D 3865 - 82, 1983.
- 15.2 *Standard General Methods for Detector Calibration and Analysis of Radionuclides*, ASTM E181-82, 1982.
- 15.3 *Standard Practices for the Measurement of Radioactivity*, ASTM D 3648-78, 1978.
- 15.4 *EML Procedures Manual, 27th Edition, Volume 1*, U.S. DOE Environmental Measurements Laboratory, New York, NY, HASL-300-Ed.27-Vol.1, 1990.

Radium-228 in Water and Air Filters by Beta Counting

| | |
|------------------------------|--|
| Working Linear Range: | Greater than 1 pCi/L, infinite with dilution |
| Reporting Limit: | ~ 1 pCi/L Water; TBD for Air Filters |
| Reporting Units: | Water, pCi/L; Air filters, pCi/air filter |
| Matricies: | Water, air filters |

1.0 Scope and Application

- 1.1 The method covers the determination of radium-228 (^{228}Ra) in water and air filters. The nominal sensitivity of the procedure may vary with each analysis but is approximately 1 pCi/L for water. The nominal sensitivity that may be obtained by this exact method for air filters requires additional performance data.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 The radium in the sample is coprecipitated as radium-barium sulfate. The precipitate is dissolved in a pentasodium diethylenetriamine pentaacetate solution.
- 2.2 Radium-228, a weak beta emitter, decays to actinium-228 (^{228}Ac), which is allowed to ingrow for at least 36 hours. The ^{228}Ac is then extracted into di-2-ethylhexylphosphoric acid and back-extracted with nitric acid.
- 2.3 The ^{228}Ac is beta counted in a low background proportional counter and its measured activity is used to calculate the ^{228}Ra concentration of the original sample.

3.0 Interferences

- 3.1 This procedure is very specific for the isolation of ^{228}Ra and ^{228}Ac ; no specific radionuclide interferences have been identified.
- 3.2 Moisture absorbed by the sample solids on the counting planchet alters counting and self-absorption characteristics.
- 3.3 Nonuniformity of sample residue in the counting planchet interferes with the accuracy and precision of the method.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low-level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Separatory funnels, beakers, pipettes, funnels, volumetric flasks. Class A volumetric glassware is used for carrier and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 6.2 pH Meter: scale readability of ± 0.1 pH units.
- 6.3 Scissors, reserved for cutting only air filters.
- 6.4 Platinum dish, 125 mL.
- 6.5 Muffle furnace, able to reach at least 500°C and able to maintain temperatures within $\pm 15^\circ\text{C}$.
- 6.6 Electric hot plate/magnetic stirrer. This piece of apparatus should have a built-in stirrer and stepless temperature controls that can be changed as heating requirements may demand.
- 6.7 Teflon-coated stirring bar.

- 6.8 Teflon stirring rod.
- 6.9 Ash free filter paper, Whatman No. 42, or equivalent.
- 6.10 Centrifuge: Able to hold 40-mL size centrifuge tubes and achieve at least 2,000 rpm.
- 6.11 Centrifuge tubes: 40 mL and 100 mL.
- 6.12 Vacuum filter apparatus.
- 6.13 Planchets: Planchets shall be fabricated from uniform density stainless steel. Size is dictated by the inside dimensions of the detector chamber. All planchets shall be nitric acid washed before use.
- 6.14 Desiccator: Large enough to hold dried planchets until ready for counting.
- 6.15 Low Background Alpha/Beta Proportional Counting System: Tennelec Model LB-5100, or equivalent. Detector must have a rigid sample positioning device that has accurate and reproducible geometry.
- 6.16 Large volume ($>50 \text{ cm}^3$) Ge detector with full width at one-half peak maximum (FWHM) less than 2.5 KeV at 1,332 KeV.
- 7.0 Routine Preventive Maintenance**
- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks, and replace as necessary.
- 8.0 Reagents and Calibration Standards**
- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. All radionuclide standards must be corrected for decay. In all cases acids and bases are added to water.

- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Acetic acid (CH_3COOH), 17.4 M: Glacial, reagent.
- 8.4 Acetic acid (CH_3COOH), 6 M: Dilute 345 mL of glacial reagent CH_3COOH to 1 L with water.
- 8.5 Diethylenetriamine pentacetic acid, pentasodium Salt, Na_5DTPA , 41% reagent solution.
- 8.6 Actinium wash solution: Dissolve 100 grams monochloroacetic acid and 2.4 mL of 41% Na_5DTPA in 800 mL of water and dilute to 1 liter. Adjust pH to 3.0 with NaOH pellets (approximately 25.4 grams NaOH).
- 8.7 Ammonium hydroxide (NH_4OH), 15 M: Concentrated, reagent.
- 8.8 Barium carrier, 10 mg Ba^{+2}/mL : Dissolve 17.78 grams $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 800 mL water and dilute to 1 liter. Allow to stand 24 hours and filter.
- 8.9 Barium carrier, 5 mg Ba^{+2}/mL : Dissolve 4.45 grams $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 400 mL water and dilute to 500 mL.
- 8.10 Bismuth carrier, 20 mg Bi^{+3}/mL : Dissolve 46.4 grams $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 800 mL water and dilute to 1 liter.
- 8.11 Monochloroacetic acid (ClCH_2COOH), 2 M: Add 189 grams of reagent grade monochloroacetic acid to beaker, dissolve in water, and dilute to 1 liter.
- 8.12 Diammonium citrate, 2 M: Dissolve 226.2 grams dibasic ammonium citrate, $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, in water and dilute to 500 mL.
- 8.13 Diammonium citrate/ NH_4OH wash solution: Mix equal volumes of 2 M diammonium citrate and 15 M NH_4OH .

- 8.14 Di-2-ethylhexylphosphoric acid (HDEHP), 15% in n-heptane: Dilute 150 mL HDEHP to 1 liter with n-heptane and transfer to 2-liter separatory funnel. Wash HDEHP twice with 200-mL aliquots of a 1:1 mixture of 2 M diammonium citrate and 15 M NH_4OH . Mixture is prepared by adding 100 mL 15 M NH_4OH to 100 mL 2 M diammonium citrate in a beaker and mixing. Add to separatory funnel containing HDEHP. Shake for 1 minute, releasing pressure frequently. Allow layers to separate and discard lower layer. Wash HDEHP twice with 4 M HNO_3 , discarding lower layer each time after shaking for 1 minute. Store cleaned HDEHP in polyethylene bottle. Immediately before using HDEHP solution, amount to be used is washed first with equal volume of distilled water and then with one-half volume of actinium wash. Lower layers are discarded each time after shaking for 1 minute.
- 8.15 Diethylenetriamine pentacetic acid, pentasodium Salt, Na_5DTPA , 0.17 M, pH 10: Add 209 mL of the 41% Na_5DTPA solution to 400 mL of water and filter through glass wool with suction. Dilute to 1 liter with water and adjust to pH 10 using either perchloric acid or sodium hydroxide (usually requires 10 to 12 mL perchloric acid). Store in polyethylene bottle.
- 8.16 N-Heptane: Reagent grade.
- 8.17 Hydrofluoric acid (HF): Concentrated (48% HF) reagent.
- 8.18 Lead carrier, 100 mg Pb^{+2}/mL : Dissolve 160 grams reagent grade $\text{Pb}(\text{NO}_3)_2$ in 800 mL water and dilute to 1 liter.
- 8.19 Nitric acid (HNO_3), 16 M: Concentrated (70% HNO_3) reagent.
- 8.20 Nitric acid (HNO_3), 4 M: Dilute 250 mL of concentrated HNO_3 to 1 liter with water.
- 8.21 Nitric acid (HNO_3), 3 M: Dilute 189 mL of concentrated HNO_3 to 1 liter with water.
- 8.22 Nitric acid (HNO_3), 1 M: Dilute 63 mL of concentrated HNO_3 to 1 liter with water.
- 8.23 Perchloric acid (HClO_4), 12 M: Concentrated (70% HClO_4) reagent.
- 8.24 Sodium hydroxide (NaOH): Reagent grade pellets.

- 8.25 Sodium sulfate (Na_2SO_4), 20%: Dissolve 20 grams anhydrous Na_2SO_4 in 80 mL water and dilute to 100 mL.
- 8.26 Sulfuric acid (H_2SO_4), 18 M: Concentrated (96% H_2SO_4) reagent.
- 8.27 Sulfuric acid (H_2SO_4), 4 M: Dilute 222 mL of the concentrated H_2SO_4 to 1 liter with water.
- 8.28 Radium-228 standard solution: from NIST, or NIST traceable, or from another nationally recognized agency.
- 8.29 Barium-133 tracer solution: from NIST, or NIST traceable, or from another nationally recognized agency.

9.0 Calibration Procedures

- 9.1 The beta counting system is calibrated (e.g., plateau determination, operating voltages) according to the manufacturer's instructions at least annually and after every significant change to the detector system.
- 9.2 A background count of sufficient length to meet the required uncertainty and lower limit of detection is made weekly. Daily background checks must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.3 Plateau checks are made after every gas bottle change by counting a check source at the operating voltage. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.4 Determination of counting efficiency.
- 9.4.1 To a clean planchet transfer sufficient ^{228}Ra standard to provide less than or equal to 5% uncertainty at the 1 sigma level. Record volume and activity of standard added.
- 9.4.2 Place the planchet on a hot plate and evaporate to dryness (avoid splattering).
- 9.4.3 Cool and store planchet in a desiccator for at least 48 hours.
- 9.4.4 Count the planchet and determine the net beta activity in counts per minute.

- 9.4.5 Calculate the instrument counting efficiency using the equation in Section 12.2.
- 9.5 Daily, or before use, a check source is counted to verify detector efficiency. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.

10.0 Sample Preparation

10.1 Water

- 10.1.1 Measure a volume of water sample appropriate to meet the required sensitivity, into a 1.5-L beaker. Record comment if presence of undissolved material is noted. For samples less than 1 L, dilute to 1 L with H₂O before adding carrier and tracer.
- 10.1.2 Adjust pH to approximately 1.0 with 16 M HNO₃ and add 2 mL of lead carrier.
- 10.1.3 Add appropriate quantity of ¹³³Ba tracer to the sample to provide less than or equal to 5% uncertainty at the 1 sigma level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.1.4 Continue with Sample Analysis, Section 11.0.

10.2 Glass Fiber Filters

- 10.2.1 Remove the filter from the shipping envelope or bag and hold the filter over a 125-mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside the bag to the platinum dish.
- 10.2.2 Place the dish with sample in a muffle furnace. Ash the sample for about 16 hours at 500°C \pm 15°C.
- 10.2.3 Remove the dish and allow to cool.
- 10.2.4 Completely dampen the sample with a minimum amount but no more than 10 mL of concentrated HNO₃.

- 10.2.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on a hot plate until a moist residue remains. Remove the dish and allow to cool. (**Caution:** Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
- 10.2.6 Add 10 mL of concentrated HF and evaporate until the residue is almost completely dry. Remove the dish and allow to cool.
- 10.2.7 Add 10 mL of concentrated HNO₃ and evaporate until the sample is lightly fuming and just moist. Remove the dish and allow to cool.
- 10.2.8 Repeat Step 10.2.7.
- 10.2.9 Moisten the residue on the sides and bottom of the dish with 3 M HNO₃. Scrape the residue from the sides and bottom of the dish and break it up with a Teflon rod. Wash down the sides of the dish and the Teflon rod thoroughly using 3 M HNO₃.
- 10.2.10 Return the dish to the hot plate and evaporate until about 5 mL of solution remains. Remove the dish and allow to cool.
- 10.2.11 Filter the sample using a funnel and Whatman No. 42 filter paper into a 50-mL volumetric flask.
- 10.2.12 Wash the dish using 3 small portions (less than 5 mL each) of 3 M HNO₃, filtering wash solution into volumetric flask.
- 10.2.13 Wash down the filter and residue with 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.2.14 Make up the contents of the volumetric flask to 50 mL with 3 M HNO₃, stopper, and mix thoroughly.
- 10.2.15 Transfer an appropriate volume of sample to achieve required sensitivity to a 1.5 L beaker. Record volume of sample used.
- 10.2.16 Adjust the volume to approximately 1.0 L with H₂O and add 2 mL of lead carrier.

- 10.2.17 Add appropriate quantity of ^{133}Ba tracer to the sample to provide less than or equal to 5% uncertainty at the 1 sigma level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.2.18 Continue with Sample Analysis, Section 11.0.

11.0 Sample Analysis

- 11.1 Add 100 mL 18 M H_2SO_4 and heat to $70^\circ\text{C} \pm 5^\circ\text{C}$ with stirring for 1 hour. Allow lead sulfate to settle 16 hours (or overnight).
- 11.2 Carefully decant as much clear liquid as possible without losing any precipitate. Pour equal volumes of remaining liquid and precipitate into two centrifuge tubes of equal volume (40 or 100 mL). Centrifuge and decant supernate. If necessary, repeat until all precipitate has been collected in two centrifuge tubes. Slurry precipitate in one tube with 4 M H_2SO_4 , and transfer quantitatively to the other tube using 4 M H_2SO_4 as wash. Centrifuge and discard supernate.
- 11.3 Place stirring bar in tube containing PbSO_4 , and add 1 mL of glacial acetic acid, 6 mL of 41% Na_3DTPA , and 1 mL distilled water. Heat with stirring until dissolution is complete.
- 11.4 Add while stirring 1 mL (20 mg) bismuth carrier and 2 mL 18 M H_2SO_4 . Digest 5 to 10 minutes in hot water bath, cool, centrifuge, and discard supernate.
- 11.5 Add 15 mL of 0.17 M Na_3DTPA to precipitate, place in boiling water bath, and heat with stirring to dissolve precipitate (dissolution may require 20 minutes).
- 11.6 When precipitate has dissolved, add 1 mL of barium carrier (10 mg/mL) and 1 mL Na_2SO_4 (20%), dilute to 28 mL with distilled water, and add 2 mL of 6 M acetic acid. Heat in hot water bath for 5 minutes while stirring with magnetic stirring bar.
- 11.7 Transfer to ice bath. Allow to cool for 5 minutes with stirring. Remove stirring bar and centrifuge. Decant and discard supernate.

- 11.8 Repeat steps 11.5, 11.6, and 11.7, omitting addition of Ba^{+2} in step 11.6. Record time acetic acid is added. The second BaSO_4 precipitation with acetic acid provides an actinium free precipitate and is the start of ingrowth of ^{228}Ac from ^{228}Ra present.
- 11.9 To the BaSO_4 precipitate add 15 mL 0.17 M Na_3DTPA , heat, and stir until all dissolves.
- 11.10 Allow solution to cool, stopper centrifuge tube, and store at least 36 hours to allow ^{228}Ac ingrowth.
- 11.11 After ingrowth period, place sample in boiling water bath, insert magnetic stirring bar, and stir until any precipitate that may have formed during ingrowth period has dissolved. Then add 1 mL 20% Na_2SO_4 , dilute to 28 mL with distilled water, and add 2 mL of 6 M acetic acid. Record time; this ends the ^{228}Ac ingrowth period and begins the ^{228}Ac decay period.
- 11.12 Allow mixture to heat in boiling water bath for 5 minutes with stirring, then remove stirring bar and place centrifuge tube in ice bath for 5 minutes. Centrifuge and decant supernate into clean 40-mL centrifuge tube. Rinse walls with 2 to 3 mL of water, exercising care not to disturb precipitate. Add wash to tube containing supernate.
- 11.13 Add 1 mL of barium carrier (5 mg/mL) to centrifuge tube containing supernate. Heat with stirring in boiling water bath for 5 minutes. Cool in ice water bath for 5 minutes and centrifuge. The second BaSO_4 precipitation ensures complete removal of the radium.
- 11.14 Quantitatively transfer supernate to 100-mL beaker containing 5 mL of 2 M monochloroacetic acid. Measure pH to confirm that it is 3.0. It is important that the pH of the solution containing the actinium is 3.0. If necessary, adjust pH with additional 2 M monochloroacetic acid.
- 11.15 Transfer 50 mL of 15% HDEHP to a 125 mL separatory funnel. Add 50 mL H_2O and shake for 1 minute. Allow layers to separate and discard lower aqueous layer.
- 11.16 Repeat 11.15 using 50 mL of actinium wash solution in place of H_2O .
- 11.17 Transfer sample solution from step 11.14 to the 125-mL separatory funnel.

- 11.18 Shake vigorously for 2 minutes (relieve pressure as needed). Allow layers to separate and discard aqueous (lower) phase.
- 11.19 Add 10 mL of actinium wash solution. Shake for 1 minute, allow layers to separate, and discard aqueous layer.
- 11.20 Repeat step 11.19.
- 11.21 Add 10 mL of 1 M HNO₃. Shake for 1 minute, allow layers to separate, and collect lower layer in 80-mL beaker.
- 11.22 Repeat step 11.21 using 5 mL of 1 M HNO₃. Combine lower aqueous layer in 80-mL beaker containing aqueous fraction from step 11.21. Discard organic phase.
- 11.23 Evaporate solution to dryness on planchet. Continue heating planchet until all nitric acid vapors have been removed. Carefully flame samples to a dull red glow for a few minutes to convert nitrate salts to oxides. Cool in desiccator and count promptly using the manufacturer's suggested operating procedure.
- 11.24 Recount each sample that has a positive detect. Compare the expected activity of the second count to the first count and verify, based on the half-life of ²²⁸Ac, that the activity in the sample is ²²⁸Ac.
- 11.25 Yield Determination
- 11.25.1 Transfer planchet to a calibrated gamma spectroscopy system. Measure ¹³³Ba activity.
- 11.25.2 Calculate chemical yield, Y, by dividing the ¹³³Ba activity of the sample by the ¹³³Ba activity added. Use procedure FM-RAD-0140 (Gamma Spectroscopy) to determine ¹³³Ba activity in the sample.

12.0 Calculations

- 12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

- A = activity at mid-point of counting interval, in dpm, γ/s , or pCi as appropriate,
- A_0 = activity at time of standardization in same units as A,
- λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,
- t = time elapsed from standardization to mid-point of counting interval.

- 12.2 Calculate the instrument counting efficiency using the following equation:

$$E = \frac{(\text{Net Beta cpm})}{(^{228}\text{Ra Added, dpm})}$$

- 12.3 Calculate the chemical yield, Y, of the method using the following equation:

$$\text{Yield}(Y) = \frac{(^{133}\text{Ba Measured})}{(^{133}\text{Ba Added})}$$

- 12.4 Calculate the concentration of ^{228}Ra in pCi/L or pCi/air filter using the following equation:

$$Ra = \frac{C_1 - C_B}{(2.22) (Y) (E) (V) (1 - e^{-0.113 t_1}) (e^{-0.113 t_2})}$$

Where:

| | | |
|-------|---|---|
| C_1 | = | sample counts per minute |
| C_B | = | background counts per minute |
| Y | = | chemical yield from step 12.3 |
| E | = | beta counting efficiency |
| V | = | sample size (L) (V for air filter is fraction of total filter.) |
| t_1 | = | ^{228}Ac period of ingrowth from ^{228}Ra (hr) |
| t_2 | = | ^{228}Ac decay period (hr) measured from the actinium separation to mid-time of beta count |
| 2.22 | = | dpm per pCi |

Note: pCi may be converted to Bq by using the following multiplicative factor: 3.667E-02 Bq/pCi. Final sample results shall be corrected for reagent blank contribution.

12.5 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical service contract(s). The minimum detectable concentration (MDC) in pCi/L (or pCi/air filter) shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project specific Sampling and Analysis Plan, or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|----------------------------|-------------------|------------------|-------------------|
| Reagent Blank [™] | 1/20 [*] | To be determined | Qualify Data |
| ¹³³ Ba Yield | 1/1 | To be determined | Qualify Data |
| LCS | 1/20 [*] | To be determined | Qualify Data |
| Duplicate [™] | 1/20 [*] | To be determined | Qualify Data |

^{*} or per batch or fraction thereof

[™] per matrix

15.0 Reference

Eastern Environmental Radiation Facility Radiochemistry Procedures Manual.
Montgomery, Alabama. U.S. EPA, EPA-520/5-84-006. 1984.

Radium-226 in Water by Emanation/Scintillation Counting

Working Linear Range: Greater than 0.1 pCi/L, infinite with dilution
Reporting Limit: ~0.1 pCi/L
Reporting Units: pCi/L
Matrix: Water

1.0 Scope and Application

- 1.1 The method is used for the determination of low-level radium-226 activity in water. The nominal sensitivity of the procedure may vary with each analysis but is approximately 0.1 pCi/L in water.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 The method is based on the emanation and scintillation counting of the radon-222 (^{222}Rn) progeny of radium-226 (^{226}Ra). It is made specific for ^{226}Ra by allowing the shorter-lived radon progeny of other radium isotopes to decay before counting.
- 2.2 Radium is coprecipitated with barium sulfate and the resulting barium-radium sulfate is decomposed with phosphoric acid. The glassy melt product is dissolved to form soluble barium-radium salts. The salts are dissolved and the solution stored to allow the ^{222}Rn to ingrow. After the ingrowth period, the radon gas is purged from the solution, collected in a counting cell, and counted after a 4-hour wait. Radium-226 yield is determined by using a ^{133}Ba tracer.

3.0 Interferences

Gaseous alpha-emitting radionuclides such as radon-219 and radon-220 or their alpha-emitting progeny could interfere.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling low-level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Radon bubbler and assembly. See Figures 1 and 2.
- 6.2 Radon scintillation chamber. See references 15.1 and 15.2 for examples.
- 6.3 Gas purification tube, containing ascarite and magnesium perchlorate. See Figure 2.
- 6.4 Manometer, 0 to 760 mm Hg, having a volume that is small compared to the scintillation chamber.
- 6.5 Scintillation counter assembly: a photomultiplier tube (PMT) coupled to an appropriate preamplifier, HV supply, and scaler.
- 6.6 Membrane filters: 0.45 μ m pore size, millipore or equivalent.
- 6.7 Silicone grease, high vacuum.
- 6.8 Platinum crucibles.
- 6.9 Gamma spectrometer to count ¹³³Ba tracer: Large volume (> 50 cm³) Ge detector with full width at one-half the peak maximum (FWHM) less than 2.5 keV at 1,332 keV, and associated electronics.
- 6.10 Class A Volumetric Glassware: For carrier and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.

7.0 Routine Preventive Maintenance

- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents

- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. All radionuclide standards must be corrected for decay. In all cases, acids and bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Ammonium sulfate solution ($(\text{NH}_4)_2\text{SO}_4$), 100 g/L: Dissolve 10 grams $(\text{NH}_4)_2\text{SO}_4$ in water and dilute to 100 mL.
- 8.4 Barium chloride carrier stock solution (BaCl_2), 10 grams Ba/L: Dissolve 17.8 grams $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water. Dilute to 1 L with water.
- 8.5 ^{133}Ba tracer solution: NIST, NIST-traceable, or another nationally recognized agency.
- 8.6 Barium chloride carrier working solution (BaCl_2), 1 gram Ba/L: Dilute 100 mL of barium chloride stock solution to 1 L with water and mix thoroughly. Allow to stand for 24 hours, and filter through membrane filter.
- 8.7 EDTA/Sodium carbonate cleaning solution: Dissolve 10 grams of disodium ethylenediaminetetraacetate and 10 grams of sodium carbonate (Na_2CO_3) in water. Dilute to 1 L.
- 8.8 Hydrochloric acid (HCl), 12 M: Concentrated reagent.
- 8.9 Hydrochloric acid solution (HCl), 6M: Dilute 500 mL concentrated HCl to 1 L with H_2O .

- 8.10 Hydrochloric acid solution (HCl), 1 M: Dilute 83 mL concentrated HCl to 1 L with H₂O.
- 8.11 Hydrochloric acid solution (HCl), 0.25 M: Dilute 20.8 mL concentrated HCl to 1 L with H₂O.
- 8.12 Hydrochloric acid solution (HCl), 0.1 M: Dilute 8.3 mL concentrated HCl to 1 L with H₂O.
- 8.13 Hydrofluoric acid (HF), Concentrated (48% HF) reagent.
- 8.14 Hydrogen peroxide (H₂O₂): Mix 1 volume 30% H₂O₂ with 9 volumes H₂O.
- 8.15 Phosphoric acid (H₃PO₄), Concentrated.
- 8.16 Magnesium perchlorate (Mg(ClO₄)₂), Anhydrous reagent.
- 8.17 Radium-226 standard solution: from NIST, NIST-traceable, or from another nationally recognized agency.
- 8.18 Sulfuric acid (H₂SO₄), 18 M: Concentrated reagent.
- 8.19 Sulfuric acid solution (H₂SO₄), 0.05 M: Dilute 2.7 mL concentrated H₂SO₄ to 1 L with H₂O.
- 8.20 Aerosol OT: 0.1% aqueous mixture.
- 8.21 Washing solution, add 0.1% Aerosol OT to 0.05 M H₂SO₄ to achieve a final dilution of 10 mL 0.1% Aerosol OT per liter H₂SO₄.
- 8.22 Ascarite: 8 to 20 mesh.
- 8.23 Helium: High pressure, dual-regulated cylinder.
- 8.24 Nitric acid (HNO₃), 16 M: Concentrated reagent.
- 9.0 Calibration Procedures**
- 9.1 All apparatus should be thoroughly checked before use to ensure it is free from defects and works properly.

- 9.2 Test each bubbler before use by adding about 10 mL water and passing air through it at a rate of 3 to 5 mL/min. The procedure should produce many fine bubbles rather than a few large ones. Do not use bubblers requiring excess pressure to initiate bubbling.
- 9.3 The counting efficiency for each combination of scintillation cell, PMT, and electronics used must be determined.
- 9.3.1 Place 5 mL barium carrier working solution, 1 mL concentrated HCl, and 3 mL radium standard solution (10 pCi/mL) in the bubbler. Fill bubbler two-thirds to three-fourths full with water.
- 9.3.2 Continue scintillation cell calibration beginning at step 11.4.
- 9.3.3 Calculate efficiency using the equation in Section 12.1.
- 9.3.4 Label cell with efficiency value, date of calibration, and PMT system identification.
- 9.3.5 Perform steps 9.3.1 to 9.3.4 initially for every new scintillation cell before use and after every 20 uses or semi-annually, whichever is more frequent.
- 9.3.6 If the PMT system is changed (i.e., components replaced or repaired) in any way, counting efficiency must be reestablished.
- 9.4 A background is measured for each scintillation chamber used. A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed before using the cell. The results must be within established limits (e.g., $\pm 3 \sigma$) before commencing analyses.
- 10.0 Sample Preparation**
- 10.1 Transfer an aliquot of thoroughly mixed water sample sufficient to achieve the required sensitivity to a 1,500-mL beaker. For samples less than 1 L, dilute up to 1 L with 0.25 M HCl.
- 10.1.1 Record volume of sample used. Record comment if presence of any undissolved material is noted.

- 10.2 Acidify sample with 20 mL concentrated HCl. While vigorously stirring, add 50 mL barium carrier working solution and sufficient ^{133}Ba tracer to provide less than or equal to 5% uncertainty at the 1 sigma level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.3 While stirring rapidly, cautiously add 20 mL concentrated H_2SO_4 and continue to stir for 1 hour. Cover beaker and allow precipitate to develop overnight.
- 10.4 Filter sample through membrane filter using washing solution to transfer solids to filter. Wash solids twice with washing solution.
- 10.5 Place membrane filter in a 30-mL platinum crucible, add 0.5 mL of concentrated HF and 3 drops (0.15 mL) of $(\text{NH}_4)_2\text{SO}_4$ solution, and evaporate to dryness.
- 10.6 Carefully ignite filter and residue over small flame until carbon is burned off.
- 10.7 Cool and add 1 mL of concentrated H_3PO_4 and heat on hot plate to about 200°C . Gradually raise temperature to 300° to 400°C for 30 minutes.
- 10.8 Swirl crucible over a low bunsen flame, adjusted to avoid spattering. Swirl so that crucible walls are covered with hot, concentrated H_3PO_4 . Continue to heat until BaSO_4 dissolves to give a clear melt (just below redness), and then heat for 1 minute more to ensure removal of SO_3 .
- 10.9 Cool crucible, fill it one-half full with 6M HCl, heat on steam bath, then gradually add water to within 2 mm of top of crucible.
- 10.10 Evaporate on steam bath until there are no more vapors of HCl.
- 10.11 Add 6 mL 1 M HCl, swirl, and warm to dissolve BaCl_2 crystals.

11.0 Sample Analysis

- 11.1 To prepare a scintillation cell for use, evacuate and cautiously refill with helium. Repeat evacuation and refill cycle twice, more often following samples with high ^{222}Rn activities.
- 11.2 Clean bubblers by rinsing with 0.25 M HCl. If previous sample activity exceeded 10 pCi (^{226}Ra), then remove stopcock grease and soak in $90^\circ\text{C} \pm 10^\circ\text{C}$ EDTA/

Na_2CO_3 solution for 1 hour. Remove, cool, and rinse with distilled water. Soak in warm 1M HCl for about 30 minutes, remove, cool, and rinse with distilled water. Dry and regrease the stopcocks.

- 11.3 Close inlet stopcock of greased and tested radon bubbler. Add a drop of water to fritted disk, and transfer sample from centrifuge tube to bubbler using medicine dropper. Rinse tube with at least three 2-mL portions of water. Add water until bubbler is two-thirds to three-fourths full.
- 11.4 Insert outlet stopcock into bubbler with stopcock open.
- 11.5 Adjust helium regulator so a very small stream of gas will flow with the needle valve open. Attach helium supply to bubbler inlet, and adjust inlet pressure to produce a froth a few millimeters thick. Establish a "zero" ingrowth time by purging liquid with helium for 15 to 20 minutes.
- 11.6 In rapid succession, close inlet stopcock, remove gas connection, and close outlet stopcock. Record date and time and store bubbler, for at least 2 weeks, before collecting and counting the radon. For higher activity samples, shorter ingrowth times are acceptable if the required sensitivity can be met.
- 11.7 Radon Counting
 - 11.7.1 Attach a prepared scintillation chamber (see Section 11.1) to bubbler assembly. Substitute glass tube with stopcock for bubbler so helium gas can be turned off conveniently. Open stopcock on scintillation chamber, close stopcock to gas, and gradually open stopcock to vacuum source to evacuate cell.
 - 11.7.2 Close stopcock to vacuum source, and check manometer reading for 2 minutes to check system for leaks.
 - 11.7.3 Open stopcock to helium gas and cautiously allow scintillation chamber to reach atmospheric pressure. Close all stopcocks.
 - 11.7.4 Place scintillation cell on PMT in light-tight housing. Wait 10 minutes and collect a background count for at least 100 minutes.
 - 11.7.5 Remove scintillation cell from PMT, and attach it to radon bubbler with all stopcocks closed.

- 11.7.6 Open stopcock to vacuum and then to scintillation chamber, and allow chamber and gas purification system to evacuate. Close vacuum stopcock and check manometer for leaks.
- 11.7.7 Adjust helium regulator so that a very slow stream of gas will flow with needle valve open. Attach helium supply to inlet of bubbler.
- 11.7.8 Cautiously open bubbler outlet stopcock and allow pressure to equalize to transfer all or most of the liquid in bubbler side-arm to the bubbler chamber.
- 11.7.9 Close outlet stopcock and very cautiously open inlet stopcock to flush remaining fluid from side-arm and fritted disk. Close inlet stopcock.
- 11.7.10 Perform steps 11.7.8 and 11.7.9 several times to achieve nearly equal pressure on the two sides of the bubbler.
- 11.7.11 With outlet stopcock fully open, cautiously open inlet stopcock so that flow of gas produces a froth a few millimeters thick at surface of bubbler solution. Maintain flow rate by adjusting pressure with regulator valve and continue de-emanation until pressure in scintillation chamber reaches atmospheric (15 to 20 minutes).
- 11.7.12 In rapid succession, close stopcocks to scintillation chamber, bubbler inlet, and bubbler outlet. Shut off and disconnect gas supply. Record time and date, which is the end of ingrowth and beginning of decay.
- 11.7.13 Four hours after de-emanation, place scintillation chamber on PMT, wait 10 minutes, and count. Record date and time counting was started and finished.
- 11.8 Yield Determination
- 11.8.1 Use procedure FM-RAD-0140 (Gamma Spectrometry) to determine the ^{133}Ba activity in the sample.
- 11.8.2 Transfer solution in bubbler to gamma counting container. Wash bubbler thoroughly with 1M HCl, and combine with sample in container.
- 11.8.3 Calculate sample yield, Z, by dividing the ^{133}Ba activity of the sample by the ^{133}Ba activity of a 50-mL aliquot of BaCl_2 carrier working solution counted under identical conditions (volume, geometry, matrix) as the sample.
- 11.8.4 Sample may be stored for a second counting or discarded.

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12.0 Calculations

- 12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

- A = activity at mid-point of counting interval, in dpm, γ/s , or pCi as appropriate,
- A_0 = activity at time of standardization in same units as A,
- λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,
- t = time elapsed from standardization to mid-point of counting interval.

- 12.2 Counting Efficiency. Calculate efficiency for each scintillation cell and PMT system combination as:

$$E = \frac{\left[\frac{S}{t_1} - \left(\frac{S_B}{t_B} \right) \right] [\lambda] t_1}{(R) (1 - e^{-\lambda t_1}) (1 - e^{-\lambda t_B}) (e^{-\lambda t_1})}$$

Where:

- E = efficiency of scintillation chamber (cpm/dpm)
- S = number of counts accumulated from standard
- S_B = number of background counts
- t_B = background counting time (min)
- t_1 = counting time of standard (min)

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- t_2 = ingrowth period of ^{222}Rn (min)
 t_3 = decay time of ^{222}Rn from de-emanation until counting (min)
 λ = ^{222}Rn decay constant, $1.26 \times 10^{-4} \text{ min}^{-1}$
 R = activity of radium standard added (dpm)

Note: Use the same units for all times, and decay constant.

12.3 Yield

Calculate chemical yield as:

$$\text{YIELD}(Z) = \frac{(^{133}\text{Ba Measured})}{(^{133}\text{Ba Added})}$$

12.4 Radium-226 Concentration

$$\text{Radium} = \frac{\left(\frac{C}{(E)(V)(Z)} - B\right)}{2.22} \text{ pCi/L}$$

Where:

- 2.22 = conversion factor from dpm to pCi
 E = scintillation cell efficiency
 B = reagent blank result (dpm/L)

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- V = volume of sample (L)
 Z = chemical yield of method

and,

$$C = \frac{\left[\frac{N}{t_1} - \left(\frac{N_B}{t_B} \right) \right] [\lambda] t_1}{(1 - e^{-\lambda t_1}) (1 - e^{-\lambda t_2}) (e^{-\lambda t_3})}$$

Where:

- C = net counts per minute
 N = number of sample counts accumulated
 N_B = number of background counts determined prior to use
 t_B = background counting time (min)
 t_1 = counting time of sample (min)
 t_2 = ingrowth period of ^{222}Rn (min)
 t_3 = decay time of ^{222}Rn from de-emanation until counting (min)
 λ = ^{222}Rn decay constant, $1.26 \times 10^{-4} \text{ min}^{-1}$

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels and are outlined in the FEMP QAPjP or specified in the project-specific Sampling and Analysis Plan, or the analytical laboratory services contract(s).

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Levels and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

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Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Correctove Action |
|-------------------------|-------------------|------------------|-------------------|
| Reagent Blank* | 1/20 ^m | To be determined | Qualify Data |
| ¹³³ Ba Yield | 1/1 | To be determined | Qualify Data |
| LCS | 1/20 ^m | To be determined | Qualify Data |
| Duplicate* | 1/20 ^m | To be determined | Qualify Data |

* per matrix

^m or per batch or fraction thereof

15.0 References

- 15.1 U.S. Department of Energy Environmental Measurements Laboratory. *EML Procedures Manual*. HASL-300, 27th ed. 1990.
- 15.2 American Society for Testing and Materials. *1991 Annual Book of ASTM Standards*. Method D3454, Standard Test Method for Radium-226 in Water. Vol. 11.02.

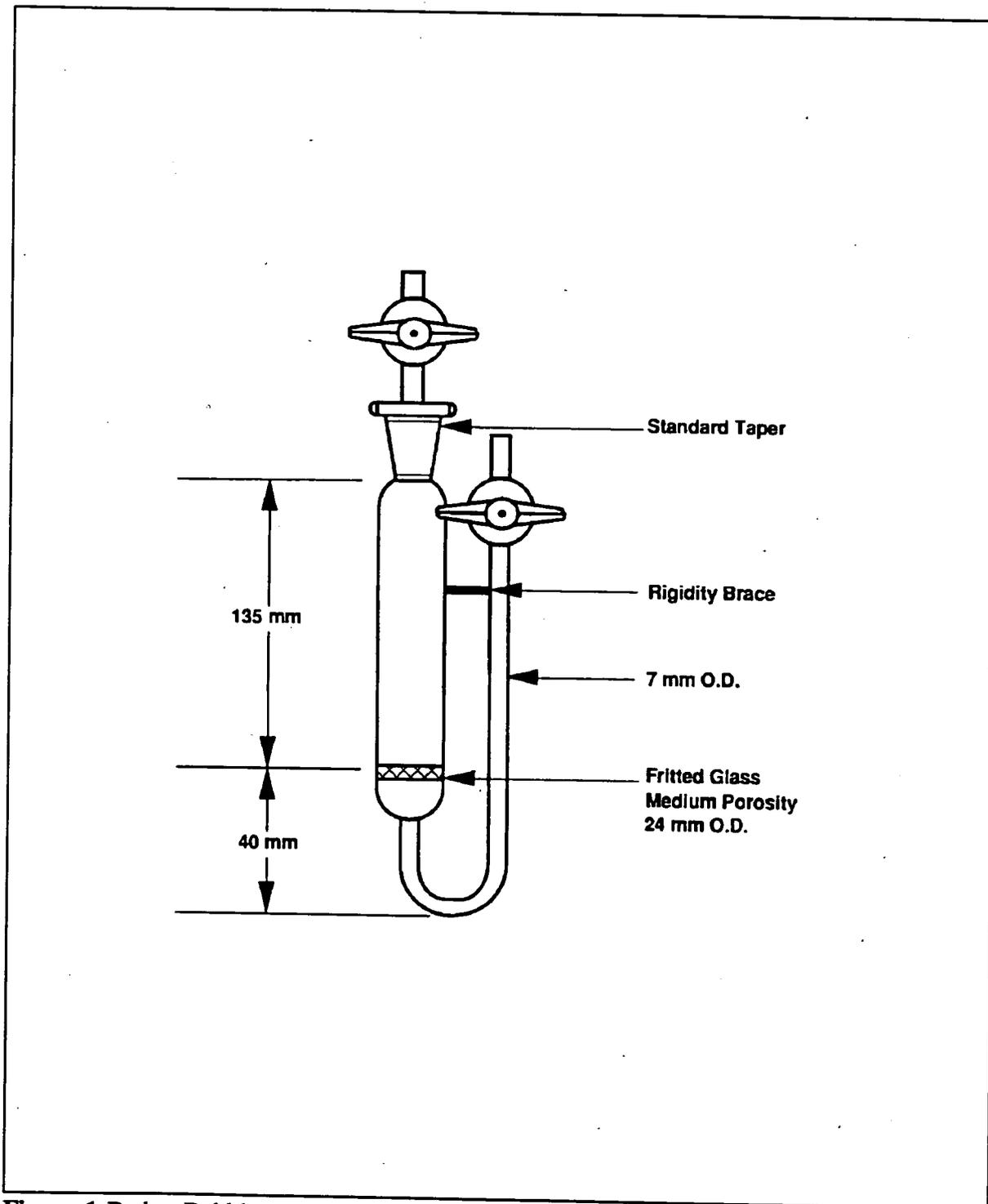


Figure 1 Radon Bubbler

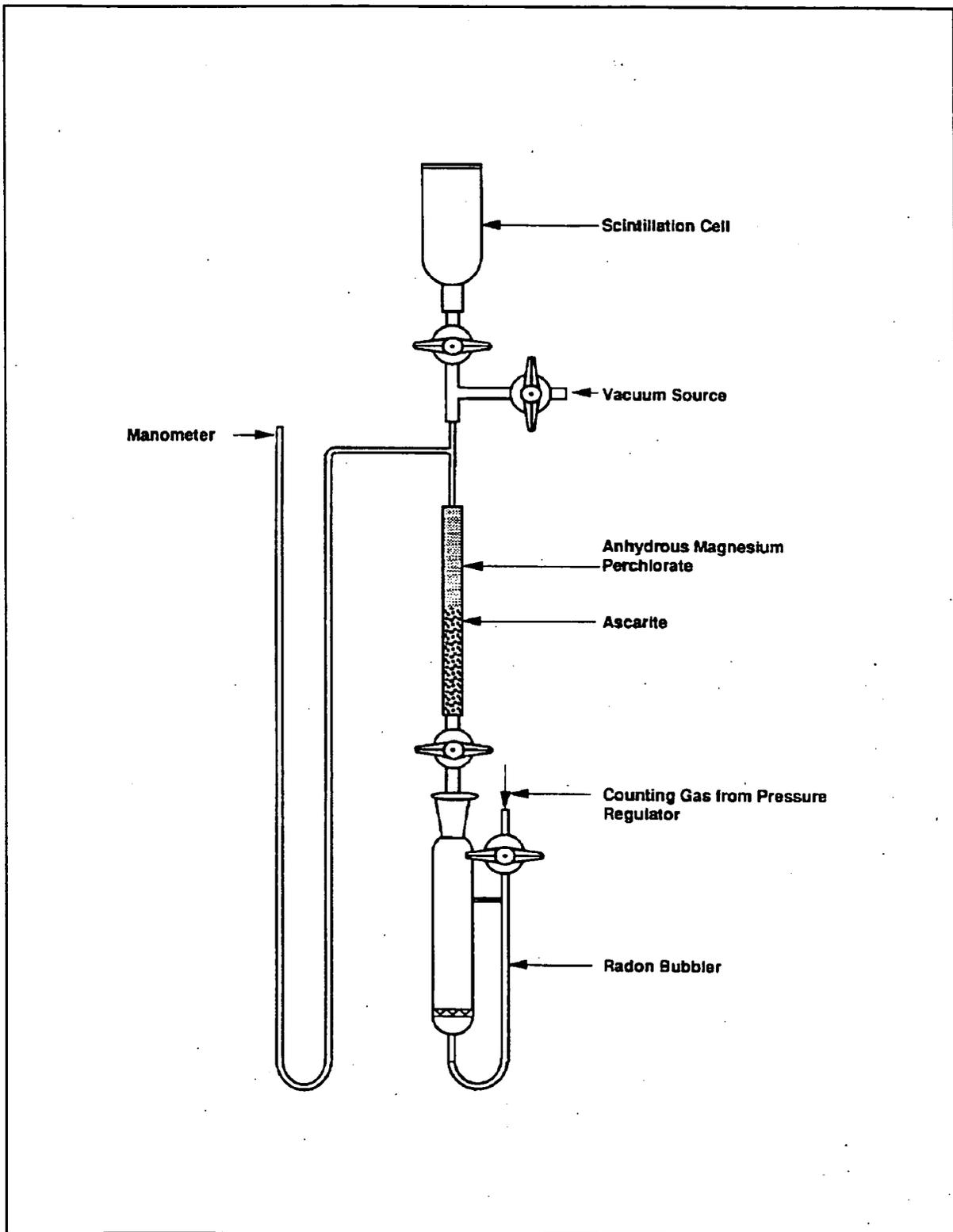


Figure 2 Radon Bubbler Assembly

Radium-226 in Soil/Sediment, Milk, and Air Filters by Emanation/Scintillation Counting

Working Linear Range: Infinite with dilution
Reporting Limit: ~0.1 pCi/L Milk, ~0.04 pCi/g Solids, TBD Air Filters
Reporting Units: Milk, pCi/L; Solids, pCi/g; Air filters, pCi/air filter
Matrices: Milk, soil/sediment, air filters

1.0 Scope and Application

- 1.1 The method is used for the determination of low-level radium-226 activity in soil/sediment, milk, and air filters. The technique may be applied to almost any material that can be converted to a homogeneous solution. The nominal sensitivity of the procedure may vary with each analysis but is approximately 0.04 pCi/g for soil/sediment and 0.1 pCi/L for milk. The nominal sensitivity that may be obtained by this exact method for air filters needs performance data.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 The method is based on the emanation and scintillation counting of the radon-222 (^{222}Rn) progeny of radium-226 (^{226}Ra). It is made specific for ^{226}Ra by allowing the shorter-lived radon progeny of other radium isotopes to decay before counting.
- 2.2 After sample pretreatment, most interferences are removed by successive fuming nitric acid separations. Radium is then coprecipitated with barium chromate and dissolved in perchloric acid and water. The solution is stored to allow the ^{222}Rn to ingrow. After the ingrowth period, the radon gas is purged from the solution, collected in a counting cell, and counted after a 4-hour wait. Radium-226 yield is determined by using a ^{133}Ba tracer.
- 2.3 The method differs for the sample matrices only in the sample preparation steps.

3.0 Interferences

Gaseous alpha emitting radionuclides, such as radon-219 and radon-220 or their alpha emitting progeny could interfere.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low-level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Radon bubbler and assembly. See Figures 1 and 2.
- 6.2 Radon scintillation chamber. See references for examples.
- 6.3 Gas purification tube, containing ascarite and magnesium perchlorate. See Figure 2.
- 6.4 Manometer, 0-760 mm Hg, having a volume that is small compared to the scintillation chamber.
- 6.5 Scintillation counter assembly: a photomultiplier tube (PMT) coupled to the appropriate preamplifier, HV supply, and scaler.
- 6.6 Membrane filters: 0.45- μm pore size, Millipore or equivalent.
- 6.7 Silicone grease, high vacuum.
- 6.8 Platinum crucibles.

- 6.9 Gamma spectrometer to count ^{133}Ba tracer: Large volume ($> 50 \text{ cm}^3$) Ge detector with full width at one-half the peak maximum (FWHM) less than 2.5 keV at 1,332 keV, and associated electronics.
- 6.10 Glass fiber filters, Gelman type A/E or equivalent, 9 cm, 5.5 cm, 15 cm, and 4 cm, and 2.8 cm.
- 6.11 Whatman No. 42 filter paper, 9 cm and 15 cm.
- 6.12 Teflon-coated stirring bar.
- 6.13 Electric hot plate/magnetic stirrer: Apparatus should have built in stirrer and stepless temperature controls that can be changed as heating requirements demand.
- 6.14 Drying oven: The gravity convection type oven is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 125°C and able to maintain temperatures within $\pm 5^\circ\text{C}$.
- 6.15 Muffle furnace: Able to reach and maintain at least 900° and able to maintain temperatures within $\pm 15^\circ\text{C}$.
- 6.16 Fisher filtrator unit (or equivalent).
- 6.17 Funnels, beakers, flasks
- 6.18 pH meter: Scale Readability to ± 0.1 pH units.
- 6.19 Class A volumetric glassware: For carrier and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 7.0 Routine Preventive Maintenance**
- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents

- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. All radionuclide standards must be corrected for decay. In all cases, acids and bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Barium chloride carrier (BaCl_2), 20 mg Ba/mL: Dissolve 30.4 grams BaCl_2 per liter of 0.12 M HCl.
- 8.4 Yttrium nitrate carrier ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), 10 mg Y/mL: Dissolve 43.5 grams of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ per liter of H_2O . Note: See Reference Attachment A for yttrium carrier cleanup procedure.
- 8.5 ^{133}Ba tracer solution: from NIST, NIST-traceable, or from another nationally recognized agency.
- 8.6 Acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), 6M: Dilute 345 mL of glacial $\text{C}_2\text{H}_4\text{O}_2$ to 1 L with H_2O .
- 8.7 Ammonium acetate solution ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$), 6M: Dissolve 462 grams $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ per Liter of H_2O .
- 8.8 Sodium chromate solution (Na_2CrO_4): Dissolve 100 grams Na_2CrO_4 per Liter of H_2O .
- 8.9 Hydrochloric acid (HCl), 12 M: Concentrated reagent.
- 8.10 Hydrochloric acid solution (HCl), 6M: Dilute 500 mL concentrated HCl to 1 L with H_2O .
- 8.11 Hydrochloric acid solution (HCl), 1 M: Dilute 83 mL concentrated HCl to 1 L with H_2O .
- 8.12 Hydrochloric acid solution (HCl), 0.25 M: Dilute 20.8 mL concentrated HCl to 1 L with H_2O .
- 8.13 Perchloric acid (HClO_4), Concentrated reagent.
- 8.14 Hydrogen peroxide (H_2O_2), 30%.

- 8.15 Phosphoric acid (HPO_4), Concentrated reagent.
- 8.16 Magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$), anhydrous, reagent.
- 8.17 Radium-226 standard solution: NIST, NIST-traceable, or another nationally recognized agency.
- 8.18 Ascarite: 8 to 20 mesh.
- 8.19 Helium: High pressure, dual-regulated cylinder.
- 8.20 Nitric acid (HNO_3), 16 M: Concentrated reagent.
- 8.21 Nitric acid (HNO_3), 90% fuming.
- 8.22 Nitric Acid (HNO_3), 8 M: Dilute 500 mL of concentrated HNO_3 to 1 L with H_2O .
- 8.23 Nitric Acid (HNO_3), 3 M: Dilute 188 mL of concentrated HNO_3 to 1 L with H_2O .
- 8.24 0.1% Aerosol OT
- 8.25 Sodium carbonate (Na_2CO_3), reagent.

Note: Reagent grade sodium carbonate Na_2CO_3 has inherent ^{226}Ra activity. It is necessary to analyze the Na_2CO_3 reagent used with each batch of samples for ^{226}Ra so that blank corrections can be made. If necessary the reagents must be purified.

Simple purification of the Na_2CO_3 will reduce the ^{226}Ra content of the reagent by an appreciable factor. Dissolve a bulk quantity of Na_2CO_3 with H_2O in a 3-L beaker. Heat and stir until Na_2CO_3 is completely dissolved. Add about 50 mL of barium carrier to precipitate BaCO_3 and continue heating and stirring for about 30 minutes. Filter and discard precipitate. Evaporate filtrate to dryness, grind to powder with mortar and pestle, and use resulting refined Na_2CO_3 for fusions.

- 8.26 Sodium hydroxide (NaOH), 240 g/L: Dissolve 240 grams of NaOH per 1 Liter of H_2O .
- 8.27 Hydrofluoric Acid (HF), concentrated reagent.
- 8.28 Ammonium Hydroxide (NH_4OH), 15 M: Concentrated reagent.

8.29 Ammonium Hydroxide (NH_4OH), 7.5 M: Dilute 500 mL NH_4OH to 1 L with H_2O .

9.0 Calibration Procedures

9.1 All apparatus should be thoroughly checked before use to ensure it works properly and is free of defects.

9.2 Test each bubbler before use by adding about 10 mL water and passing air through it at a rate of 3 to 5 mL/min. This procedure should produce many fine bubbles rather than a few large ones. Do not use bubblers requiring excess pressure to initiate bubbling.

9.3 The counting efficiency for each combination of scintillation cell, PMT, and electronics used must be determined.

9.3.1 Place 5 mL barium carrier working solution, 1 mL concentrated HCl, and 3 mL radium standard solution (10 pCi/mL) in the bubbler. Fill bubbler two-thirds to three-fourths full with water.

9.3.2 Continue scintillation cell calibration by continuing the procedure at step 11.4.

9.3.3 Calculate efficiency using the equation in Section 12.1.

9.3.4 Label cell with efficiency value, date of calibration, and PMT system identification.

9.3.5 Perform steps 9.3.1 to 9.3.4 initially for every new scintillation cell before use and after every 20 uses or semi-annually, whichever is more frequent.

9.3.6 If the PMT system is changed (i.e., components replaced or repaired) in any way, counting efficiency must be reestablished.

9.3.7 A background is measured for each scintillation chamber used. A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed before using the cell. The results must be within established limits (e.g., $\pm 3 \sigma$) before commencing analyses.

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10.0 Sample Preparation

10.1 Soil/Sediment

10.1.1 Dry sample overnight at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$. Pass dried sample (typically 100 grams) through a 2-mm sieve to remove stones, etc. Pass sieved sample through grinder, ball mill, or pulverizer to reduce sample to pass 15-mesh screen. Blend until thoroughly mixed.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

10.1.2 Transfer an appropriate amount of sample to achieve required sensitivity to a platinum crucible. Record weight (dry) of sample used. Add four times the sample weight of Na_2CO_3 and mix thoroughly. Process an equal amount of Na_2CO_3 as a blank through the entire analysis.

10.1.3 Fuse to a clear melt in an electric muffle furnace at $900^{\circ}\text{C} \pm 15^{\circ}\text{C}$. Cool by quenching crucible in cold water.

10.1.4 Crush and grind the melt to powder with mortar and pestle.

10.1.5 Transfer ground material to 600-mL beaker and add 400 mL of H_2O . Police crucible thoroughly with H_2O . Retain crucible.

10.1.6 Add 1 mL of Ba carrier and sufficient ^{133}Ba tracer to provide less than or equal to 5% uncertainty at the 1 sigma level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

10.1.7 Heat to $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and stir for about 1 hour.

10.1.8 Cool and filter with suction through Buchner funnel with 9-cm glass fiber filter backed by 9-cm Whatman No. 42 filter paper into 1-L sidearm flask. Wash filter with H_2O . Remove funnel and discard filtrate. Replace funnel on flask.

10.1.9 Dissolve carbonates on paper with 8 M HNO_3 with suction off, collecting the solution. Apply suction and wash with 8 M HNO_3 . Dissolve any material adhering to sides of platinum crucible with 8 M HNO_3 , and combine with sample by passing through filter. Discard filters.

- 10.1.10 Transfer solution of alkaline earth nitrates to original 600-mL beaker and evaporate to dryness.
- 10.1.11 Add 40 mL of H₂O and stir. Slowly add 40 mL of 90% fuming HNO₃ to dissolve solid matter, then add an additional 400 mL of 90% fuming HNO₃. Stir for 20 minutes.
- 10.1.12 Continue with Section 10.4.
- 10.2 Milk
- 10.2.1 Measure appropriate volume of milk to achieve required sensitivity (typically 0.7 kg) into a ceramic or vycor container. Record volume of sample used.
- 10.2.2 Evaporate sample to dryness. Evaporation must be done carefully to avoid spattering. A drying oven at 110° to 125°C or a controlled drip apparatus, e.g. a buret and hot plate, may be used.
- 10.2.3 Place container with dried sample in muffle furnace and increase temperature slowly up to 325°C to avoid ignition of sample. Increase temperature to 550°C ± 15°C and continue ashing until ash appears white. Total ashing time could be 16 hours or more.
- 10.2.4 If entire sample is to be used, do not grind or blend ash. If sample will be split or only a portion used, grind ash to pass a 40-mesh screen followed by thorough blending. Transfer entire sample or aliquot to a 600-mL beaker.
- 10.2.5 Add enough 8 M HNO₃ to dissolve the ash (usually about 50 mL).
- 10.2.6 Add 1 mL of barium carrier solution and sufficient ¹³³Ba tracer solution to achieve less than or equal to 5% uncertainty at the 1 sigma level.
- Note:** The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.
- 10.2.7 Heat to boiling and digest for 5 minutes. Solution should be complete except for traces of carbon and silica.
- 10.2.8 Filter by suction through a 5.5-cm glass fiber filter to remove insoluble material. Wash the residue with 8 M HNO₃. Discard the residue.
- 10.2.9 Return solution to original beaker, and dilute to about 400 mL with H₂O.

- 10.2.10 Add 2 to 3 mL of H_3PO_4 .
- 10.2.11 Add NaOH pellets slowly with stirring to a pH of 5 to 6 (point at which turbidity just persists). Slowly add NaOH solution (240 g/L) to a pH of 10. Stir for 30 minutes.
- Note:** The blank for the procedure should be prepared by taking the same amount of solid NaOH as used in this step and dissolving it at a minimum of 8 M HNO_3 . The barium carrier and ^{133}Ba tracer should be added, then 2 to 3 mL of H_3PO_4 , and the pH should be adjusted to 10 with NaOH solution. The blank is then carried through the rest of the procedure.
- 10.2.12 Allow phosphate precipitate to settle and cool (3 to 4 hours). Filter by suction on a 15-cm glass fiber filter backed by a 15-cm Whatman No. 42 filter paper. Discard filtrate.
- 10.2.13 Slowly add 150 mL of hot 8 M HNO_3 to phosphate precipitate, dissolving it completely. Apply suction and wash filter with 8 M HNO_3 . Discard filter and any residue.
- 10.2.14 Transfer solution to original 600-mL beaker and evaporate almost to dryness (use low heat to avoid bumping).
- 10.2.15 Add 40 mL of H_2O and stir on combination hot/plate magnetic stirrer using Teflon-coated stirring bar. Slowly add 40 mL of 90% fuming HNO_3 to dissolve solid matter, then add an additional 100 mL of 90% fuming HNO_3 . Stir for 20 minutes.
- 10.2.16 Continue with Section 10.4.
- 10.3 Glass Fiber Filters
- 10.3.1 Remove the filter from the shipping envelope or bag and hold the filter over a 125 mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside the bag to the platinum dish.
- 10.3.2 Place the dish with sample in a muffle furnace. Ash the sample for about 16 hours at $500^\circ\text{C} \pm 15^\circ\text{C}$.
- 10.3.3 Remove the dish and allow to cool.

- 10.3.4 Completely dampen the sample with a minimum amount but no more than 10 mL of concentrated HNO_3 .
- 10.3.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on a hot plate until a moist residue remains. Remove the dish and allow to cool. (**Caution:** Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
- 10.3.6 Add 10 mL of concentrated HF and evaporate until the residue is almost completely dry. Remove the dish and allow to cool.
- 10.3.7 Add 10 mL of concentrated HNO_3 and evaporate until the sample is lightly fuming and just moist. Remove the dish and allow to cool.
- 10.3.8 Repeat above step (step 10.3.7).
- 10.3.9 Moisten the residue on the sides and bottom of the dish with 3 M HNO_3 . Scrape the residue from the sides and bottom of the dish and break it up with a teflon rod. Wash down the sides of the dish and the Teflon rod thoroughly using 3 M HNO_3 .
- 10.3.10 Return the dish to the hot plate and evaporate until about 5 mL of solution remains. Remove the dish and allow to cool.
- 10.3.11 Filter the sample using a funnel and Whatman No. 42 filter paper into a 50 mL volumetric flask.
- 10.3.12 Wash out the dish using 3 small portions (less than 5 mL each) of 3 M HNO_3 .
- 10.3.13 Wash down the filter and residue with 3 small portions (less than 5 mL each) of 3 M HNO_3 .
- 10.3.14 Make up the contents of the volumetric flask to 50 mL with 3 M HNO_3 , stopper, and mix thoroughly.
- 10.3.15 Transfer an appropriate amount of sample to achieve required sensitivity to a beaker and evaporate almost to dryness. Record sample volume used.

- 10.3.16 Add 1 mL of barium carrier solution and sufficient ^{133}Ba tracer solution to achieve less than or equal to 5% uncertainty at the 1 sigma level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.3.17 Add 40 mL of water and stir on a hot plate/magnetic stirrer using a Teflon coated bar. Slowly add 40 mL of 90% fuming HNO_3 to dissolve solid matter, then add an additional 100 mL of 90% fuming HNO_3 . Stir for 20 minutes.

- 10.3.18 Continue with Section 10.4.

10.4 Final HNO_3 separation

- 10.4.1 Cool and allow calcium and barium nitrates to settle. Using a Buchner funnel, filter by suction through 4-cm glass fiber filter into 250-mL side-arm flask. Drain thoroughly, remove funnel from flask, and discard filtrate. Place funnel in Fisher filtrator unit with 150-mL beaker as collection vessel.

- 10.4.2 With suction on, transfer remaining precipitate in beaker to funnel with H_2O . Wash filter with H_2O and drain funnel thoroughly. Discard filter and any residue.

- 10.4.3 Evaporate solution slowly to dryness, then dissolve residue with 23 mL of H_2O .

- 10.4.4 Add 77 mL of 90% fuming HNO_3 with magnetic stirring, using Teflon-coated stirring bar. Stir for 20 minutes.

- 10.4.5 Cool and allow nitrate precipitate to settle. Filter through Buchner funnel onto 2.8-cm glass fiber filter into 250-mL side-arm flask. Remove as much acid as possible with suction. Remove funnel and discard filtrate.

- 10.4.6 Dissolve remaining precipitate in beaker with a few mL of H_2O . Place funnel on Fisher filtrator, pour through funnel, and collect solution in 40-mL short cone, heavy walled centrifuge tube. Wash filter with H_2O , keeping total volume below 20 mL. If larger volume is collected, reduce volume to about 20 mL by heating on hot water bath ($90^\circ\text{C} \pm 10^\circ\text{C}$). The volume needs to be small to ease the later separations by centrifugation.

- 10.4.7 Add 1 mL of yttrium carrier solution. Heat in water bath at $90^\circ\text{C} \pm 10^\circ\text{C}$.

- 10.4.8 Adjust pH to 8 with 7.5 M NH_4OH . Cool to room temperature and allow precipitate to settle.
- 10.4.9 Centrifuge and decant supernate into another 40-mL centrifuge tube.
- 10.4.10 Dissolve precipitate with about four drops of concentrated HCl and dilute to 10 mL. Heat in $90^\circ\text{C} \pm 10^\circ\text{C}$ water bath.
- 10.4.11 Adjust pH to 8 with 7.5 M NH_4OH . Cool to room temperature and allow precipitate to settle.
- 10.4.12 Centrifuge and decant, combining supernate with that from step 10.4.9. Discard precipitate.
- 10.4.13 Add 1 mL of 6 M $\text{C}_2\text{H}_4\text{O}_2$ and 2 mL of 6 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. Adjust pH to 5.5 with 6 M HCl or 7.5 M NH_4OH . The pH of the solution is critical at this point. Barium chromate will not precipitate completely at lower pH.
- 10.4.14 Heat in a water bath to $90^\circ\text{C} \pm 10^\circ\text{C}$. Add 1 mL of Na_2CrO_4 solution dropwise while stirring. Allow the precipitate to settle. Add up to, but no more than 2 mL, excess Na_2CrO_4 solution to give the supernate a yellow chromate color.
- 10.4.15 Heat to $90^\circ\text{C} \pm 10^\circ\text{C}$ in water bath for 30 minutes. Cool, centrifuge, and discard supernate. Just before decanting the supernate, add a few drops of 0.1% aerosol OT solution to prevent a film of BaCrO_4 from forming on the surface.
- 10.4.16 Add 1 mL HClO_4 and about 15 mL of H_2O to precipitate in centrifuge tube. Heat in water bath and add 6 drops of H_2O_2 (30%). Continue heating to remove excess H_2O_2 . Allow sample to cool.

11.0 Sample Analysis

- 11.1 To prepare a scintillation cell for use, evacuate and cautiously refill with helium. Repeat evacuation and refill cycle twice, more often following samples with high ^{222}Rn activities.

- 11.2 Clean bubblers by rinsing with 0.25 M HCl. If previous sample activity exceeded 10 pCi (^{226}Ra), then remove stopcock grease and soak in $90^\circ\text{C} \pm 10^\circ\text{C}$ EDTA/ Na_2CO_3 solution for 1 hour. Remove, cool, and rinse with distilled water. Soak in warm 1M HCl for about 30 minutes, remove, cool, and rinse with distilled water. Dry and regrease the stopcocks.
- 11.3 Close inlet stopcock of greased and tested radon bubbler. Add a drop of water to fritted disk, and transfer sample from centrifuge tube to bubbler using medicine dropper. Rinse tube with at least three 2-mL portions of water. Add water until bubbler is two-thirds to three-fourths full.
- 11.4 Insert outlet stopcock into bubbler with stopcock open.
- 11.5 Adjust helium regulator so a very small stream of gas will flow with the needle valve open. Attach helium supply to bubbler inlet, and adjust inlet pressure to produce a froth a few millimeters thick. Establish a "zero" ingrowth time by purging liquid with helium for 15 to 20 minutes.
- 11.6 In rapid succession, close inlet stopcock, remove gas connection, and close outlet stopcock. Record date and time and store bubbler, for at least 2 weeks, before collecting and counting the radon. For higher activity samples, shorter ingrowth times are acceptable if the required sensitivity can be met.
- 11.7 Radon Counting
- 11.7.1 Attach a prepared scintillation chamber (see Section 11.1) to bubbler assembly. Substitute glass tube with stopcock for bubbler so helium gas can be turned off conveniently. Open stopcock on scintillation chamber, close stopcock to gas, and gradually open stopcock to vacuum source to evacuate cell.
- 11.7.2 Close stopcock to vacuum source, and check manometer reading for 2 minutes to check system for leaks.
- 11.7.3 Open stopcock to helium gas and cautiously allow scintillation chamber to reach atmospheric pressure. Close all stopcocks.
- 11.7.4 Place scintillation cell on PMT in light-tight housing. Wait 10 minutes and collect a background count for at least 100 minutes.
- 11.7.5 Remove scintillation cell from PMT, and attach it to radon bubbler with all stopcocks closed.

- 11.7.6 Open stopcock to vacuum and then to scintillation chamber, and allow chamber and gas purification system to evacuate. Close vacuum stopcock and check manometer for leaks.
- 11.7.7 Adjust helium regulator so that a very slow stream of gas will flow with needle valve open. Attach helium supply to inlet of bubbler.
- 11.7.8 Cautiously open bubbler outlet stopcock and allow pressure to equalize to transfer all or most of the liquid in bubbler side-arm to the bubbler chamber.
- 11.7.9 Close outlet stopcock and very cautiously open inlet stopcock to flush remaining fluid from side-arm and fritted disk. Close inlet stopcock.
- 11.7.10 Perform steps 11.7.8 and 11.7.9 several times to achieve nearly equal pressure on the two sides of the bubbler.
- 11.7.11 With outlet stopcock fully open, cautiously open inlet stopcock so that flow of gas produces a froth a few millimeters thick at surface of bubbler solution. Maintain flow rate by adjusting pressure with regulator valve and continue de-emanation until pressure in scintillation chamber reaches atmospheric (15 to 20 minutes).
- 11.7.12 In rapid succession, close stopcocks to scintillation chamber, bubbler inlet, and bubbler outlet. Shut off and disconnect gas supply. Record time and date, which is the end of ingrowth and beginning of decay.
- 11.7.13 Four hours after de-emanation, place scintillation chamber on PMT, wait 10 minutes, and count. Record date and time counting was started and finished.
- 11.8 Yield Determination
- 11.8.1 Use procedure FM-RAD-0140 (Gamma Spectrometry) to determine the ^{133}Ba activity in the sample.
- 11.8.2 Transfer solution in bubbler to gamma counting container. Wash bubbler thoroughly with 1M HCl, and combine with sample in container. Measure ^{133}Ba activity in gamma counter.
- 11.8.3 Calculate sample yield, Z, by dividing the ^{133}Ba activity of the sample by the ^{133}Ba activity of a 50-mL aliquot of BaCl_2 carrier working solution counted under identical conditions (volume, geometry, matrix) as the sample.

11.8.4 Sample may be stored for a second counting or discarded.

12.0 Calculations

12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

A = activity at mid-point of counting interval, in dpm, γ/s , or pCi as appropriate,

A_0 = activity at time of standardization in same units as A,

λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,

t = time elapsed from standardization to mid-point of counting interval.

12.2 Counting Efficiency. Calculate efficiency for each scintillation cell and PMT system combination as:

$$E = \frac{\left[\frac{S}{t_1} - \left(\frac{S_B}{t_B} \right) \right] [\lambda] t_1}{(R) (1 - e^{-\lambda t_1}) (1 - e^{-\lambda t_2}) (e^{-\lambda t_3})}$$

Where:

E = efficiency of scintillation chamber (cpm/dpm)

S = number of counts accumulated from standard

S_B = number of background counts

| | | |
|-----------|---|--|
| t_B | = | background counting time (min) |
| t_1 | = | counting time of standard (min) |
| t_2 | = | ingrowth period of ^{222}Rn (min) |
| t_3 | = | decay time of ^{222}Rn from de-emanation until counting (min) |
| λ | = | ^{222}Rn decay constant, $1.26 \times 10^{-4} \text{ min}^{-1}$ |
| R | = | activity of radium standard added (dpm) |

Note: Use the same units for all times and decay constant.

12.3 Calculate chemical yield, Z, as:

$$\text{YIELD}(Z) = \frac{(^{133}\text{Ba Measured})}{(^{133}\text{Ba Added})}$$

12.4 Radium-226 Concentration

$$\text{Radium} = \frac{\left(\frac{C}{(E)(V)(Z)} - B\right)}{2.22}$$

(pCi/g, pCi/L, or pCi/air filter)

Where:

| | | |
|------|---|---|
| 2.22 | = | conversion factor from dpm to pCi |
| E | = | scintillation cell efficiency |
| B | = | reagent blank result (dpm/L, g or air filter) |

V = volume or weight of sample (V for air filters is fraction of total filter)

Z = chemical yield of method

and,

$$C = \frac{\left[\frac{N}{t_1} - \left(\frac{N_B}{t_B} \right) \right] [\lambda] t_1}{(1 - e^{-\lambda t_1}) (1 - e^{-\lambda t_2}) (e^{-\lambda t_3})}$$

Where:

C = net counts per minute

N = number of counts accumulated

N_B = number of background counts determined prior to use

t_B = background counting time (min)

t_1 = counting time of sample (min)

t_2 = ingrowth period of ^{222}Rn (min)

t_3 = decay time of ^{222}Rn from de-emanation until counting (min)

λ = ^{222}Rn decay constant, $1.26 \times 10^{-4} \text{ min}^{-1}$

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project-specific Sampling and Analysis Plan, or the analytical laboratory services contract(s).

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|-------------------------|-------------------|------------------|-------------------|
| Reagent Blank* | 1/20 ^m | To be determined | Qualify Data |
| ¹³³ Ba Yield | 1/1 | To be determined | Qualify Data |
| LCS | 1/20 ^m | To be determined | Qualify Data |
| Duplicate* | 1/20 ^m | To be determined | Qualify Data |

* per matrix

^m or per batch or fraction thereof

15.0 References

- 15.1 U.S. Department of Energy Environmental Measurements Laboratory. *EML Procedures Manual*. HASL-300, 27th ed. 1990.
- 15.2 American Society for Testing and Materials. *1991 Annual Book of ASTM Standards*. Method D3454, Standard Test Method for Radium-226 in Water. Vol. 11.02.

Attachment A**A. Purification of Yttrium Carrier**

- A.1 Dissolve 100 grams of yttrium nitrate, $(Y(NO_3)_3 \cdot 6H_2O)$, in 80 mL of H_2O . Add a few drops of HNO_3 . Transfer to 1-L separatory funnel using two 20-mL portions of H_2O .
- A.2 Add 120 mL of saturated NH_4NO_3 to the separatory funnel. Add 240 mL of tributyl phosphate (TBP) to separatory funnel and shake for 5 minutes. Allow phases to separate for 10 minutes.
- A.3 Draw off aqueous (lower) layer into second separatory funnel. Add 240 mL of fresh TBP and shake for 5 minutes. Allow phases to separate and discard aqueous layer.
- A.4 Combine both TBP phases in one separatory funnel, add 20 mL of H_2O , and shake for 5 minutes. Allow phases to separate and transfer aqueous layer to clean separatory funnel.
- A.5 Repeat H_2O wash and combine aqueous fractions. Discard TBP.
- A.6 Add 50 mL of CCl_4 to H_2O solution, shake for 1 minute, and allow to separate. Discard CCl_4 .
- A.7 Dilute to 2 L with H_2O and store in polyethylene.

B. Yttrium Carrier Counting Check

- B.1 Pipette 1 mL of yttrium carrier into each of three 40-mL centrifuge tubes. Dilute to 20 mL with H_2O .
- B.2 Heat in water bath to about $90^\circ C \pm 5^\circ C$. With stirring, adjust pH to 8 with NH_4OH . Digest for 10 minutes and cool in cold water bath.
- B.3 Centrifuge for 5 minutes. Decant and discard supernate.

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- B.4 Break up precipitate with a few mL of H₂O. Dilute to 20 mL with H₂O. Add a few drops of concentrated HCl to just dissolve precipitate. Heat solution in water bath to about 90°C ± 5°C, and add 1 mL of saturated H₂C₂O₄ (oxalic acid) dropwise while stirring.
- B.5 Allow precipitate to digest for about 1 hour. Cool to room temperature and filter on a 2.8-cm Whatman No. 42 filter paper. Discard filtrate.
- B.6 Dry in 110°C ± 5°C oven. Mount with nylon ring and disc and count.

3204

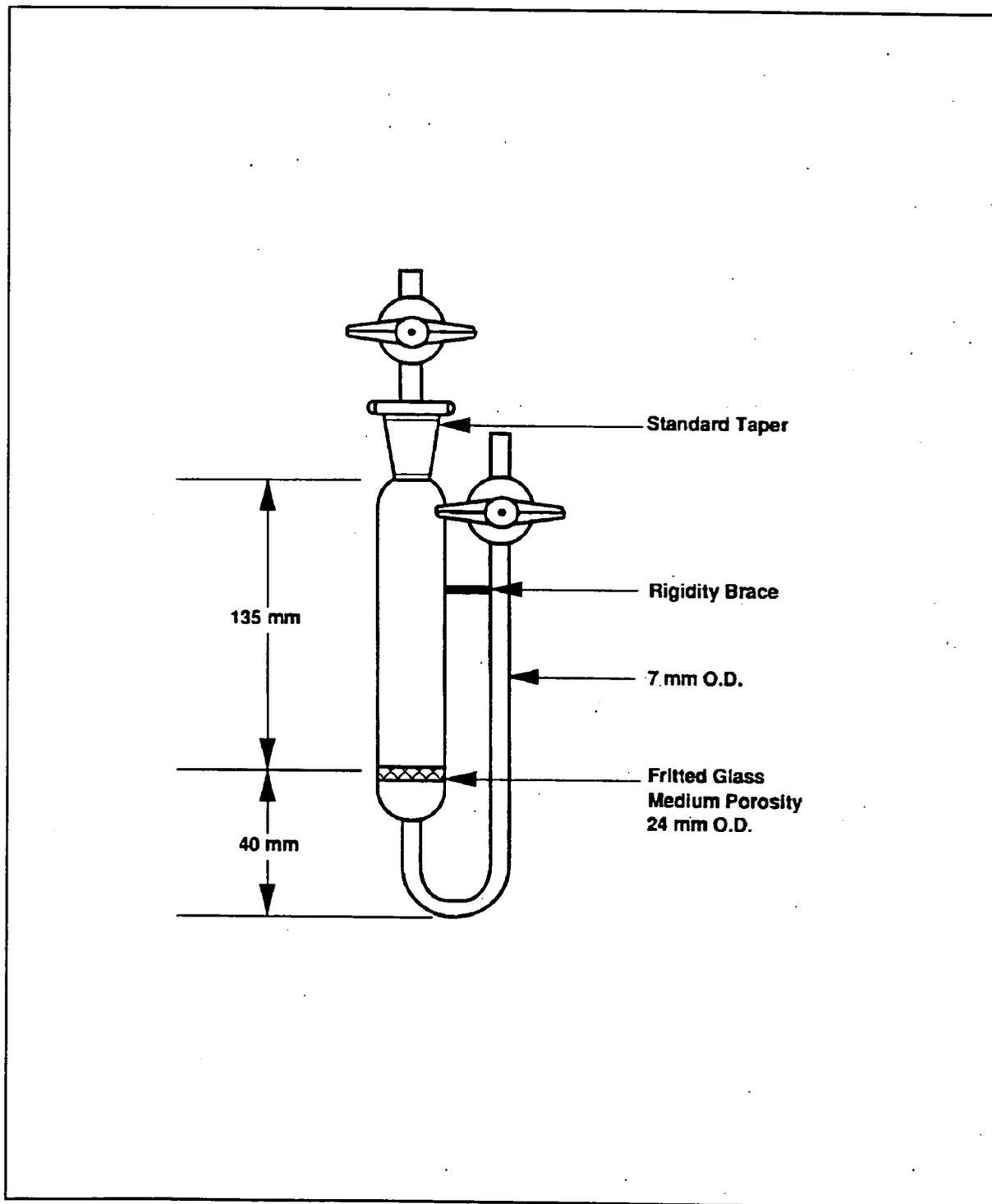


Figure 1 Radon Bubbler

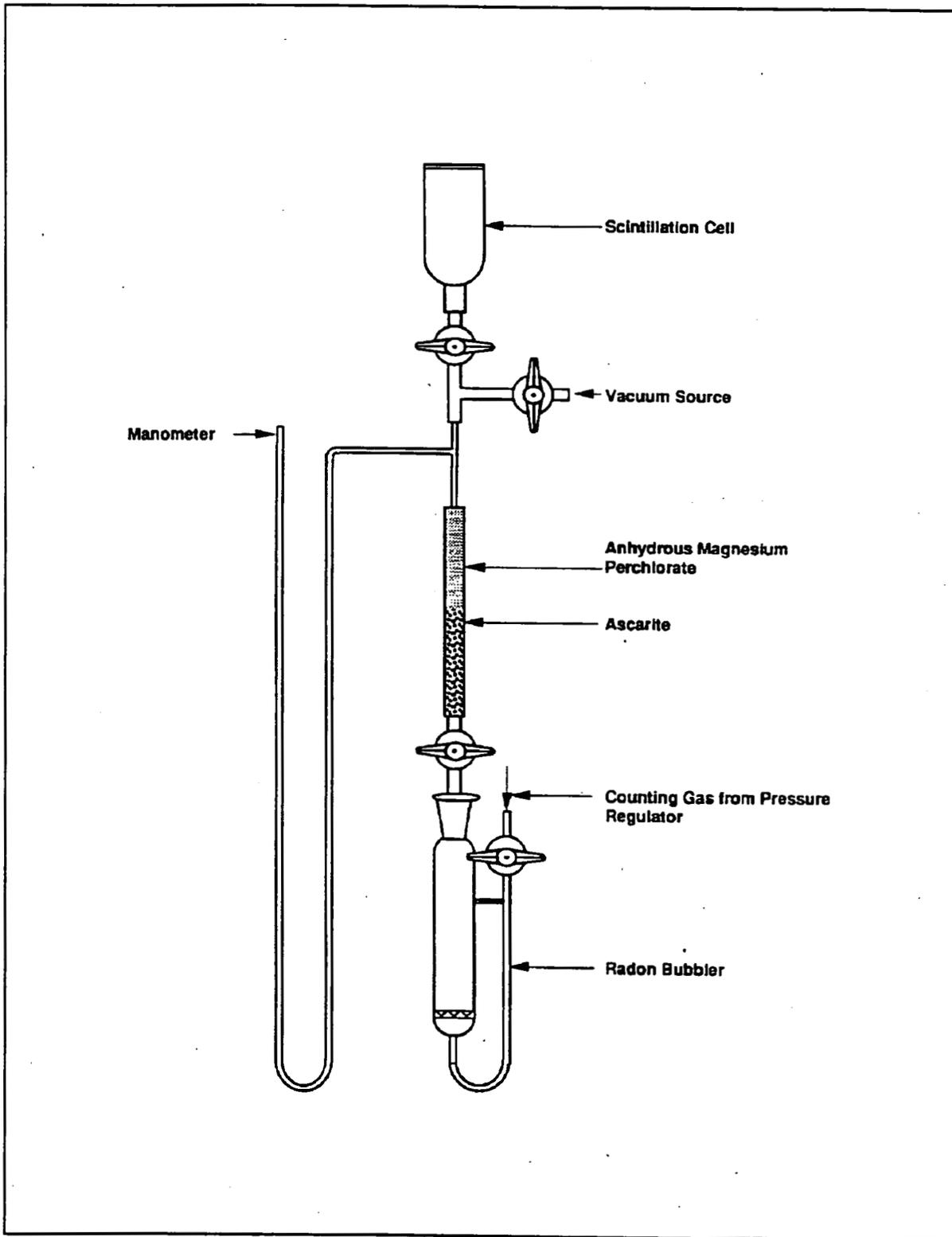


Figure 2 Radon Bubbler Assembly

3204

Lead-210 in Water by Beta Counting

Working Linear Range: Greater than 7 pCi/L, infinite with dilution
Reporting Limit: ~7 pCi/L
Reporting Units: Water, pCi/L
Matrix: Water

1.0 Scope and Application

- 1.1 The method is applicable to the analysis of ^{210}Pb in water. The nominal sensitivity of the procedure may vary with each analysis but is approximately 7 pCi/L for water.
- 1.2 The method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 Bismuth-210 is counted to determine the amount of ^{210}Pb present in the sample.
- 2.2 Lead carrier is added to a water sample. The lead is separated as a lead bromide complex by solvent extraction with methyltricaprylammonium chloride in toluene. Bismuth carrier is added, and the sample preparation is stored to allow the ingrowth of ^{210}Bi . The ^{210}Bi progeny is separated from the ^{210}Pb parent by precipitation as bismuth oxychloride and is measured using a low background beta counter. A simplified flow chart is shown in Figure 1. Chemical yields are determined by atomic absorption for lead and gravimetrically for bismuth. A calibration standard and reagent blank are processed concurrently with the samples.

3.0 Interferences

- 3.1 The stable lead content of the sample may bias the lead recovery measurement made by atomic absorption. A portion of the sample is reserved before adding the lead carrier to determine the amount of lead to correct for in the recovery (yield) calculation.
- 3.2 The contribution from any alpha emitters and the low energy beta from any ^{210}Pb present in the final sample preparation are removed by counting the sample through an aluminum or equivalent absorber.

- 3.3 Moisture absorbed by the sample solids on the counting planchet alters counting and self-absorption characteristics.
- 3.4 Nonuniformity of sample residue in the counting planchet interferes with the accuracy and precision of the method.

1. Sample
 - 1.a 10 mL taken for stable Pb analysis
2. Add Pb carrier to remaining sample
3. Evaporate and dissolve in acids
4. Prepare organic extractant
5. Extract Pb into organic (with HBr)
6. Extract Pb into aqueous (with HCl)
7. Evaporate and dissolve in acids
8. Add Bi carrier
9. Separate Bi from Pb by precipitating BiOCl
 - 9.a Discard (old) Bi as precipitate
10. Start ingrowth of (new) ^{210}Bi from cleaned Pb
11. Add Bi carrier
12. Bring to 100 mL volume
 - 12.a Take 1 mL, dilute to 10 mL; analyze for Pb yield
13. Wait about 20 days
14. Separate Bi from Pb by precipitating BiOCl
 - 14.a Discard Pb as supernate (or save for re-analysis)
15. Start decay time of ^{210}Bi
16. Weigh BiOCl precipitate for Bi yield
17. Count ^{210}Bi activity

Figure 1 Simplified Process Flow for ^{210}Pb Analysis

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Separatory funnels, beakers, pipettes, centrifuge tubes, and volumetric flasks. Class A volumetric glassware is used for carrier and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 6.2 Electric hot plate/magnetic stirrer: With built-in stirrer and stepless temperature controls that can be changed as heating requirements may demand.
- 6.3 pH Meter: Accurate to ± 0.1 pH units.
- 6.4 Centrifuge: Able to hold 40-mL size centrifuge tubes and achieve at least 2,000 rpm.
- 6.5 Filter papers: Whatman No. 42, or equivalent.
- 6.6 Vacuum filtering apparatus.
- 6.7 Drying oven: The gravity convection type oven is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 110°C and able to maintain temperature within $\pm 5^\circ\text{C}$.

- 6.8 Analytical balance: Scale readability ± 0.1 mg.
- 6.9 Planchets: For mounting final sample preparation. Planchets should be fabricated from uniform density stainless steel. Size is dictated by inside dimensions of the detector chamber. All planchets shall be nitric acid washed before use.
- 6.10 Aluminum foil: 7.0 to 7.2 mg/cm².
- 6.11 Low background alpha/beta proportional counting system: Tennelec Model LB-5100, or equivalent. Detector must have a rigid sample positioning device that has accurate and reproducible geometry.
- 6.12 Atomic absorption spectrophotometer: Working range 0 to 50 ppm Pb.
- 7.0 Routine Preventive Maintenance**
- 7.1 Perform routine preventive maintenance for the instruments according to the manufacturers' directions.
- 7.2 Document all instrument maintenance in the instrument specific maintenance logbook, as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks, and replace as necessary.
- 8.0 Reagents and Calibration Standards**
- 8.1 Chemicals must be reagent grade, meeting American Chemical Society specifications. In all cases acids or bases are added to water. All radionuclide standards must be corrected for decay.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 ²¹⁰Pb calibration standard: Dilute 10 mL of ²¹⁰Pb primary standard using 2 M HNO₃ to give nominal concentration of 10 pCi/mL.
- 8.4 ²¹⁰Pb primary standard from NIST, or NIST-traceable, or from other nationally recognized agency.

- 8.5 Lead carrier, 20 mg Pb^{+2} /mL: Dissolve 32 grams of $Pb(NO_3)_2$ in 0.8 M HNO_3 , and dilute to 1 L with 0.8 M HNO_3 .
- 8.6 Lead nitrate ($Pb(NO_3)_2$): Reagent grade.
- 8.7 Nitric acid (HNO_3): Concentrated (70% by weight) reagent.
- 8.8 Hydrobromic acid (HBr), 3 M: Dilute 333 mL of concentrated HBr to 1 L with water.
- 8.9 Hydrobromic acid (HBr): Concentrated, reagent grade (48% by weight, in water).
- 8.10 Aliquot 336, 30% v/v in toluene: Combine 300 mL of Aliquot 336 with 700 mL of toluene. Just before use, wash solution twice with an equal volume of 1.5 M HBr.
- 8.11 Aliquot 336, methyltricaprylammonium chloride ($CH_3NCl(C_8H_{17})_3$): Reagent grade.
- 8.12 Toluene ($C_6H_5CH_3$): Reagent grade.
- 8.13 Hydrobromic acid (HBr), 1.5 M: Dilute 167 mL of concentrated HBr to 1 L with water.
- 8.14 Hydrobromic acid (HBr), 0.1 M: Dilute 11 mL of concentrated HBr to 1 L with water.
- 8.15 Hydrochloric acid (HCl): Concentrated reagent (37% by weight).
- 8.16 Hydrochloric acid (HCl), 8 M: Dilute 667 mL of concentrated HCl to 1 L with water.
- 8.17 Perchloric acid ($HClO_4$): Concentrated (70% by weight) reagent.
- 8.18 Bismuth carrier, 10 mg Bi^{+2} /mL: Dissolve 23.2 grams of $Bi(NO_3)_3 \cdot 5H_2O$ in 0.8 M HNO_3 , and dilute to 1 L with 0.8 M HNO_3 .
- 8.19 Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$): Reagent grade.
- 8.20 Nitric acid (HNO_3), 0.8 M: Dilute 50 mL of concentrated HNO_3 to 1 L with water.

- 8.21 Ammonium hydroxide (NH₄OH): Concentrated (28% NH₃ by weight) reagent.
- 8.22 Hydrochloric acid (HCl), 0.5 M: Dilute 41.7 mL of concentrated HCl to 1 L with water.
- 8.23 Methanol (CH₃OH): Anhydrous, reagent grade (99.8% by weight).

9.0 Calibration Procedures

- 9.1 The calibration (energy efficiency determination plus self-absorption and backscatter) of the beta counting system specifically for this procedure is done by counting a known amount of ²¹⁰Bi obtained from a ²¹⁰Pb standard. The ²¹⁰Bi preparation must be counted on the same detector system, in the same position, with the same type of mounting, and through the same absorber materials used for samples.
- 9.2 The beta counting system is generally calibrated (e.g., plateau determination, operating voltages) according to the manufacturer's instructions at least annually and after every significant change to the detector system.
- 9.3 A background count of sufficient length to meet the required uncertainty and lower limit of detection is made weekly. Daily background checks must be within the established limits, e.g., $\pm 3 \sigma$ before commencing analyses.
- 9.4 Plateau checks are made after every gas bottle change by counting a check source at the operating voltage. The results must be within the established limits, e.g., $\pm 3 \sigma$ before commencing analyses.
- 9.5 Daily, or before use, a check source is counted to verify detector efficiency. The results must be within the established limits, e.g., $\pm 3 \sigma$ before commencing analyses.
- 9.6 The AA instrument used for stable Pb analysis and determination of Pb yield is calibrated as per Method No. FM-INO-0020.

10.0 Sample Preparation

10.1 Measure a volume of water sample appropriate to meet the required sensitivity, up to 1-L, into a 2-L beaker. Record comment if presence of undissolved material is noted. Reserve 10 mL of sample for stable Pb analysis. (Use FEMP Procedure FM-INO-0020 for Pb analysis.) Record volume of sample after subtracting aliquot removed for stable Pb analysis.

10.1.1 Process 1 L of ASTM Type II water through entire procedure as if it were a sample for each batch or fraction there of. This will be used as a reagent blank.

10.1.2 Process 10 mL of ^{210}Pb calibration standard added to 990 mL of water containing the same type and amount of preservative present in the samples through entire procedure as if it were a sample.

Note: The standard solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

10.2 Pipette 1 mL of lead carrier and 5 mL of concentrated HNO_3 into each sample beaker.

10.3 Place sample on hot plate and evaporate it to approximately 100 mL.

10.4 Add 100 mL of concentrated HNO_3 to sample and evaporate it to dryness.

10.5 Remove beaker from hot plate and allow it to cool to room temperature.

10.6 Add 25 mL of 3 M HBr to sample, place beaker on hot plate, and allow solution to evaporate to dryness.

10.7 Remove beaker from hot plate and allow it to cool to room temperature.

10.8 Add 100 mL of 3 M HBr to sample. Heat if necessary to redissolve residue, and allow sample to cool to room temperature.

11.0 Sample Analysis

11.1 Lead Extraction

11.1.1 Add 75 mL of Aliquot 336 solution (30%) to 250-mL separatory funnel.

- 11.1.2 Add 75 mL of 1.5 M HBr to separatory funnel.
- 11.1.3 Stopper and shake separatory funnel for 1 minute.
- 11.1.4 Allow phases to separate and discard aqueous (lower) phase.
- 11.1.5 Repeat steps 11.1.2 through 11.1.4.
- 11.1.6 Transfer sample from step 10.8 to 250-mL separatory funnel containing 75 mL of the just washed Aliquot 336 solution.
- 11.1.7 Shake separatory funnel for 30 seconds.
- 11.1.8 Let phases separate and discard the aqueous phase.
- 11.1.9 Add 50 mL of 0.1 M HBr to separatory funnel.
- 11.1.10 Shake separatory funnel for 30 seconds.
- 11.1.11 Let phases separate and discard aqueous phase.
- 11.1.12 Repeat steps 11.1.9 through 11.1.11 twice to remove residual impurities.
- 11.1.13 Add 50 mL of concentrated HCl to separatory funnel.
- 11.1.14 Shake separatory funnel for 30 seconds.
- 11.1.15 Let phases separate, and transfer aqueous phase containing lead into 400-mL beaker.
- 11.1.16 Repeat steps 11.1.13 through 11.1.15, combining aqueous fractions into 400-mL beaker. This is necessary to improve Pb recovery (now in aqueous phase). Discard organic phases.
- 11.1.17 Add 100 mL of concentrated HNO₃ to beaker and heat to dryness on hot plate.
- 11.1.18 Cool sample and add 5 mL of 8 M HCl and 5 mL of concentrated perchloric (HClO₄) acid to residue. **Caution:** This operation should be done in a fume hood suitable for heating perchloric acid.
- 11.1.19 Heat sample to dryness on hot plate to oxidize Pb.

11.1.20 Cool sample and add 10 mL of concentrated HNO₃ to beaker.

11.1.21 Heat sample to dryness on hot plate.

11.1.22 Cool sample and add 10 mL of concentrated HCl to beaker.

11.1.23 Heat sample to dryness on hot plate.

11.1.24 Cool sample and add 10 mL of concentrated HNO₃ and 10 mL of concentrated HCl to beaker.

11.1.25 Heat until volume is reduced to about 10 mL.

11.2 Bismuth Separation

11.2.1 Transfer sample to 40-mL centrifuge tube with water rinse. Pipette 1 mL of bismuth carrier into tube and stir for 60 seconds with magnetic stirrer.

11.2.2 Adjust pH of sample to 8.0 ± 0.1 using concentrated NH₄OH or concentrated HCl. **Caution:** Add NH₄OH slowly since heat will be generated during initial addition. Use properly calibrated pH meter to monitor pH. Stir solution using magnetic stirrer while adjusting pH.

11.2.3 Heat sample (while stirring) in hot water bath.

11.2.4 Cool and centrifuge sample for 10 minutes and discard supernate, which contains residue trace impurities. Precipitate contains both lead and bismuth.

11.2.5 Dissolve precipitate in 5 drops of concentrated HCl.

11.2.6 Add 40 mL of water to centrifuge tube and heat with constant stirring. The sample will form the insoluble product BiOCl.

11.2.7 Cool, centrifuge for 10 minutes, and collect supernate in 250-mL beaker. The supernate contains the lead.

11.2.8 Repeat steps 11.2.5 through 11.2.7 twice more to remove residual lead. Discard precipitate.

11.2.9 Record time and date for start of ²¹⁰Bi ingrowth.

- 11.2.10 Add 1 mL of Bi carrier and 5 mL of concentrated HCl to combined supernates. Reduce volume to less than 100 mL.
- 11.2.11 Cool and transfer to 100-mL volumetric flask and bring to volume with 0.5 M HCl.
- 11.2.12 Dilute 1 mL of the sample preparation to 10 mL in volumetric flask with 0.5 M HCl.
- 11.2.13 Determine lead carrier recovery by analyzing sample in 10-mL volumetric flask. Use FM-INO-0020 for lead analysis.
- 11.2.14 Store remaining sample preparation in 100-mL volumetric flask (step 11.2.11) for about 20 days to allow ingrowth of the ^{210}Bi progeny.
- 11.3 Bismuth Collection
- 11.3.1 Transfer solution from 100-mL volumetric flask to 250-mL beaker and evaporate to about 15 mL.
- 11.3.2 Transfer sample to a 40-mL centrifuge tube and adjust pH to 8.0 ± 0.1 with NH_4OH . Centrifuge for 10 minutes and discard supernate. **Caution:** Add NH_4OH slowly since heat will be generated during initial addition. Use properly calibrated pH meter to monitor pH. Stir solution using magnetic stirrer while adjusting pH.
- 11.3.3 Dissolve precipitate with five drops of concentrated HCl, and bring sample volume to 30 mL with water. Record day and time for start of decay of ^{210}Bi .
- 11.3.4 Heat with constant stirring in hot water bath. Cool and centrifuge for 10 minutes. (Supernate may be saved for additional ^{210}Pb analysis.)
- 11.3.5 Dissolve precipitate with five drops of concentrated HCl, and bring sample volume to 30 mL with water.
- 11.3.6 Heat with constant stirring in hot water bath. Cool and centrifuge for 10 minutes. (Add supernate to that from step 11.3.4 for additional ^{210}Pb analysis.)
- 11.3.7 Dissolve precipitate with five drops of concentrated HCl, and bring sample volume to 30 mL with water.

- 11.3.8 Heat with constant stirring in hot water bath. Cool and filter with suction through a weighed Whatman No. 42 filter paper.
- 11.3.9 Wash tube and precipitate with water and methanol.
- 11.3.10 Dry paper and precipitate for 30 minutes at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ in drying oven.
- 11.3.11 Cool and reweigh to determine Bi yield (BiOCl precipitate).
- 11.4 Beta Counting
- 11.4.1 Mount filter paper on planchet with adhesive and cover with thin plastic tape or film or collodion solution. Cover the sample with aluminium foil so that the sample mounting, or detector's window, or a combination thereof, provides a nominal 7.0 mg/cm^2 absorber.
- 11.4.2 Count sample on low background proportional counter for nominal 400 minutes. Actual counting time required to meet the minimum detectable concentration will depend on detector background and counting efficiency.

12.0 Calculations

- 12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

A = activity at mid-point of counting interval, in dpm, γ/s , or pCi as appropriate,

A_0 = activity at time of standardization in same units as A,

λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,

t = time elapsed from standardization to mid-point of counting interval.

- 12.2 Calculate activity of ^{210}Pb in sample as follows (Note: Correcting the ^{210}Pb activity in the sample back to the date and time of sample collection must be done if the elapsed time is greater than 6 months.):

$$\text{Pb-210} = \frac{(X - R)}{(2.22) (V) (E) (P) (B) (D) (I)} \text{ pCi/L}$$

Where:

- V = Amount of sample (L), adjusted for amount of preservative added and aliquots removed for stable Pb analysis and Pb recovery (yield) determination.
- E = Beta counter efficiency (cpm/dpm), determined with each batch by counting ^{210}Bi from a ^{210}Pb standard prepared as a sample.
- X = Sample net count rate (cpm)
- R = Reagent blank net count rate (cpm) counted on same system as sample with same background and efficiency
- P = Chemical yield of lead carrier (determined by AA measurement). The Pb yield calculation must be adjusted for the amount of lead present in the original sample.
- B = Chemical (gravimetric) yield of bismuth carrier. The yield is determined by multiplying the net weight of the BiOCl precipitate by 0.8024 and dividing by the weight of Bi added, nominally 10 mg.
- D = Decay factor of ^{210}Bi , $e^{-\lambda_2 t}$, where t is elapsed time from Pb/Bi separation (Step 11.3.3) to midpoint of counting interval, and λ_2 is $\ln 2$ /half-life of ^{210}Bi in same units as t
- I = Ingrowth factor of ^{210}Bi , $e^{-\lambda_1 t} - e^{-\lambda_2 t}$, where λ_1 is $\ln 2$ /half-life of ^{210}Pb in the same units as t and t is elapsed time from Step 11.2.9 to Step 11.3.3
- 2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the multiplicative factor $3.667\text{E-}02$ Bq/pCi.

12.3 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical services contract(s). The minimum detectable concentration (MDC) in pCi/L shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project-specific Sampling and Analysis Plan or the analytical laboratory contract specifications.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Levels and the project-specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|---------------|-----------|------------------|-------------------|
| Reagent Blank | 1/20* | To be determined | Qualify data |
| Pb Yield | 1/1 | To be determined | Qualify data |
| Bi Yield | 1/1 | To be determined | Qualify data |
| Pb Standard | 1/20* | To be determined | Qualify data |
| Duplicate | 1/20* | To be determined | Qualify data |

* or per batch or fraction thereof

15.0 References

- 15.1 *Radiochemistry Procedures Manual*. U.S. EPA, Eastern Environmental Radiation Facility. Report No. EPA 520/5-84-006. 1984.
- 15.2 *The Radiometric Determination of Pb-210 in Various Matrices*. Method No. 4009. Westinghouse Materials Company of Ohio-FMPC. September 26, 1989.

- 15.3 *EML Procedures Manual*. 27th ed., Volume 1. U.S. DOE Environmental Measurements Laboratory. New York, NY, HASL-300-Ed.27-Vol.1. 1990.
- 15.4 *Standard Practices for the Measurement of Radioactivity*, ASTM D 3648-78. Philadelphia: American Society for Testing and Materials. 1987.

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Isotopic Thorium in Milk, Vegetation, Soil/Sediment, Water, and Air Filters by Alpha Spectrometry

| | |
|-----------------------|--|
| Working Linear Range: | Infinite with dilution |
| Reporting Limit: | To be determined |
| Reporting Units: | Milk, Water, pCi/L; Solids, pCi/g; Air filters, pCi/air filter |
| Matrices: | Milk, vegetation, water, soil/sediment, air filters |

1.0 Scope and Application

1.1 The method covers the measurement of thorium isotopes 228, 230, and 232 in milk, vegetation, soil/sediment, water, and air filters. The mass of the isotopes can be calculated from the measured activities using the specific activity factors for each isotope. The nominal sensitivity that may be obtained by this exact method for the media requires performance data. Note that the beta emitting ^{234}Th isotope is not covered by the method.

1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

The sample is dissolved in acid or ashed, and the residue is dissolved in acid. Thorium is separated from uranium by organic extraction and purified by adsorption on anion exchange resin from nitric acid. It is stripped from the resin with HCl and electrodeposited onto a stainless steel disk. The disk is counted on a solid state detector (e.g., a silicon surface barrier) to determine the thorium isotopes by alpha spectrometry. The recovery of the thorium isotopes is measured using a ^{229}Th tracer.

3.0 Interferences

3.1 In determining very low levels of thorium isotopes in environmental samples, detector backgrounds and laboratory blanks must be determined accurately. Reagent blank determinations must be made to ascertain that contamination from reagents, glassware, and other laboratory sources is negligible compared to the sample being analyzed. A blank determination should be made in exactly the same way a sample determination is made.

- 3.2 Samples that have excess iron or other material deposited with the sample will undergo self-absorption. Self-absorption is indicated by poor resolution and low-energy tailing (peak straggling) in the sample spectrum.
- 3.3 Samples with high concentrations of ^{233}U may have quantities of ^{229}Th that would be sufficient to bias tracer recovery.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids, and/or bases must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Separatory funnels, beakers, pipettes, burets, funnels, volumetric flasks. Class A volumetric glassware is used for tracer and standard preparation, unless otherwise specified. Unless otherwise noted, nitric acid should be used to wash all glassware.
- 6.2 Electric hot plate/magnetic stirrer: With built-in stirrer and stepless temperature controls that can be changed as heating requirements may demand.
- 6.3 Ceramic or Vycor containers.
- 6.4 Drying oven: Gravity convection type is recommended, with thermostatic controls to maintain desired temperature and able to reach at least 125°C and able to

maintain temperature within $\pm 5^{\circ}\text{C}$.

- 6.5 Muffle furnace: Able to reach and maintain 900°C and able to maintain temperature within $\pm 15^{\circ}\text{C}$.
- 6.6 Top-loading balance: Scale readability of ± 0.1 g.
- 6.7 Analytical balance: Scale readability of ± 0.1 mg.
- 6.8 Teflon beakers and stirring rod.
- 6.9 Sieves: 2-mm and 15 mesh.
- 6.10 Grinder or Ball mill: Sufficient to reduce soil/sediment sample to pass 15 mesh sieve.
- 6.11 Platinum dishes: 100- and 125-mL with cover.
- 6.12 Ash-free filter paper: Whatman No. 42, or equivalent.
- 6.13 Scissors: Reserved for cutting only air filters.
- 6.14 Ion exchange column: 2-cm I.D. \times 10 cm long.
- 6.15 Electrodeposition apparatus: 0 to 12 V dc, 0 to 2 A, using disposable deposition cells. Cathode is stainless steel disk with mirror finish. Anode is platinum wire loop. See reference 15.2 for example apparatus. All electroplating disks are washed with nitric acid before use.
- 6.16 Alpha spectrometry system: Consisting of solid state alpha detector, multichannel analyzer (or PC or minicomputer), electronics, printer, and vacuum chamber. System must be capable of providing a spectral resolution of 60 keV or better.

7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the instruments according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine Class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. In all cases, acids or bases are added to water.

8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.

8.3 Hydrochloric acid (HCl), 12 M: Concentrated, reagent.

8.4 ^{229}Th Tracer solution: From NIST, or NIST-traceable, or from another nationally recognized agency.

8.5 Hydrochloric acid (HCl), 9 M: Dilute 750 mL of concentrated HCl to 1 L with water.

8.6 Nitric acid (HNO_3), 16 M: Concentrated, reagent.

8.7 Hydrofluoric acid (HF): Concentrated, 48% reagent.

8.8 Sodium carbonate (Na_2CO_3): Reagent.

8.9 Perchloric acid (HClO_4), 12 M: Concentrated, reagent.

8.10 Nitric acid (HNO_3), 8 M: Dilute 500 mL of concentrated HNO_3 to 1 L with water.

8.11 Nitric acid (HNO_3), 3 M: Dilute 187.5 mL of concentrated HNO_3 to 1 L with water.

8.12 Tri-iso-octylamine (TIOA): Reagent grade.

8.13 TIOA Solution in p-Xylene, 10%: Dissolve 100 mL of TIOA in p-xylene and dilute to 1 L with p-xylene.

8.14 p-Xylene: Reagent grade.

8.15 Nitric acid, (HNO_3) 6 M: Dilute 375 mL of concentrated HNO_3 to 1 L with water.

- 8.16 Anion exchange resin: BioRad AG1-X8, 200-400 mesh, or equivalent. Convert to nitrate form for thorium analysis by washing resin with 6 M HNO₃ until washing shows no trace of chloride when tested with AgNO₃.
- 8.17 Silver nitrate (AgNO₃): Reagent.
- 8.18 Hydrochloric acid (HCl), 6 M: Dilute 500 mL of the concentrated HCl to 1 L with water.
- 8.19 Sodium hydrogen sulfate—sulfuric acid solution (NaHSO₄ · H₂SO₄): Dissolve 10 g of sodium hydrogen sulfate in 100 mL of water, then carefully add 100 mL of concentrated H₂SO₄ while stirring. This solution contains about 5% NaHSO₄ in 9 M H₂SO₄.
- 8.20 Preadjusted ammonium sulfate electrolyte ((NH₄)₂SO₄), 1 M: Dissolve 132 g of ammonium sulfate in water and dilute to 1 L. While stirring, adjust the pH to 3.5 with 15 M NH₄OH or 18 M H₂SO₄.
- 8.21 Thymol blue indicator, 0.04% Solution: Dissolve 0.1 gram thymolsulfonephthalein in 21.5 mL 0.01 M NaOH and 228.5 mL water.
- 8.22 Ammonium hydroxide (NH₄OH), 15 M: Concentrated reagent.
- 8.23 Sulfuric Acid (H₂SO₄), 18 M: Concentrated reagent.
- 8.24 Sulfuric Acid (H₂SO₄), 1.8 M: Dilute 100 mL of 18 M H₂SO₄ to 1 L with water.
- 8.25 Ammonium hydroxide (NH₄OH), 1.5 M: Dilute 100 mL of 15 M NH₄OH to 1 L with water.
- 8.26 Ammonium hydroxide (NH₄OH), 0.15 M: Dilute 10 mL of 15 M NH₄OH to 1 L with water.
- 8.27 Ethanol (C₂H₅OH), 98% reagent: Made slightly basic with 3 to 5 drops of 15 M NH₄OH per 100 mL of alcohol.
- 8.28 Mixed alpha standard (e.g., ²³⁸Pu, ²³⁹Pu, ²⁴²Pu, or ²³⁰Th, ²³²Th): From NIST, or NIST-traceable or from another nationally recognized agency.
- 8.29 Alpha check source (e.g., ²⁴¹Am or ²¹⁰Po).

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9.0 Calibration Procedures

- 9.1 Use a mixed alpha emitting standard (e.g., ^{238}Pu , ^{239}Pu , ^{242}Pu , or ^{230}Th , ^{232}Th , traceable to NIST or another nationally recognized agency) to calibrate each detector in counting system. Refer to manufacturer's instructions for specific calibration procedure.
- 9.2 Using an alpha check source, verify detector efficiency, detector resolution, and energy calibration daily or before use. Results must be within established limits (e.g., $\pm 3 \sigma$) before commencing analyses.
- 9.3 Calibrate alpha counting system (i.e., operating voltages, etc.) according to manufacturer's instructions at least annually and after every significant change to the counting system.
- 9.4 Perform a background count weekly of sufficient length to meet the required uncertainty and lower limit of detection. Results must be within established limits (e.g., $\pm 3 \sigma$) before commencing analyses.

10.0 Sample Preparation

10.1 Water

- 10.1.1 Add 50 mL of 12 M HCl and appropriate quantity of ^{229}Th tracer to a measured volume of water sample appropriate to meet the required sensitivity. The ^{229}Th tracer activity added should be about 5 pCi or sufficient to provide 5% uncertainty or less at the 1σ level. Record volume of water used before adding tracer, tracer activity, and amount of tracer added. Note whether any undissolved material is present.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.1.2 Evaporate sample to 100 mL volume. Add 300 mL of 12 M HCl to make sample concentration 9 M in HCl. Continue with Sample Analysis, Section 11.0.

10.2 Milk

- 10.2.1 Measure volume of milk appropriate to meet the required sensitivity into a ceramic or vycor container and add appropriate quantity of ^{229}Th tracer. The activity of the ^{229}Th tracer added should be about 5 pCi or sufficient to provide 5% uncertainty or less at the 1σ level. Record volume of milk used before adding tracer, tracer activity, and amount of tracer added.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.2.2 Evaporate sample to dryness. Evaporation must be done carefully to avoid spattering. A drying oven at 110° to 125°C , or a controlled drip apparatus, e.g., a buret, and hot plate may be used.

- 10.2.3 Place container with dried sample in muffle furnace, and increase temperature slowly up to 325°C to avoid ignition of the sample. Increase temperature to $550^\circ\text{C} \pm 15^\circ\text{C}$ and continue ashing until ash appears white. Total ashing time could be 16 hours or more.

- 10.2.4 Cool ash, add 9 M HCl, and heat to bring sample into solution. Quantitatively transfer using 9 M HCl to 1-L beaker.

- 10.2.5 Add 9 M HCl to sample in beaker to approximate volume of 500 mL. Continue with Sample Analysis, Section 11.0.

10.3 Vegetation and Produce

- 10.3.1 Place a measured weight of vegetation/produce appropriate to meet the required sensitivity in a ceramic or vycor container. Dry at $100^\circ\text{C} \pm 5^\circ\text{C}$, reweigh, and grind. Record both wet weight and dry weight.

- 10.3.2 Add appropriate quantity of ^{229}Th tracer to sample. The activity of the ^{229}Th tracer added should be about 5 pCi or sufficient to provide 5% uncertainty or less at the 1σ level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.3.3 Transfer to muffle furnace and raise temperature slowly over 8 hours (to prevent ignition) to 250°C , then increase less slowly to 500°C . Sample is ashed at $500^\circ\text{C} \pm 15^\circ\text{C}$ for 16 hours or more to produce a white ash.

- 10.3.4 Cool and weigh the vegetation/produce ash. Record exact weight.

10.3.5 Dissolve ash in concentrated HNO_3 and quantitatively transfer to 400-mL beaker to a final volume of about 200 mL. Evaporate slowly to dryness.

10.3.6 Add 25 mL of concentrated HNO_3 to beaker and evaporate slowly to dryness. Repeat 25-mL additions of acid and evaporation until a white residue is obtained.

Note: If silicious material is present, transfer sample to 100-mL Teflon beaker with HNO_3 . Add 10 mL HF and evaporate to dryness. Repeat additions of 25 mL HNO_3 —10 mL HF as necessary to remove silica. Remove HF by 3 successive additions of 10 mL HNO_3 and evaporation.

10.3.7 Add 25 mL of concentrated HCl and evaporate to dryness. Repeat two more times.

10.3.8 Dissolve residue in 100 mL of 9 M HCl. Heat if necessary.

10.3.9 Continue with Sample Analysis, Section 11.0.

10.4 Soil/Sediment

10.4.1 Dry sample at 100°C for about 12 hours. Pass sample (typically 100 g) through a 2-mm sieve to remove roots, stones, etc. Grind, mill, or pulverize soil to pass 15 mesh screen. Blend until thoroughly mixed.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

10.4.2 Weigh an appropriate amount of 15 mesh soil/sediment sample to meet the required sensitivity and transfer to a 100-mL platinum dish. Record (dry) weight used.

10.4.3 Add appropriate quantity of ^{229}Th tracer. The ^{229}Th tracer activity added should be about 5 pCi or sufficient to provide 5% uncertainty or less at the 1σ level.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

10.4.4 Heat platinum dish containing sample in muffle furnace. Increase temperature at 1-hour intervals to 300° , 450° , and 550°C . Muffle for 2 or 3 hours at $550^\circ\text{C} \pm 15^\circ\text{C}$ or until only a brown, powdery ash remains. Remove and cool.

10.4.5 Fuse with four times the sample weight of Na_2CO_3 in electric muffle furnace at $900^\circ\text{C} \pm 15^\circ\text{C}$.

- 10.4.6 Cool and transfer melt to 400-mL beaker containing a magnetic stir bar.
- 10.4.7 Wash platinum dish with 25 mL of HCl. Slowly add washings to beaker. Repeat three more times. Cover and place on hot plate/stirrer.
- 10.4.8 Heat while stirring until volume is reduced to about 75 mL.
- 10.4.9 Cool and carefully add 150 mL of water. Filter by gravity through Whatman No. 42 filter paper.
- 10.4.10 Wash precipitate with 100 mL of hot 6 M HCl, followed by equal volume of hot water. Discard residue.
- 10.4.11 Evaporate filtrate slowly to dryness.
- 10.4.12 Dissolve residue in 100 mL of 9 M HCl.
- 10.4.13 Continue with Section 11.0, Sample Analysis.
- 10.5 Glass Fiber Filters
- 10.5.1 Remove filter from shipping envelope or bag and hold the filter over a 125 mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside the bag to the platinum dish.
- 10.5.2 Place the dish with sample in a muffle furnace. Ash the sample for about 16 hours at $500^{\circ}\text{C} \pm 15^{\circ}\text{C}$.
- 10.5.3 Remove the dish and allow to cool.
- 10.5.4 Completely dampen sample with a minimum amount but no more than 10 mL of concentrated HNO_3 .
- 10.5.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on a hot plate until a moist residue remains. Remove the dish and allow to cool. (Caution: Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
- 10.5.6 Add 10 mL of concentrated HF and evaporate until the residue is almost completely dry. Remove the dish and allow to cool.

- 10.5.7 Add 10 mL of concentrated HNO₃ and evaporate until the sample is lightly fuming and just moist. Remove the dish and allow to cool.
- 10.5.8 Repeat step 10.5.7.
- 10.5.9 Moisten the residue on the sides and bottom of the dish with 3 M HNO₃. Scrape the residue from the sides and bottom of the dish and break it up with a teflon rod. Wash down the sides of the dish and the teflon rod thoroughly using 3 M HNO₃.
- 10.5.10 Return the dish to the hot plate and evaporate until about 5 mL of solution remains. Remove the dish and allow to cool.
- 10.5.11 Filter the sample using a funnel and Whatman No. 42 filter paper into a 50 mL volumetric flask.
- 10.5.12 Wash out the dish using 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.5.13 Wash down the filter and residue with 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.5.14 Make up the contents of the volumetric flask to 50 mL with 3 M HNO₃, stopper, and mix thoroughly.
- 10.5.15 Transfer appropriate volume to meet the required sensitivity of the sample solution from the volumetric flask to a beaker. Record volume of sample transferred. Add appropriate quantity of ²²⁹Th tracer to sample. The ²²⁹Th tracer activity added should be about 5 pCi or sufficient to provide 5% uncertainty or less at the 1 σ level. Evaporate to dryness.
- Note:** The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.
- 10.5.16 Dissolve residue in 9 M HCl, heating if necessary.
- 10.5.17 Continue with Sample Analysis, Section 11.0.
- 11.0 Sample Analysis**
- 11.1 Thorium Extraction

- 11.1.1 Place volume of 10% TIOA solution equal to sample volume in an appropriate size separatory funnel. Add 50 mL 9 M HCl per 100 mL of 10% TIOA solution and shake funnel for 1 minute. Drain and discard aqueous (lower) acid phase after clean separation of the two phases.
- 11.1.2 Quantitatively transfer sample with 9 M HCl to TIOA in separatory funnel, and shake funnel vigorously for 2 minutes. Vent funnel stopcock to prevent pressure buildup in funnel.
- 11.1.3 Allow phases to separate cleanly and draw off aqueous acid phase.
- 11.1.4 Evaporate aqueous acid fraction to dryness.
- 11.1.5 Add 10 mL 16 M HNO₃ and evaporate to dryness.
- 11.1.6 Add 5 mL 9 M HCl and 5 mL 12 M HClO₄ and evaporate to dryness. **Caution:** This operation should be performed in a fume hood suitable for heating perchloric acid.
- 11.1.7 Add 10 mL of 16 M HNO₃ and evaporate to dryness.
- 11.1.8 Repeat step 11.1.7.
- 11.1.9 Dissolve sample, heating if necessary, in 10 mL of 6 M HNO₃.
- 11.2 Ion Exchange
- 11.2.1 Prepare ion exchange column with 25-mL ion exchange resin. Wash resin with 250 mL of 6 M HNO₃.
- 11.2.2 Decant sample into column at gravity flow (approximately 3 mL/min), and rinse sample on column with an additional 50 mL of 6 M HNO₃. Discard wash.
- 11.2.3 Elute thorium from column with 200 mL of 6 M HCl at flow rate of 3 mL/minute.
- 11.2.4 Evaporate thorium eluate to near dryness.
- 11.2.5 Add 5 mL 16 M HNO₃ to residue and evaporate to near dryness.
- 11.3 Electrodeposition
- 11.3.1 Add 2 mL of a 5% solution of NaHSO₄ in 9 M H₂SO₄ to sample.

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- 11.3.2 Add 5 mL of 16 M HNO₃, mix well, and evaporate to dryness but do not bake.
- 11.3.3 Dissolve sample in 5 mL of preadjusted ammonium sulfate electrolyte, warming to hasten dissolution.
- 11.3.4 Transfer solution to electrodeposition cell using an additional 5 to 10 mL of electrolyte in small increments to rinse sample container.
- 11.3.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H₂SO₄ (or 1.5 M NH₄OH) until color is obtained.
- 11.3.6 Place platinum anode into solution so that it is about 1 cm above stainless steel disk that serves as cathode.
- 11.3.7 Connect electrodes to source of current, turn power on, and adjust power supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustments during the electrodeposition.)
- 11.3.8 Continue electrodeposition for 1 hour.
- 11.3.9 When electrodeposition is to be terminated, add 1 mL of 15 M NH₄OH and continue electrodeposition for 1 minute.
- 11.3.10 Remove anode from cell, and then turn power off.
- 11.3.11 Remove solution from cell, and rinse cell 2 or 3 times with 0.15 M NH₄OH.
- 11.3.12 Disassemble cell, and wash disk with ethyl alcohol made basic with NH₄OH.
- 11.3.13 Touch edge of disk to tissue to absorb alcohol from disk.
- 11.3.14 Dry disk, label it for counting, and place it in a designated holding/staging area before counting. If disk is not completely dry, moisture may adversely affect spectral resolution.
- 11.4 Alpha Spectrometry
- 11.4.1 Using the manufacturer's suggested operating procedure, count samples for as long as necessary to meet the minimum detectable concentration requirements specified in the analytical laboratory service contract or Sampling and Analysis Plan. Counting times may have to be further adjusted if sample counting efficiency is

low, if the tracer recovery is less than expected, or if the anticipated thorium activity is less than 1 dpm/sample.

- 11.4.2 Check α spectrum for peaks at the ^{228}Th , ^{229}Th , ^{230}Th , or ^{232}Th α energies and determine the total counts in each peak.

| Thorium Isotope | Primary Alpha Energies (MeV) | Probability per Decay |
|-----------------|------------------------------|-----------------------|
| 228 | 5.42 | 0.73 |
| | 5.34 | 0.27 |
| 229 | 5.05 | 0.07 |
| | 4.97 | 0.10 |
| | 4.90 | 0.11 |
| | 4.84 | 0.61 |
| | 4.81 | 0.10 |
| 230 | 4.68 | 0.76 |
| | 4.62 | 0.24 |
| 232 | 3.95 | 0.24 |
| | 4.01 | 0.76 |

- 11.4.3 Samples with poorly resolved tracer or analyte peaks may indicate excessive self-absorption and the need to replat or repurify the sample.

12.0 Calculations

- 12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

A = activity at mid-point of counting interval, in dpm, γ /s, or pCi as appropriate,

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A_0 = activity at time of standardization in same units as A,

λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,

t = time elapsed from standardization to mid-point of counting interval.

12.2 Calculate thorium concentration in pCi/L (or pCi/g or pCi/air filter) as follows:

$$\text{Th} = \frac{(A - A_1) (F) (Y_t)}{(2.22) (B - B_1) (V) (Y_s)}$$

Where:

A = gross sample counts per minute in ^{228}Th , ^{229}Th , ^{230}Th , or ^{232}Th α peaks

A_1 = detector background counts per minute in same α peaks as A above

B = gross tracer counts per minute that appear in α peaks of tracer isotope

B_1 = detector background counts per minute in the same α peaks as B above

F = activity of tracer added (dpm)

V = sample volume (L), or weight (g); V for air filter is fraction of total filter

Y_t = probability of α emission per decay for α of interest (in tracer) in B above

Y_s = probability of alpha emission per decay for α of interest (in sample) in A above

2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the multiplicative factor 3.667E-02 Bq/pCi. The overall recovery for the tracer is included in the above equation as [(F) (Y_t)]/(B- B_1). Final sample results must be corrected for reagent blank contribution.

- 12.2.1 The activity of ^{228}Th ($T_{1/2} = 1.91$ years) found in the samples must be corrected for decay back to the time of sample collection. The half lives of the other thorium isotopes being measured are so long that decay corrections need not be applied.
- 12.2.2 The concentration for each thorium isotope is determined by the above equation using the sample counts of the main alpha peak for that isotope.
- 12.2.3 The thorium concentration in $\mu\text{g/L}$ (or g or air filter) can be calculated by dividing each isotopic activity by the isotopic specific activity and summing the results as:

$$(1 \mu\text{g } ^{228}\text{Th} / 8.21 \times 10^8 \text{ pCi } ^{228}\text{Th}) (x \text{ pCi } ^{228}\text{Th/L}) = X \mu\text{g } ^{228}\text{Th/L}$$

$$(1 \mu\text{g } ^{230}\text{Th} / 1.94 \times 10^4 \text{ pCi } ^{230}\text{Th}) (y \text{ pCi } ^{230}\text{Th/L}) = Y \mu\text{g } ^{230}\text{Th/L}$$

$$(1 \mu\text{g } ^{232}\text{Th} / 1.09 \times 10^{-1} \text{ pCi } ^{232}\text{Th}) (z \text{ pCi } ^{232}\text{Th/L}) = Z \mu\text{g } ^{232}\text{Th/L}$$

$$\text{The total } \mu\text{g/L} = X + Y + Z.$$

- 12.3 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical services contract(s). The minimum detectable concentration (MDC) in pCi/L (or g or air filter) shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels and are outlined in the QAPjP or specified in the project-specific Sampling and Analysis Plan or the analytical laboratory services contracts.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Levels and the project-specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|------------------------------|-------------------|------------------|-------------------|
| Reagent Blank ⁻⁻⁻ | 1/20 [*] | To be determined | Qualify Data |
| ^{229}Th Tracer | 1/1 | To be determined | Qualify Data |

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| | | | |
|-------------|-------|------------------|--------------|
| LCS | 1/20* | To be determined | Qualify Data |
| Duplicate** | 1/20* | To be determined | Qualify Data |

* or per batch or fraction thereof
 ** per matrix

15.0 References

- 15.1 *Eastern Environmental Radiation Facility Radiochemistry Procedures Manual.* Montgomery, Alabama. U.S. EPA, EPA-520/5-84-006. 1984.
- 15.2 *EML Procedures Manual, 27th ed., Vol. 1.* New York: U.S. DOE Environmental Measurements Laboratory. HASL-300-Ed.27-Vol.1. 1990.
- 15.3 *Standard General Methods for Detector Calibration and Analysis of Radionuclides,* ASTM E181-82. 1982.
- 15.4 *Standard Practices for the Measurement of Radioactivity,* ASTM D 3648-78. 1978.
- 15.5 C. M. Lederer and V. S. Shirley, ed. *Table of Isotopes,* 7th ed. New York: Wiley and Sons. 1978.

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Isotopic Uranium in Vegetation, Milk, Water, and Air Filters by Alpha Spectrometry

| | |
|------------------------------|--|
| Working Linear Range: | Greater than 1 pCi/L, infinite with dilution |
| Reporting Limit: | ~ 1 pCi/L (water); TBD for other materials |
| Reporting Units: | Milk, Water, pCi/L; Solids, pCi/g; Air filters, pCi/air filter |
| Matrices: | Milk, vegetation, water, air filters |

1.0 Scope and Application

- 1.1 This procedure applies to determination of isotopic uranium in milk, water, vegetation, and air filters. Total uranium activity is determined by adding the results for the individual isotopes ($^{233/234}\text{U}$, $^{235/236}\text{U}$, ^{238}U). Total uranium mass may be determined with the specific activity factors for each isotope. The nominal sensitivity may vary with each analysis but is approximately 0.06 pCi/L ($^{235,238}\text{U}$), 1 pCi/L (^{234}U) for water. The nominal sensitivity that may be obtained by this exact method for the other media requires additional performance data.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

A uranium tracer (^{232}U) is added to the sample. A milk or vegetation sample is oven dried and ashed, a water sample is evaporated, and an air filter is dissolved. The sample residue is dissolved in strong HCl. Uranium is extracted into tri-iso-octylamine (TIOA) and then stripped from the TIOA with dilute nitric acid. Polonium is removed by absorption onto Ni foil. The uranium is electrodeposited onto a stainless steel disk, and the disk is counted on a solid state detector, e.g., silicon surface barrier, to determine the uranium isotopes by alpha spectrometry.

3.0 Interferences

- 3.1 Measurement of the concentration of ^{235}U in a sample will be less certain than measurement of other uranium isotopes because of the tailing of the ^{234}U counts into the spectrum area of ^{235}U . Additional evaluation of the spectrum may be required to subtract the contribution of the ^{234}U tailing into the spectrum area corresponding to the ^{235}U activity. Additional measurements using longer counting

periods and lower counting efficiency may also be used to achieve resolution of ^{235}U counts.

- 3.2 The only non-uranium alpha-emitting radionuclide that may come through the chemistry and cause interference with the determination of ^{233}U or ^{234}U is ^{231}Pa . However, ^{231}Pa is not likely to be present in environmental samples in significant quantities.
- 3.3 If a sample contains both ^{233}U and ^{234}U , it will be difficult to resolve the two isotopes since their principal alpha energies differ by only 0.05 MeV. Unless the spectrum is well resolved, combined $^{235/236}\text{U}$ results should be reported.
- 3.4 In determining very low levels of uranium isotopes in environmental samples, detector backgrounds and laboratory reagent blanks must be accurately determined. Reagent blank determinations will be made to ascertain that the contamination from reagents, glassware, and other laboratory sources is negligible compared to the sample being analyzed. A reagent blank determination will be made in exactly the same way as for a sample.
- 3.5 Samples that have excess iron or other material deposited with the sample will undergo self-absorption. Self-absorption is indicated by poor resolution and low-energy tailing (peak straggling) in the sample spectrum.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container type, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

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6.0 Apparatus

- 6.1 Separatory funnels, beakers, pipettes, funnels, volumetric flasks. Class A glassware is used for standard and tracer preparations unless noted otherwise. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 6.2 Ceramic or Vycor containers.
- 6.3 Drying oven. The gravity convection type oven is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 125°C and able to maintain temperatures to within $\pm 5^\circ\text{C}$.
- 6.4 Electric hot plate/magnetic stirrer. This piece of apparatus should have a built-in stirrer and step-less temperature controls that can be changed as heating requirements may demand.
- 6.5 Scissors, reserved for cutting only air filters.
- 6.6 Teflon stirring rod.
- 6.7 Ash free filter paper, Whatman No. 42, or equivalent.
- 6.8 Muffle furnace, able to reach at least 500°C and able to maintain temperatures to within $\pm 15^\circ\text{C}$.
- 6.9 Top loading balance, scale readability ± 0.1 g.
- 6.10 Analytical balance, scale readability ± 0.1 mg.
- 6.11 Platinum dish, 125 mL.
- 6.12 Electrodeposition apparatus, direct current, 0 to 12 V and 0 to 2 A, using disposable deposition cells. Cathode is stainless steel disk with mirror finish and anode is platinum wire loop. See reference 15.3 for example apparatus. All electroplating disks shall be cleaned with nitric acid before use.
- 6.13 Alpha spectrometry system: Consisting of solid state alpha detector, multichannel analyzer (or PC or minicomputer), electronics, printer, and vacuum chamber. System must be capable of providing a spectral resolution of 60 keV or better on a plated source.

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7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the instruments according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine Class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

- 8.1 Class A glassware is used for standard and carrier preparation unless noted otherwise. Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. In all cases acids or bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 ²³²U Tracer solution: From NIST, or NIST-traceable, or from another nationally recognized agency.
- 8.4 Hydrochloric acid (HCl), 9 M: Dilute 750 mL of 12 M HCl to 1 L with water.
- 8.5 Hydrochloric acid (HCl), 12 M, concentrated: 37% HCl reagent.
- 8.6 Nitric acid (HNO₃), 16 M: 70% HNO₃ reagent.
- 8.7 Hydrofluoric acid (HF), 29 M: 48% HF reagent.
- 8.8 Nitric acid (HNO₃), 3 M: Dilute 187.5 mL of 16 M HNO₃ to 1 L with water.
- 8.9 Perchloric acid (HClO₄), 12 M: 70% HClO₄ reagent.
- 8.10 TIOA Solution in p-Xylene, 10%: Dissolve 100 mL of TIOA in p-xylene and dilute to 1 L with p-xylene.
- 8.11 Tri-iso-octylamine (TIOA): Reagent.

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- 8.12 p-Xylene: Reagent.
- 8.13 Nickel (Ni) foil: 1.5 cm × 1 cm × 0.1 mm.
- 8.14 Nitric acid (HNO₃), 0.1 M: Dilute 6 mL of 16 M HNO₃ to 1 L with water.
- 8.15 Hydrochloric acid (HCl), 1 M: Dilute 83 mL of 12 M HCl to 1 L with water.
- 8.16 Sodium hydrogen sulfate-sulfuric acid solution (NaHSO₄ · H₂SO₄): Dissolve 10 grams of sodium hydrogen sulfate in 100 mL of water and then carefully add 100 mL of concentrated H₂SO₄ while stirring. This solution contains about 5% NaHSO₄ in 9 M H₂SO₄.
- 8.17 Sodium hydrogen sulfate (NaHSO₄), reagent.
- 8.18 Sulfuric acid (H₂SO₄), 1 M: Dilute 55.6 mL of concentrated H₂SO₄ to 1 L with water.
- 8.19 Sulfuric acid (H₂SO₄), 18 M: Concentrated reagent.
- 8.20 Preadjusted ammonium sulfate electrolyte ((NH₄)₂SO₄), 1 M: Dissolve 132 gram of ammonium sulfate in water and dilute to 1 L. While stirring, adjust the pH to 3.5 with 15 M NH₄OH or 18 M H₂SO₄.
- 8.21 Thymol blue indicator, 0.04% solution: Dissolve 0.1 gram thymolsulfonephthalein in 21.5 mL 0.01 M NaOH and 228.5 mL water.
- 8.22 Sulfuric acid (H₂SO₄), 1.8 M: Dilute 100 mL of 18 M H₂SO₄ to 1 L with water.
- 8.23 Ammonium hydroxide (NH₄OH), 15 M: Concentrated reagent.
- 8.24 Ammonium hydroxide (NH₄OH), 1.5 M: Dilute 100 mL of 15 M NH₄OH to 1 L with water.
- 8.25 Ethanol (C₂H₅OH), 98% reagent, made slightly basic with 3 to 5 drops of 15 M NH₄OH per 100 mL of alcohol.
- 8.26 Mixed alpha standard (e.g., ²³⁸Pu, ²³⁹Pu, ²⁴²Pu, or ²³⁸U, ²³⁵U, ²³³U): From NIST or traceable to NIST, or to another nationally recognized agency.
- 8.27 Alpha check source (e.g., ²⁴¹Am or ²¹⁰Po).

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9.0 Calibration Procedures

- 9.1 Use a mixed alpha emitting standard (e.g., ^{238}Pu , ^{239}Pu , ^{242}Pu , or ^{238}U , ^{235}U , ^{233}U ,) from NIST, traceable to NIST or from another nationally recognized agency) to calibrate each detector in counting system. Refer to the manufacturer's instructions for specific calibration procedure.
- 9.2 Using an alpha check source verify the detector efficiency, detector resolution, and energy calibration daily or before use. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.3 The alpha counting system is calibrated, i.e., operating voltages, etc., according to the manufacturers instructions at least annually and after every significant change to the counting system.
- 9.4 A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed weekly. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.

10.0 Sample Preparation

10.1 Milk

- 10.1.1 Measure appropriate volume of milk to meet the required sensitivity into a ceramic or vycor container and add appropriate quantity of ^{232}U tracer. If sample activity is expected to be less than 1 dpm/g or is unknown, add 10 dpm of tracer. For higher levels, add as much ^{232}U tracer as the estimated activity of uranium in the sample. Record volume of milk used prior to adding tracer, activity, and amount of tracer added.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.1.2 Evaporate sample to dryness. The evaporation must be done carefully to avoid spattering. A drying oven at 110° to 125°C, or a controlled drip apparatus, e.g., a buret and hot plate may be used.
- 10.1.3 Place container with dried sample in muffle furnace and increase temperature slowly up to 325°C \pm 15°C to avoid ignition of the sample. Increase temperature to 550°C \pm 15°C and continue ashing until ash appears white. Total ashing time could take up to 16 or more hours.

- 10.1.4 Cool ash, add 9 M HCl and heat to bring sample into solution. Quantitatively transfer using 9 M HCl to 1-L beaker.
- 10.1.5 Add 9 M HCl to sample in beaker to approximate volume of 500 mL. Continue with Sample Analysis, Section 11.0.

10.2 Water

- 10.2.1 Add 50 mL of 12 M HCl and appropriate quantity of ^{232}U tracer to a measured volume of water sample appropriate to meet the required sensitivity. If sample activity is expected to be less than 1 dpm/g or is unknown, add 10 dpm of tracer. For higher levels, add as much ^{232}U tracer as the estimated activity of uranium in the sample. Record volume of water used prior to adding tracer, activity, and amount of tracer added. Record comment if presence of any undissolved material is noted.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.2.2 Evaporate sample to 100 mL. Add 300 mL of 12 M HCl to make sample concentration 9 M in HCl. Continue with Sample Analysis, Section 11.0.

10.3 Vegetation and Produce

- 10.3.1 A measured weight of vegetation/produce appropriate to meet the required sensitivity, is placed in a ceramic or vycor container, dried at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$, reweighed and ground. Record both wet weight and dry weight.
- 10.3.2 Add appropriate quantity of ^{232}U tracer to sample. If sample activity is expected to be less than 1 dpm/g or is unknown, add 10 dpm of tracer. For higher levels, add as much ^{232}U tracer as the estimated activity of uranium in the sample.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.3.3 Transfer to a muffle furnace and raise the temperature slowly over 8 hours (to prevent ignition) to $250^{\circ}\text{C} \pm 15^{\circ}\text{C}$, then increase less slowly to $500^{\circ}\text{C} \pm 15^{\circ}\text{C}$. The sample is ashed at $500^{\circ}\text{C} \pm 15^{\circ}\text{C}$ for 16 hours or more to produce a white ash.

- 10.3.4 Cool and weigh the vegetation/produce ash. Record exact weight.

- 10.3.5 Dissolve ash in concentrated HNO_3 and quantitatively transfer to a 400 mL beaker to a final volume of approximately 200 mL. Evaporate slowly to dryness.
- 10.3.6 Add 25 mL of concentrated HNO_3 to the beaker and evaporate slowly to dryness. Repeat 25 mL additions of acid and evaporation until a white residue is obtained. (Note: If silicious material is present, transfer sample to 100-mL Teflon beaker with HNO_3 . Add 10 mL HF and evaporate to dryness. Repeat additions of 25 mL HNO_3 —10 mL HF as necessary to remove silica. Remove HF by 3 successive additions of 10 mL HNO_3 and evaporation.)
- 10.3.7 Add 25 mL of concentrated HCl and evaporate to dryness. Repeat two more times.
- 10.3.8 Dissolve residue in 100 mL of 9 M HCl. Heat if necessary.
- 10.3.9 Continue with Sample Analysis, Section 11.0.
- 10.4 Glass Fiber Filters
- 10.4.1 Remove the filter from the shipping envelope or bag and hold the filter over a 125-mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside the bag to the platinum dish.
- 10.4.2 Place the dish with sample in a muffle furnace. Ash the sample for about 16 hours at $500^\circ\text{C} \pm 15^\circ\text{C}$.
- 10.4.3 Remove the dish and allow to cool.
- 10.4.4 Completely dampen the residue with a minimum amount but no more than 10 mL of concentrated HNO_3 .
- 10.4.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on a hot plate until a moist residue remains. Remove the dish and allow to cool.
- 10.4.6 Add 10 mL of concentrated HF and evaporate until the residue is almost completely dry. Remove the dish and allow to cool.
- 10.4.7 Add 10 mL of concentrated HNO_3 and evaporate until the sample is lightly fuming and just moist. Remove the dish and allow to cool.
- 10.4.8 Repeat above step (Step 10.4.7).

- 10.4.9 Moisten the residue on the sides and bottom of the dish with 3 M HNO₃. Scrape the residue from the sides and bottom of the dish and break it up with a teflon rod. Wash down the sides of the dish and the teflon rod thoroughly using 3 M HNO₃.
- 10.4.10 Return the dish to the hot plate and evaporate until about 5 mL of solution remains. Remove the dish and allow to cool.
- 10.4.11 Filter the sample using a funnel and Whatman No. 42 filter paper into a 50 mL volumetric flask.
- 10.4.12 Wash out the dish using 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.4.13 Wash down the filter and residue with 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.4.14 Make up the contents of the volumetric flask to 50 mL with 3 M HNO₃, stopper, and mix thoroughly.
- 10.4.15 Transfer appropriate volume to meet the required sensitivity of the sample solution from the volumetric flask to a beaker. Record volume of sample transferred. Add appropriate quantity of ²³²U tracer to sample. If sample activity is expected to be less than 1 dpm/g or is unknown, add 10 dpm of tracer. For higher levels, add as much ²³²U tracer as the estimated activity of uranium in the sample. Evaporate to dryness.
- Note:** The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.
- 10.4.16 Dissolve residue in 9 M HCl, heating if necessary.
- 10.4.17 Continue with Sample Analysis, Section 11.0.

11.0 Sample Analysis

11.1 Uranium Extraction

- 11.1.1 Place volume of 10% TIOA solution equal to sample volume in an appropriate size separatory funnel. Add 50 mL of 9 M HCl per 300 mL of 10% TIOA solution and shake funnel for 1 minute. Drain and discard aqueous (lower) acid phase after clean separation of the two phases.

- 11.1.2 Quantitatively transfer sample with 9 M HCl to TIOA in separatory funnel and shake funnel vigorously for 3 minutes. Vent funnel stopcock to prevent pressure buildup in funnel.
- 11.1.3 Allow phases to separate cleanly and draw off aqueous acid phase and discard.
- 11.1.4 Add 50 mL 9 M HCl to TIOA solution in separatory funnel and shake for 1 minute.
- 11.1.5 Allow phases to separate, and withdraw and discard lower aqueous acid phase.
- 11.1.6 Repeat steps 11.1.4 and 11.1.5.
- 11.1.7 Strip uranium from TIOA solution by adding 100 mL 0.1 M HNO₃ to separatory funnel and shaking funnel for 2 minutes.
- 11.1.8 Allow phases to separate. Withdraw and transfer lower acid phase to another separatory funnel.
- 11.1.9 Repeat steps 11.1.7 and 11.1.8 and combine strip solutions. Discard TIOA solution.
- 11.1.10 Place combined acid strip solutions in separatory funnel used in step 11.1.8.
- 11.1.11 Add 100 mL p-xylene to combined strip solution and shake funnel for 1 minute. The p-xylene removes most of the TIOA carried into the aqueous acid phase.
- 11.1.12 Allow phases to separate cleanly. Withdraw aqueous acid layer into beaker. Discard p-xylene.
- 11.1.13 Evaporate combined acid solution from step 11.1.12 to dryness. Do not overheat.
- 11.1.14 Add 10 mL 16 M HNO₃ to residue and evaporate to dryness. Do not overheat.
- 11.1.15 Add 5 mL 9 M HCl and 5 mL 12 M HClO₄ to residue and evaporate to dryness. **Caution:** This operation should be performed in a fume hood suitable for heating perchloric acid.
- 11.1.16 Repeat step 11.1.15.
- 11.1.17 Add 10 mL 12 M HCl and evaporate to dryness.

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- 11.1.18 Repeat step 11.1.17.
- 11.1.19 Add 50 mL 1 M HCl to sample residue and warm gently to dissolve residue.
- 11.1.20 Heat sample solution to $80^{\circ}\text{C} \pm 5^{\circ}\text{C}$ with stirring. Do not overheat.
- 11.1.21 Suspend new, clean nickel metal strip into solution for 2 hours to remove polonium.
- 11.1.22 Remove nickel and evaporate solution to near dryness.
- 11.1.23 Add 5 mL of 16 M HNO_3 .
- 11.1.24 Evaporate sample to near dryness.
- 11.2 Electrodeposition
- 11.2.1 Add 2 mL of a 5% solution of NaHSO_4 in 9 M H_2SO_4 to sample.
- 11.2.2 Add 5 mL of 16 M HNO_3 , mix well, and evaporate to dryness but do not bake.
- 11.2.3 Dissolve sample in 5 mL of preadjusted ammonium sulfate electrolyte, warming to hasten dissolution.
- 11.2.4 Transfer solution to electrodeposition cell using an additional 5 to 10 mL of electrolyte in small increments to rinse sample container.
- 11.2.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H_2SO_4 (or 1.5 M NH_4OH) until color is obtained.
- 11.2.6 Place platinum anode into solution so that it is about 1 cm above stainless steel disk that serves as cathode.
- 11.2.7 Connect electrodes to source of current, turn power on, and adjust power supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustments during the electrodeposition.)
- 11.2.8 Continue electrodeposition for 1 hour.
- 11.2.9 When electrodeposition is to be terminated, add 1 mL of 15 M NH_4OH and continue electrodeposition for 1 minute.

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- 11.2.10 Remove anode from cell, and then turn power off.
- 11.2.11 Remove solution from cell, and rinse cell 2 or 3 times with 0.15 M NH_4OH .
- 11.2.12 Disassemble cell, and wash disk with ethanol made basic with NH_4OH .
- 11.2.13 Touch edge of disk to tissue to absorb ethanol from slide.

Note: The sample must be counted within 1 week because ^{232}U daughters grow into the sample and possibly interfere with determination of certain other uranium activities.

- 11.2.14 Dry disk, label it for counting, and place it in a designated holding/staging area before counting. If the disk is not completely dry, moisture may adversely affect spectral resolution.

11.3 Alpha Spectrometry

- 11.3.1 Using the manufacturer's suggested operating procedure, count samples for as long as necessary to meet the Minimum Detectable Concentration requirements specified in the analytical laboratory service contract(s) or Sampling and Analysis Plan. Counting times may have to be further adjusted if sample counting efficiency is low, if the tracer recovery is less than expected, or if the anticipated uranium activity is less than 1 dpm/sample.
- 11.3.2 Check the alpha spectrum for peaks at $^{233}\text{U}/^{234}\text{U}$, $^{235}/^{236}\text{U}$, and ^{238}U alpha energies (as listed below) and determine total counts in each peak. The ^{233}U and ^{234}U isotopes emit alpha particles that are too close in energy for resolution and the reported value is a sum of the two. Combined ^{235}U and ^{236}U values should be reported if the spectrum is not well resolved.

| Uranium Isotope | Primary Alpha Energies (MeV) | Probability per Decay |
|-----------------|------------------------------|-----------------------|
| 232 | 5.32 | 0.69 |
| | 5.26 | 0.31 |
| 233 | 4.78 | 0.13 |
| | 4.82 | 0.84 |
| 234 | 4.72 | 0.27 |

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| | | |
|------|------|------|
| | 4.77 | 0.72 |
| 235 | 4.36 | 0.11 |
| | 4.37 | 0.06 |
| | 4.39 | 0.55 |
| | 4.59 | 0.05 |
| 236* | 4.44 | 0.26 |
| | 4.49 | 0.74 |
| 238 | 4.15 | 0.23 |
| | 4.19 | 0.77 |

* If ^{236}U alpha peaks are not resolved, then use the ^{235}U probability per decay values for activity calculations.

11.3.3 Samples with poorly resolved tracer or analyte peaks may indicate excessive self-absorption and the need to replate or repurify the sample.

12.0 Calculations

12.1 Calculate concentration of an uranium isotope in pCi/g or pCi/L, or pCi/air filter as follows:

$$U = \frac{(A - A_1) \times F \times Y_t}{(2.22) \times (B - B_1) \times (W) \times Y_s} \quad (1)$$

Where:

A = gross sample counts per minute that appear in the $^{233/234}\text{U}$, ^{235}U , ^{236}U , or ^{238}U α peaks

A₁ = Detector background counts per minute in the same α peaks as A above

B = gross tracer counts per minute that appear in α peaks of tracer isotope

- B_1 = Detector background counts per minute in the same α peaks as B above
- F = tracer activity in dpm added to sample
- W = sample volume or weight, L or gram (W for air filter is fraction of total filter.)
- Y_s = probability of alpha emission per decay for α of interest (in sample) in A above
- Y_t = probability of α emission per decay for α of interest (in tracer)
- 2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the following multiplicative factor: $3.667E-02$ Bq/pCi. The overall recovery for the tracer is included in the above equation as $(F)(Y)/(B - B_1)$. Final sample results shall be corrected for reagent blank contribution.

- 12.2 The concentration for each uranium isotope is determined by the above equation using the sample counts of the main alpha peak for that isotope.
- 12.3 The uranium concentration in $\mu\text{g/g}$ (or L or air filter) can be calculated by dividing each isotopic activity by the isotopic specific activity and summing the results:

$$(1 \mu\text{g } ^{234}\text{U} / 6.24 \times 10^3 \text{ pCi } ^{234}\text{U}) (w \text{ pCi } ^{234}\text{U/g}) = W \mu\text{g } ^{234}\text{U/g}$$

$$(1 \mu\text{g } ^{235}\text{U} / 2.14 \text{ pCi } ^{235}\text{U}) (x \text{ pCi } ^{235}\text{U/g}) = X \mu\text{g } ^{235}\text{U/g}$$

$$(1 \mu\text{g } ^{236}\text{U} / 6.47 \times 10^2 \text{ pCi } ^{236}\text{U}) (y \text{ pCi } ^{236}\text{U/g}) = Y \mu\text{g } ^{236}\text{U/g}$$

$$(1 \mu\text{g } ^{238}\text{U} / 0.333 \text{ pCi } ^{238}\text{U}) (z \text{ pCi } ^{238}\text{U/g}) = Z \mu\text{g } ^{238}\text{U/g}$$

$$U \text{ total } \mu\text{g/g} = W + X + Y + Z.$$

- 12.4 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical services contract(s). The minimum detectable concentration (MDC) in

pCi/L (or gram or air filter) shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels and are outlined in the FEMP QAPjP or specified in the project specific Sampling and Analysis Plan, or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|-------------------------|-----------|------------------|-------------------|
| Reagent Blank** | 1/20* | To be determined | Qualify Data |
| ²³² U Tracer | 1/1 | To be determined | Qualify Data |
| LCS | 1/20* | To be determined | Qualify Data |
| Duplicate** | 1/20* | To be determined | Qualify Data |

* or per batch or fraction thereof

** per matrix

15.0 References

- 15.1 *Eastern Environmental Radiation Facility Radiochemistry Procedures Manual*. Montgomery, Alabama. U.S. EPA, EPA-520/5-84-006. 1984.
- 15.2 *Alpha Spectrometry Measurement for Radionuclides of Uranium*. Method RT800. Health and Environmental Chemistry, Los Alamos National Laboratory. Los Alamos, New Mexico. 1987.
- 15.3 *EML Procedures Manual*. 27th ed., Volume 1. U.S. DOE Environmental Measurements Laboratory. New York, New York. HASL-300-Ed.27-Vol.1. 1990.

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- 15.4 *Standard General Methods for Detector Calibration and Analysis of Radionuclides.* ASTM E181-82. 1982.
- 15.5 *Standard Practices for the Measurement of Radioactivity.* ASTM D 3648-78. 1978.

Attachment A

Preparation of ^{232}U Tracer

Uranium-232 ($T_{1/2}$ 72 years) decays to ^{228}Th , which has a half-life of 1.9 years. To prevent contamination of samples with ^{228}Th and its decay products, the ^{232}U stock must be decontaminated at least annually. The ^{232}U is extracted into tri-iso-octylamine (TIOA) and the TIOA is washed with a mixture of HCl and HF to decontaminate the tracer. The ^{232}U is stripped from the TIOA with dilute nitric acid and wet ashed. Aliquots of the cleaned tracer are electrodeposited and radioassayed by alpha spectrometry to determine the specific activity of the tracer solution.

A.0 Apparatus

Class A glassware shall be used for standard and tracer preparations unless noted otherwise. Unless otherwise noted, all glassware shall be nitric acid washed before use. All electroplating disks shall be cleaned with nitric acid.

A.1 Separatory funnels, beakers, pipettes, volumetric flasks.

A.2 Electric hot plate/magnetic stirrer. This piece of apparatus should have a built-in stirrer and stepless temperature controls that can be changed as heating requirements may demand.

B.0 Reagents

In all cases acids and bases should be added to water.

B.1 ^{232}U Tracer Solution: from NIST or NIST-traceable, or from another nationally recognized agency.

B.2 Hydrochloric Acid, HCl, 9 M: Dilute 750 mL of 12 M HCl to 1 L with water.

B.3 Hydrochloric Acid, HCl, 12 M, concentrated: 37% HCl reagent.

B.4 TIOA Solution in p-Xylene, 10%: Dissolve 100 mL of TIOA in p-xylene and dilute to 1 L with p-xylene.

B.5 p-Xylene: Reagent.

B.6 Hydrochloric Acid, HCl, 1 M: Dilute 83 mL of 12 M HCl to 1 L with water.

B.7 Hydrochloric Acid HCl 3 M—Hydrofluoric Acid HF 0.1 M mixture: Dilute 250 mL of concentrated HCl and 3.5 mL of concentrated HF to 1 L with water. Store in a plastic bottle.

B.8 Hydrogen peroxide, H₂O₂, 50 %, reagent.

B.9 Nitric Acid HNO₃, 0.1 M: Dilute 6 mL of the concentrated HNO₃ to 1 L with water.

C.0 Procedure

C.1 From the specific activity of the ²³²U stock solution, determine the size of the aliquot to be used so that when diluted it will result in a final solution of approximately 1 pCi ²³²U/L.

C.2 Evaporate the aliquot of ²³²U to dryness in a beaker.

C.3 Add 10 mL of 12 M HCl and evaporate to dryness.

C.4 Add 10 mL 9 M HCl to the beaker and warm to 50°C.

C.5 Add 10 drops of 50 percent hydrogen peroxide to the solution.

C.6 Equilibrate 100 mL of the 10 percent TIOA solution with 50 mL of warm 9 M HCl by shaking in a separatory funnel for one minute.

C.7 Allow the layers to separate and discard the lower aqueous acid phase.

C.8 Add the solution from step C.5 to the TIOA in the separatory funnel and shake funnel for two minutes.

C.9 Allow phases to separate and discard the lower aqueous acid phase.

C.10 Wash the TIOA solution with 50 mL 9 M HCl warmed to 50°C. Shake for one minute and discard lower aqueous acid phase when separated.

C.11 Wash the TIOA solution with 75 mL of 3 M HCl/0.1 M HF warmed to 50°C ± 5°C. Shake funnel for two minutes and discard lower acid phase when separated. Repeat this step.

- C.12 Strip the uranium tracer from the TIOA solution by adding 100 mL 0.1 M HNO₃ to the separatory funnel and shaking the funnel for two minutes.
- C.13 Allow phases to separate; withdraw and save lower acid phase.
- C.14 Repeat steps C.12 and C.13 and combine strip solutions.
- C.15 Place combined strip solutions in clean separatory funnel.
- C.16 Add 100 mL p-xylene to combined strip solution and shake funnel for one minute.
- C.17 Allow phases to separate cleanly; withdraw lower aqueous acid layer into a beaker. Discard p-xylene.
- C.18 Evaporate solution from step C.17 to dryness. Do not overheat.
- C.19 Add 10 mL 12 M HCl to residue in beaker and take to dryness. Do not overheat.
- C.20 Take up solution in 250 mL of 1 M HCl and filter through a membrane filter using suction. Store the cleaned tracer stock solution.
- C.21 Take a 1 mL aliquot of the stock solution from Step C.20 and evaporate to dryness.
- C.22 Add 5 mL of concentrated HNO₃ and evaporate to near dryness.
- C.23 Continue with electrodeposition Section 11.2 in the main procedure.
- C.24 Verify from the alpha spectrum that the ²³²U tracer is free from interfering alpha emitters before use.
- C.25 The cleaned ²³²U tracer must also be standardized before use. See references 15.4 and 15.5 for guidance on determining the absolute activity.

Isotopic Uranium in Soil/Sediment by Alpha Spectrometry

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Working Linear Range: Infinite with dilution
Reporting Limit: ~0.04 pCi/g (^{235}U), ~0.8 pCi/g (^{238}U)
Reporting Units: pCi/g
Matricies: Soil/sediment

1.0 Scope

1.1 The method applies to the determination of uranium isotopes in soil/sediment samples. It has been applied to soils from various parts of the United States. Total uranium activity is determined by adding the results for the individual isotopes ($^{233/234}\text{U}$, $^{235/236}\text{U}$, ^{238}U). Total uranium mass may be determined with the specific activity factors for each isotope. The nominal sensitivity may vary with each analysis but is approximately 0.8 pCi/g for ^{238}U and 0.04 pCi/g for ^{235}U .

1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

2.1 After adding ^{232}U tracer, organic matter is removed from the sample by heating. The sample is then decomposed by nitric acid-hydrofluoric acid digestion, and uranium is coprecipitated by making the solution basic with ammonium hydroxide (carbonate free). The hydroxide precipitate is dissolved in 8 M HCl, which is extracted with isopropyl ether to remove the bulk of the iron present. For samples with relatively low iron concentrations, this extraction can be omitted.

2.2 The 8 M HCl solution is passed through an anion exchange resin column. Uranium, polonium, and bismuth will be adsorbed on the resin, but thorium and radium will pass through the column. Plutonium and any unextracted iron are also retained by the resin but are eluted with 6 M HCl containing hydrogen iodide. The iodide ion reduces plutonium (IV) to plutonium (III) and reduces the iron (III) to iron (II); neither ion is retained by the ion exchange resin in 6 M HCl. The uranium is eluted from the column with 1.0 M HCl, whereas any zinc adsorbed on the column will remain. The uranium is electrodeposited onto a stainless steel planchet, and the planchet is counted on a silicon surface barrier detector to determine the uranium isotopes by alpha spectrometry.

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3.0 Interferences

- 3.1 Measurement of the concentration of ^{235}U in a sample will be less certain than measurement of other uranium isotopes because of the tailing of ^{234}U counts into the spectrum area of ^{235}U . Additional evaluation of the spectrum may be required to subtract the contribution of the ^{234}U tailing into the spectrum area corresponding to the ^{235}U activity. Additional measurements using longer counting periods and lower counting efficiency may also be used to achieve resolution of ^{235}U counts.
- 3.2 The only non-uranium alpha-emitting radionuclide that may come through the chemistry and cause interference with the determination of ^{233}U or ^{234}U is ^{231}Pa . However, ^{231}Pa is not likely to be present in environmental samples in significant quantities.
- 3.3 If a sample contains both ^{233}U and ^{234}U , it may be difficult to resolve the two isotopes since their principal alpha energies differ by only 0.05 MeV. Unless the spectrum is well resolved, combined ^{235}U and ^{236}U results should be reported.
- 3.4 In determining very low levels of uranium isotopes in environmental samples, detector backgrounds and laboratory blanks must be accurately determined. Reagent blank determinations shall be made to ascertain that contamination from reagents, glassware, and other laboratory sources is negligible compared to the sample being analyzed. A blank determination shall be made in exactly the same way a sample determination is made.
- 3.5 Samples that have excess iron or other material deposited with the sample will undergo self-absorption. Self-absorption is indicated by poor resolution and low-energy tailing (peak straggling) in the sample spectrum.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

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5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Separatory funnels, beakers, pipettes, volumetric flasks, ceramic or Vycor containers (casseroles), centrifuge bottles. Class A volumetric glassware is used for tracer and standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be acid washed before use.
- 6.2 Teflon beakers and watch glasses.
- 6.3 Drying oven: The gravity convection type oven is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 125°C and able to maintain temperatures to within $\pm 5^\circ\text{C}$.
- 6.4 Sieves: 2-mm and 15 mesh
- 6.5 Grinder or Ball mill: Sufficient to reduce sample to pass 15 mesh sieve.
- 6.6 Electric hot plate/magnetic stirrer: With built-in stirrer and stepless temperature controls that can be changed as heating requirements may demand.
- 6.7 Muffle furnace: Able to reach at least 550°C and maintain temperatures within $\pm 15^\circ\text{C}$.
- 6.8 Top-loading balance: Scale readability ± 0.1 g.
- 6.9 Analytical balance: Scale readability ± 0.1 mg.
- 6.10 Electrodeposition apparatus: 0 to 12 V dc, 0 to 2 A, using disposable deposition cells. Cathode is stainless steel disk with mirror finish and anode is platinum wire loop. See reference 15.3 for example apparatus. All electroplating disks shall be cleaned with nitric acid before use.
- 6.11 Alpha spectrometry system: Consisting of solid state alpha detector, multichannel analyzer (or PC or minicomputer), electronics, printer, and vacuum chamber. System must be capable of providing a spectral resolution of 60 keV or better on a plated source.

- 6.12 Vacuum filter apparatus: For use with 47-mm filters.
- 6.13 Ion exchange columns: Approximately 1.3 cm I.D., 15-cm long, with 100-mL reservoir.

7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the instruments according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine Class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents

- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. In all cases, acids or bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Standardized ^{232}U solution: From NIST, or NIST traceable, or another nationally recognized agency.
- 8.4 Nitric acid (HNO_3), 16 M: Reagent.
- 8.5 Hydrochloric acid (HCl), 12 M: Reagent.
- 8.6 Hydrochloric acid (HCl), 1 M: Dilute 83 mL of 12 M HCl to 1 L with water.
- 8.7 Hydrochloric acid (HCl), 6 M: Dilute 500 mL of 12 M HCl to 1 L with water.
- 8.8 Hydrochloric acid (HCl), 0.5 M: Dilute 41.5 mL of 12 M HCl to 1 L with water.
- 8.9 Hydrochloric acid (HCl), 8 M: Dilute 664 mL of 12 M HCl to 1 L with water.

- 8.10 Isopropyl ether $[(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2]$: Concentrated reagent.
- 8.11 Sulfuric acid (H_2SO_4), 18 M: Concentrated reagent.
- 8.12 Sulfuric acid (H_2SO_4), 1.8 M: Dilute 100 mL of 18 M H_2SO_4 to 1 L with water.
- 8.13 Hydrofluoric acid (HF): Concentrated (48% solution) reagent.
- 8.14 Hydriodic acid (HI): Concentrated (48% solution) reagent.
- 8.15 Hydriodic/hydrochloric acid solution: Mix 1 mL of concentrated HI with 50 mL of 6 M HCl. Prepare immediately before use.
- 8.16 Ferric chloride carrier solution (10 mg Fe/mL): Dissolve 4.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a mixture of 4.2 mL of concentrated hydrochloric acid and 95.8 mL of water.
- 8.17 Ammonium hydroxide (NH_4OH), 15 M: Concentrated reagent.
- 8.18 Ammonium hydroxide (NH_4OH), 1.5 M: Dilute 100 mL of 15 M NH_4OH to 1 L with water.
- 8.19 Ammonium hydroxide (NH_4OH), 0.15 M: Dilute 10 mL of 15 M NH_4OH to 1 L with water.
- 8.20 Anion exchange resin: Bio Rad AG1-X4 (100-200 mesh) chloride form, or equivalent. Prepare column by slurring resin with 8 M HCl and pouring it on column of approximately 1.3 cm I.D. Column height resin shall be about 10 cm.
- 8.21 Sodium hydrogen sulfate—sulfuric acid solution ($\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$): Dissolve 10 g of sodium hydrogen sulfate in 100 mL of water and then carefully add 100 mL of concentrated H_2SO_4 while stirring. This solution contains about 5% NaHSO_4 in 9 M H_2SO_4 .
- 8.22 Preadjusted ammonium sulfate electrolyte ($(\text{NH}_4)_2\text{SO}_4$), 1 M: Dissolve 132 g of ammonium sulfate in water and dilute to 1 L. While stirring, adjust the pH to 3.5 with 15 M NH_4OH or 18 M H_2SO_4 .
- 8.23 Thymol blue indicator, 0.04% solution: Dissolve 0.1 gram thymolsulfonephthalein in 21.5 mL 0.01 M NaOH and 228.5 mL water.
- 8.24 Ethanol ($\text{C}_2\text{H}_5\text{OH}$) 98% reagent: Made slightly basic with 3 to 5 drops of 15 M NH_4OH per 100 mL of alcohol.

8.25 Mixed alpha standard (e.g., ^{238}Pu , ^{239}Pu , ^{242}Pu , or ^{238}U , ^{235}U , ^{233}U): From NIST, or NIST traceable, or from another nationally recognized agency.

8.26 Alpha check source (e.g., ^{210}Pb , ^{241}Am).

9.0 Calibration Procedures

9.1 Use a mixed alpha emitting standard (e.g., ^{238}Pu , ^{239}Pu , ^{242}Pu , or ^{238}U , ^{235}U , ^{233}U , traceable to NIST or another nationally recognized agency) to calibrate each detector in counting system. Refer to the manufacturer's instructions for specific calibration procedure.

9.2 Using an alpha check source verify the detector efficiency, detector resolution, and energy calibration daily or before use. The results must be within the established limits (e.g., $\pm 3 \sigma$) before commencing analyses.

9.3 Calibrate the alpha counting system (i.e., operating voltages, etc.) according to the manufacturer's instructions at least annually and after every significant change to the counting system.

9.4 A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed weekly. The results must be within established limits (e.g., $\pm 3 \sigma$) before commencing analyses.

10.0 Sample Preparation

10.1 Dry sample at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for about 12 hours. Pass sample (typically 100 g) through a 2-mm sieve to remove roots, stones, etc. Grind, mill, or pulverize to reduce sample to pass 15 mesh screen. Blend until thoroughly mixed.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

10.2 Weigh an appropriate amount of 15 mesh soil/sediment sample to meet the required sensitivity and transfer to a casserole. Record (dry) weight used.

10.3 Add appropriate quantity of ^{232}U tracer. If sample activity is expected to be less than 1 dpm/g or is unknown, add 10 dpm of tracer. For higher levels, add as much ^{232}U tracer as the estimated activity of uranium in the sample.

Note: The tracer solution must have sufficient activity concentration such that the volume added does not exceed 20% of the sample volume.

- 10.4 Heat casserole containing sample in muffle furnace. Increase temperature at 1-hour intervals to 300°, 400°, and 550°C. Muffle for 2 or 3 hours at 550°C ± 15°C or until only a brown powdery ash remains. Remove and cool.
 - 10.5 Transfer sample to 250-mL Teflon beaker, rinsing casserole with 10-mL portions of 16 M HNO₃, to a final volume of 60 mL of nitric acid.
 - 10.6 Carefully add 30 mL of 48% hydrofluoric acid, cover with Teflon watchglass, and heat on hot plate with frequent stirring for about 1 hour. Remove from hot plate and cool. (**Caution:** Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
 - 10.7 Carefully add 30 mL each of 16 M HNO₃ and HF (48%), and digest on a hot plate with some stirring for an additional hour.
 - 10.8 Remove from hot plate and cool to room temperature. Slowly add 20 mL of 12 M HCl, and heat on hot plate with some stirring until solution has evaporated to liquid volume of approximately 10 mL.
 - 10.9 Add 50 mL of water, and digest on hot plate with stirring for 10 minutes to dissolve soluble salts.
 - 10.10 Cool and transfer total sample into 250-mL centrifuge bottle with minimum of distilled water from wash bottle. If any insoluble residue is present, centrifuge sample and transfer supernate into another centrifuge bottle. The residue shall be washed with 10 mL of 1.0 M HCl that is added to the supernate. If any residue remains, repeat steps 10.4 through 10.10 combining supernates. Proceed to Sample Analysis, Section 11.0.
- 11.0 **Sample Analysis**
 - 11.1 Coprecipitation
 - 11.1.1 Add 2 mL of FeCl₃ carrier solution to centrifuge bottle and stir.

- 11.1.2 Add 15 M NH_4OH (CO_2 free) while stirring to precipitate iron. Continue adding 15 M NH_4OH to raise pH to 9 to 10 as determined by pH paper; then add 5 mL in excess.
- 11.1.3 Centrifuge for 5 minutes, decant, and discard supernate.
- 11.1.4 Dissolve precipitate with a minimum of 12 M HCl, and add 8 M HCl to a volume of about 50 mL. Transfer solution to 250-mL separatory funnel using two 5-mL rinses of 8 M HCl and proceed to Section 11.2.
- 11.2 Ether Extraction
- 11.2.1 Add 60 mL of isopropyl ether to separatory funnel, and shake solution for 2 minutes. Allow phases to separate; then transfer aqueous (lower) phase to second separatory funnel. Add 5 mL of 12 M HCl to aqueous phase.
- 11.2.2 Repeat ether extraction two more times. The bulk of the iron is removed as evidenced by the appearance of a yellow color in the organic phase. If sample has a very high concentration of iron, additional extractions may be necessary.
- 11.2.3 Transfer aqueous phase to 150-mL beaker, boil for 15 minutes, and proceed with Section 11.3.
- 11.3 Anion Exchange Separation
- 11.3.1 Condition anion exchange resin column by rinsing column with four column volumes of 8 M HCl.
- 11.3.2 Transfer sample from step 11.2.3 to conditioned anion exchange resin.
- 11.3.3 After sample has passed through column, elute any unextracted iron (and plutonium if present) with six column volumes of 6 M HCl containing 1 mL of concentrated HI per 50 mL of 6 M HCl (freshly prepared).
- 11.3.4 Rinse column with additional two column volumes of 6 M HCl.
- 11.3.5 Elute uranium with six column volumes of 1.0 M HCl.
- 11.3.6 Evaporate sample to about 20 mL and add 5 mL of 16 M HNO_3 .
- 11.3.7 Evaporate sample to near dryness.

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11.4 Electrodeposition

- 11.4.1 Add 2 mL of a 5% solution of NaHSO₄ in 9 M H₂SO₄ to sample.
- 11.4.2 Add 5 mL of 16 M HNO₃, mix well, and evaporate to dryness but do not bake.
- 11.4.3 Dissolve sample in 5 mL of preadjusted ammonium sulfate electrolyte, warming to hasten dissolution.
- 11.4.4 Transfer solution to electrodeposition cell using an additional 5 to 10 mL of electrolyte in small increments to rinse sample container.
- 11.4.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H₂SO₄ (or 1.5 M NH₄OH) until color is obtained.
- 11.4.6 Place platinum anode into solution so that it is about 1 cm above stainless steel disk that serves as cathode.
- 11.4.7 Connect electrodes to source of current, turn power on, and adjust power supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustments during the electrodeposition.)
- 11.4.8 Continue electrodeposition for 1 hour.
- 11.4.9 When electrodeposition is to be terminated, add 1 mL of 15 M NH₄OH and continue electrodeposition for 1 minute.
- 11.4.10 Remove anode from cell, and then turn power off.
- 11.4.11 Remove solution from cell, and rinse cell 2 or 3 times with 0.15 M NH₄OH.
- 11.4.12 Disassemble cell, and wash disk with ethyl alcohol made basic with NH₄OH.
- 11.4.13 Touch edge of disk to tissue to absorb alcohol from slide.

Note: The sample must be counted within 1 week because ²³²U daughters grow into the sample and possibly interfere with determination of certain other uranium activities.

- 11.4.14 Dry disk, label it for counting, and place it in a designated holding/staging area before counting. If disk is not completely dry, moisture may adversely affect spectral resolution.

11.5 Alpha Spectrometry

- 11.5.1 Using the manufacturer's suggested operating procedure count samples as long as necessary to meet the minimum detectable concentration requirements specified in the analytical laboratory service contract(s) or Sampling and Analysis Plan. Counting times may have to be further adjusted if sample counting efficiency is low, if tracer recovery is less than expected, or if anticipated uranium activity is less than 1 dpm/sample.
- 11.5.2 Check the alpha spectrum for peaks at $^{233/234}\text{U}$, $^{235/236}\text{U}$, and ^{238}U alpha energies (as listed below) and determine total counts in each peak. The ^{233}U and ^{234}U isotopes emit alpha particles that are too close in energy for resolution and the reported value is a sum of the two. Combined ^{235}U and ^{236}U values should be reported if the spectrum is not well resolved.
- 11.5.3 Samples with poorly resolved tracer or analyte peaks may indicate excessive self-absorption and the need to replate or repurify the sample.

| Uranium Isotope | Primary Alpha Energies (MeV) | Probability per Decay |
|-----------------|------------------------------|-----------------------|
| 232 | 5.32 | 0.69 |
| | 5.26 | 0.31 |
| 233 | 4.78 | 0.13 |
| | 4.82 | 0.84 |
| 234 | 4.72 | 0.27 |
| | 4.77 | 0.72 |
| 235 | 4.36 | 0.11 |
| | 4.37 | 0.06 |
| | 4.39 | 0.55 |
| | 4.59 | 0.05 |
| 236* | 4.44 | 0.26 |
| | 4.49 | 0.74 |
| 238 | 4.15 | 0.23 |
| | 4.19 | 0.77 |

*If ^{235}U and ^{236}U alpha peaks are not resolved, then use the ^{235}U probability per decay values for activity calculations.

12.0 Calculations

12.1 Calculate concentration of uranium in pCi/g of soil as:

$$U = \frac{(A - A_1) \times F \times Y_t}{(2.22) \times (B - B_1) \times (W) Y_s} \text{ pCi/g}$$

Where:

A = gross sample counts per minute in $^{233/234}\text{U}$, ^{235}U , ^{236}U , or ^{238}U α peaks

A_1 = detector background counts per minute in the same α peaks as A above

B = gross tracer counts per minute that appear in the α peaks of the tracer isotope

B_1 = detector background counts per minute in the same α peaks as B above

F = tracer activity in dpm added to the sample

W = sample (dry) weight, grams

Y_s = probability of α emission per decay for α of interest (in sample) in A above

Y_t = probability of α emission per decay for α of interest (in tracer) in B above

2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the multiplicative factor $3.667\text{E-}02$ Bq/pCi. Overall recovery for the tracer is included in the above equation as $(F)(Y_t)/(B - B_1)$. Final sample results shall be corrected for reagent blank contribution.

12.2 The concentration for each uranium isotope is determined by the above equation using the sample counts of the main alpha peak for that isotope.

- 12.3 The uranium concentration in $\mu\text{g/g}$ can be calculated by dividing each isotopic activity by the isotopic specific activity and summing the results:

$$(1 \mu\text{g } ^{234}\text{U} / 6.24 \times 10^3 \text{ pCi } ^{234}\text{U}) (w \text{ pCi } ^{234}\text{U/g}) = W \mu\text{g } ^{234}\text{U/g}$$

$$(1 \mu\text{g } ^{235}\text{U} / 2.14 \text{ pCi } ^{235}\text{U}) (x \text{ pCi } ^{235}\text{U/g}) = X \mu\text{g } ^{235}\text{U/g}$$

$$(1 \mu\text{g } ^{236}\text{U} / 6.47 \text{ pCi } ^{236}\text{U}) (y \text{ pCi } ^{236}\text{U/g}) = Y \mu\text{g } ^{236}\text{U/g}$$

$$(1 \mu\text{g } ^{238}\text{U} / 0.333 \text{ pCi } ^{238}\text{U}) (z \text{ pCi } ^{238}\text{U/g}) = Z \mu\text{g } ^{238}\text{U/g}$$

$$\text{Total U } (\mu\text{g/g}) = W + X + Y + Z.$$

- 12.4 The total propagated uncertainty shall be determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical services contract(s). The minimum detectable concentration (MDC) in pCi/g must be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels and are outlined in the QAPjP or specified in the project specific Sampling and Analysis Plan or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|-------------------------|-----------|------------------|-------------------|
| Reagent Blank | 1/20* | To be determined | Qualify Data |
| ²³² U Tracer | 1/1 | To be determined | Qualify Data |
| LCS | 1/20* | To be determined | Qualify Data |
| Duplicate | 1/20* | To be determined | Qualify Data |

* or per batch or fraction thereof

15.0 References

- 15.1 *Radionuclide Method for the Determination of Uranium in Soil and Air.* U.S. EPA Environmental Monitoring and Support Laboratory. Las Vegas, Nevada. EPA-600/7-80-019. 1980.
- 15.2 *Alpha Spectrometry Measurement for Radionuclides of Uranium.* Method RT800. Health and Environmental Chemistry, Los Alamos National Laboratory. Los Alamos, New Mexico. 1987.
- 15.3 *Radiochemical Determination of Uranium Isotopes in Soil by Alpha Spectrometry.* ASTM Method C 1000-83. 1983.
- 15.4 *EML Procedures Manual.* 27th ed., Volume 1. U.S. DOE Environmental Measurements Laboratory. New York, New York. Analytical Support Level-300-Ed.27-Vol.1. 1990.
- 15.5 *Standard General Methods for Detector Calibration and Analysis of Radionuclides,* ASTM E181-82, 1982
- 15.6 *Standard Practices for the Measurement of Radioactivity,* ASTM D 3648-78, 1978.

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Attachment A
Preparation of ^{232}U Tracer

Uranium-232 ($T_{1/2} = 72$ years) decays to thorium-228 ($T_{1/2} = 1.9$ years). To prevent contamination of samples with ^{228}Th and its decay products, the ^{232}U stock must be decontaminated at least annually. The ^{232}U is extracted into tri-iso-octylamine (TIOA) and the TIOA is washed with a mixture of HCl and HF to decontaminate the tracer. The ^{232}U is stripped from the TIOA with dilute nitric acid and wet ashed. Aliquots of the cleaned tracer are electrodeposited and radioassayed by alpha spectrometry to determine the specific activity of the tracer solution.

A.0 Apparatus

- A.1 Class A glassware shall be used for standard and tracer preparations unless noted otherwise. Unless otherwise noted, all glassware shall be nitric acid washed before use. All electroplating disks shall be cleaned with nitric acid.
- A.2 Separatory Funnels, Beakers, Pipettes, Volumetric Flasks.
- A.3 Electric Hot Plate/Magnetic Stirrer: With builtin stirrer and stepless temperature controls that can be changed as heating requirements may demand.

B.0 Reagents

- B.1 In all cases, acids and bases will be added to water.
- B.2 ^{232}U Tracer Solution: From NIST or NIST-traceable.
- B.3 Hydrochloric Acid (HCl), 9 M: Dilute 750 mL of 12 M HCl to 1 L with water.
- B.4 Hydrochloric Acid (HCl), 12 M concentrated: 37% HCl reagent.
- B.5 TIOA Solution in p-Xylene, 10%: Dissolve 100 mL of TIOA in p-xylene and dilute to 1 L with p-xylene.
- B.6 p-Xylene: Reagent.
- B.7 Hydrochloric Acid (HCl), 1 M: Dilute 83 mL of 12 M HCl to 1 L with water.

- B.8 Hydrochloric Acid (HCl) 3 M—Hydrofluoric Acid (HF) 0.1 M mixture: Dilute 250 mL of concentrated HCl and 3.5 mL of concentrated HF to 1 L with water. Store in a plastic bottle.
- B.9 Hydrogen Peroxide (H₂O₂), 50 %: Reagent.
- B.10 Nitric Acid (HNO₃), 0.1 M: Dilute 6 mL of the concentrated HNO₃ to 1 L with water.
- C.0 Procedure
- C.1 From the specific activity of the ²³²U stock solution, determine the size of the aliquot to be used so that when diluted it will result in a final solution of approximately 1 pCi ²³²U/mL.
- C.2 Evaporate the aliquot of ²³²U to dryness in a beaker.
- C.3 Add 10 mL of 12 M HCl and evaporate to dryness.
- C.4 Add 10 mL 9 M HCl to the beaker and warm to 50°C.
- C.5 Add 10 drops of 50 percent hydrogen peroxide to the solution.
- C.6 Equilibrate 100 mL of the 10 percent TIOA solution with 50 mL of warm 9 M HCl by shaking in a separatory funnel for one minute.
- C.7 Allow the layers to separate and discard the lower aqueous acid phase.
- C.8 Add the solution from step C.5 to the TIOA in the separatory funnel and shake funnel for two minutes.
- C.9 Allow phases to separate and discard the lower aqueous acid phase.
- C.10 Wash the TIOA solution with 50 mL 9 M HCl warmed to 50°C. Shake for one minute and discard lower aqueous acid phase when separated.
- C.11 Wash the TIOA solution with 75 mL of 3 M HCl/0.1 M HF warmed to 50°C. Shake funnel for two minutes and discard lower acid phase when separated. Repeat this step.
- C.12 Strip the uranium tracer from the TIOA solution by adding 100 mL 0.1 M HNO₃ to the separatory funnel and shaking the funnel for two minutes.

- C.13 Allow phases to separate; withdraw and save lower acid phase.
- C.14 Repeat steps C.12 and C.13 and combine strip solutions.
- C.15 Place combined strip solutions in clean separatory funnel.
- C.16 Add 100 mL p-xylene to combined strip solution and shake funnel for one minute.
- C.17 Allow phases to separate cleanly; withdraw lower aqueous acid layer into a beaker. Discard p-xylene.
- C.18 Evaporate solution from step C.17 to dryness. Do not overheat.
- C.19 Add 10 mL 12 M HCl to residue in beaker and take to dryness. Do not overheat.
- C.20 Take up solution in 250 mL of 1 M HCl and filter through a membrane filter using suction. Store the cleaned tracer stock solution.
- C.21 Take a 1 mL aliquot of the stock solution from Step C.20 and evaporate to dryness.
- C.22 Add 5 mL of concentrated HNO₃ and evaporate to near dryness.
- C.23 Continue with electrodeposition Section 11.2 in the main procedure.
- C.24 Verify from the alpha spectrum that the ²³²U tracer is free from interfering alpha emitters before use.
- C.25 The cleaned ²³²U tracer must also be standardized before use. See references 15.5 and 15.6 for guidance on determining the absolute activity.

FM-RAD-0120

Uranium in Water, Soil/Sediment, and Air Filters by Pulsed-Laser Phosphorimetry

| | |
|------------------------------|---|
| Working Linear Range: | Greater than 50 ng/L, infinite with dilution |
| Reporting Limit: | 50 ng/L Water; TBD for other matrices |
| Reporting Units: | Water, mg/L; Solids, mg/g; Air filters, mg/air filter |
| Matrices: | Water, soil/sediment, air filters |

1.0 Scope and Application

- 1.1 The method covers the determination of uranium in water, soil/sediment, and air filters in the range of 50 ng/L or greater. Samples with uranium levels above the laser phosphorimeter dynamic range may be diluted to bring the concentration to a measurable level. The minimum detectable concentration is approximately 50 ng U/L of water. The nominal sensitivity that may be obtained by this exact method for the other media requires additional performance data.
- 1.2 The method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 The method is based on the use of commercially available laser phosphorimeters to analyze uranium in the sample media.
- 2.2 The method is useful for the analysis of water either directly, following dilution, or following wet-ashing as required by the sample media.

3.0 Interferences

- 3.1 Possible interference modes in uranium assays with consist of four types:
- 3.1.1 Absorption (Inner Filter Effect): Absorption of ultraviolet excitation light (337 nm) is more severe than visible excitation because many prevalent compounds have pi-bonding and absorb strongly in that region. Ferric iron and oxy-anions such as nitrate and organic acids are examples. Visible excitation (425 nm) may be absorbed by yellow solutions; e.g., chromate. Interferences may cause reduced signals and low results.

- 3.1.2 Lumiphors: Many organic substances, such as humic acids and organic degradation products from incomplete ashing, emit luminescence of varying lifetimes after excitation. Such effects are handled according to the manufacturer's instructions.
- 3.1.3 Quenching: Shortened triplet-state lifetime and reduced phosphorescence intensities of the excited uranyl complex result when quenching occurs. Reliable results can not be obtained when quenching exceeds 80 to 90%. Reducing agents, such as alcohols, halides except fluoride, and metals with electronic energy levels overlapping those of uranyl ion, are strong quenching agents. Examples are silver, lead, iron (II), manganese (II), and thallium. Results from single time-gated instruments are particularly sensitive to even mild quenching agents such as Al (III), Mg (II), Ca (II), and Sr (II). See the manufacturer's literature for more specific information.
- 3.1.4 Competing Reactions: For the method to perform well, the uranyl ion must be protected from various intermolecular mechanisms that rapidly quench the uranyl luminescence. Complexation fulfills this need, and examples of effective agents are phosphoric acid, polyphosphates (Fluran), and Uraplex (Chemchek Instruments). The use of polyphosphates for uranium analysis is patented by Scintrex, Ltd.; they are very acid sensitive. Nitric acid as low as one molar concentration suppresses complexation of uranyl ion with phosphoric acid, which permits increased quenching effects. Uraplex is a stronger complexing agent and is effective in samples containing up to two molar nitric acid.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

6.1 Laser phosphorimeter, meeting the following criteria:

6.1.1 Detection limit: The detectable level for uranium must be 50 ng/L or less.

6.1.2 Dynamic range: The phosphorimeter must handle an analytical range from 50 to 20,000 ng/L. Samples with higher concentrations may be diluted.

6.1.3 Instrumental precision: The precision of repetitive measurements must be within 15% R.S.D.

6.2 Beakers, pipettes, funnels, and volumetric flasks. Class A volumetric glassware is used for standard preparation unless otherwise specified. If samples containing less than 100 ng/L uranium are to be analyzed, digestion vessels (both Teflon and glassware) if used, should be leached in hot, dilute nitric acid to reduce sample contamination from leachable uranium. Liquid scintillation vials, for example, should be hot-acid leached for at least 3 days before use in digestions.

6.3 Ceramic or Vycor containers (casseroles).

6.4 Scissors: Reserved for cutting only air filters.

6.5 Teflon beakers and stirring rod.

6.6 Platinum dish: 125-mL.

6.7 Drying oven: Gravity convection type is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 125°C and able to maintain temperatures within $\pm 5^\circ\text{C}$.

6.8 Ash-free filter paper: Whatman No. 42, or equivalent.

6.9 Muffle furnace: Able to reach at least 500°C and able to maintain temperatures within $\pm 15^\circ\text{C}$.

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- 6.10 Analytical balance: Scale readability of ± 0.1 mg.
- 6.11 Sieves: 2-mm and 15 mesh.
- 6.12 Grinder or Ball mill: Sufficient to reduce sample to pass 15 mesh sieve.
- 6.13 Electric hot plate/magnetic stirrer: Apparatus should have built in stirrer and stepless temperature controls that can be changed as heating requirements demand.

7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the laser phosphorimeter according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine Class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents

- 8.1 Chemicals must be reagent grade, meeting American Chemical Society (ACS) specifications. In all cases, acids or bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Nitric acid (HNO_3): Concentrated.
- 8.4 Nitric acid (HNO_3), 1 M: Dilute 60 mL of concentrated HNO_3 to 1 L with water.
- 8.5 Nitric acid (HNO_3), 3 M: Dilute 189.5 mL of concentrated HNO_3 to 1 L with water.
- 8.6 Hydrofluoric acid (HF): Concentrated (48% solution).
- 8.7 Uranium complexant: The source of phosphoric acid, if used, must be selected with care because it has varying levels of uranium impurity. Reagents supplied by

laser phosphorimeter manufacturers are recommended because of lower uranium background. Use of URAPLEX can produce better precision and lower detection limits because of the longer phosphorescence lifetimes of the uranyl complex as well as stronger complexes for resistance to quenching.

- 8.8 Uranium standard: From NIST, or NIST-traceable, or from another nationally recognized agency.
- 8.9 Hydrogen peroxide (H_2O_2), 30%: Reagent.
- 8.10 Perchloric acid ($HClO_4$), 12 M: Concentrated, reagent.

9.0 Calibration Procedures

Follow the manufacturer's instructions to calibrate the laser phosphorimeter.

10.0 Sample Preparation

- 10.1 Samples may be analyzed with any of three levels of pretreatment. The choice depends on desired detection limit, what is known about the sample source, and the content of quenchers and lumiphors. General guidelines below are followed by specific sample media preparation steps.
 - 10.1.1 Direct: Clear water from municipal supplies or streams can usually be analyzed without dilution. Follow the instructions provided by the phosphorimeter manufacturer.
 - 10.1.2 Dilution: If the desired lower level of determination permits a large dilution, this may be the only sample treatment necessary. Both quenching agents and lumiphors can be diluted to levels of negligible effect. Analyze the dilution according to the instructions provided by the phosphorimeter manufacturer.
 - 10.1.3 Ashing: Most quenching agents are either volatilized or oxidized, and luminescing substances can be decomposed.
- 10.2 Water: If sample cannot be analyzed directly or by dilution, wet ash the sample as follows.
 - 10.2.1 Transfer desired aliquot of sample to a beaker and add at least 10% by volume of nitric acid. Record volume of sample used.

- 10.2.2 Record comment if presence of any undissolved material is noted.
- 10.2.3 Carefully evaporate the sample solution to dryness. **Caution:** Rapid boiling will cause spattering and poor precision.
- Note:** Substantial organic material will require addition of a second oxidant, either hydrogen peroxide or perchloric acid. The nitric acid/oxidant may need to be replenished to complete the ashing.
- 10.2.4 Dissolve residue with dilute (e.g., 1 M) nitric acid and warm; transfer to volumetric flask and dilute to the desired final volume using dilute nitric acid. Record final volume.
- 10.3 Glass Fiber Filters
- 10.3.1 Remove filter from shipping envelope or bag and hold filter over a 125-mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside bag to platinum dish.
- 10.3.2 Place dish with sample in muffle furnace. Ash sample for about 16 hours at 500°C ± 15°C.
- 10.3.3 Remove dish and allow to cool.
- 10.3.4 Completely dampen the sample with a minimum amount but no more than 10 mL of concentrated HNO₃.
- 10.3.5 Add 15 mL of concentrated HF in 5-mL portions. Evaporate on hot plate until moist residue remains. Remove dish and allow to cool.
- 10.3.6 Add 10 mL of concentrated HF and evaporate until residue is almost completely dry. Remove dish and allow to cool.
- 10.3.7 Add 10 mL of concentrated HNO₃ and evaporate until sample is lightly fuming and just moist. Remove dish and allow to cool.
- 10.3.8 Repeat above step (step 10.3.7).
- 10.3.9 Moisten residue on sides and bottom of dish with 3 M HNO₃. Scrape residue from sides and bottom of dish, and break it up with a Teflon rod. Wash down sides of dish and Teflon rod thoroughly using 3 M HNO₃.

- 10.3.10 Return dish to hot plate and evaporate until about 5 mL of solution remains. Remove dish and allow to cool.
- 10.3.11 Filter sample using a funnel and Whatman No. 42 filter paper into 50-mL volumetric flask.
- 10.3.12 Wash out dish using three small portions (less than 5 mL each) of 3 M HNO₃.
- 10.3.13 Wash down filter and residue with three small portions (less than 5 mL each) of 3 M HNO₃.
- 10.3.14 Make up contents of volumetric flask to 50 mL with 3 M HNO₃, stopper, and mix thoroughly.
- 10.3.15 Continue with Sample Analysis, Section 11.0.

10.4 Soil/Sediment

- 10.4.1 Dry sample at 100°C ± 5°C for about 12 hours. Pass sample (typically 100 g) through 2-mm sieve to remove roots, stones, etc. Grind, mill, or pulverize to reduce sample to pass 15 mesh screen. Blend until thoroughly mixed.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

- 10.4.2 Weigh an appropriate amount of 15 mesh soil/sediment sample to meet the required sensitivity and transfer to casserole. Record exact (dry) weight used.
- 10.4.3 Heat casserole containing sample in muffle furnace. Increase temperature at 1-hour intervals to 300°, 400°, and 550°C. Muffle for 2 or 3 hours at 550°C ± 15°C or until only a brown powdery ash remains. Remove and cool.
- 10.4.4 Transfer sample to 250-mL Teflon beaker, rinsing casserole with 10-mL portions of 16 M HNO₃, to a final volume of 60 mL of nitric acid.
- 10.4.5 Carefully add 30 mL of 48% HF, cover with Teflon watch glass, and heat on hot plate with frequent stirring for about 1 hour. Remove from hot plate and cool. (Caution: Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)

- 10.4.6 Carefully add 30 mL each of 16 M HNO₃ and 48% HF, and digest on a hot plate with some stirring for an additional hour.
- 10.4.7 Remove from hot plate and cool to room temperature. Slowly add 20 mL of 16 M HNO₃, and heat on hot plate with some stirring until solution has evaporated to liquid volume of approximately 10 mL.
- 10.4.8 Add 50 mL of water, and digest on hot plate with stirring for 10 minutes to dissolve soluble salts.
- 10.4.9 Cool and filter sample using Whatman No. 42 filter paper into 100-mL volumetric flask with minimum of 3 M HNO₃. Wash residue with 3 M HNO₃.
- 10.4.10 If any residue remains, repeat steps 10.4.3 through 10.4.9, combining filtrates in the 100-mL volumetric flask.
- 10.4.11 Make volume up to 100 mL with 3 M HNO₃. Proceed to Sample Analysis Section 11.0. Sample may require additional dilution before analysis.

11.0 Sample Analysis

Analyze the solution according to the instructions provided by the laser phosphorimeter manufacturer.

12.0 Calculations

- 12.1 Refer to the laser phosphorimeter manual for appropriate calculation, which varies depending on the instrument model and brand.
- 12.2 Final results are automatically calculated by computerized instruments. Sample volume for air filter is fraction of total.

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project specific Sampling and Analysis Plan or the analytical laboratory services contract.

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14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency* | Acceptance Range | Corrective Action |
|-----------------------------|------------|------------------|-------------------|
| Reagent Blank ^{**} | 1/20 | To be determined | Qualify data |
| LCS | 1/20 | To be determined | Qualify data |
| Duplicate ^{**} | 1/20 | To be determined | Qualify data |

* or per batch or fraction thereof

** per matrix

15.0 References

Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry, (Draft)
ASTM Standard D19.04.005R0. 1992.

FERNALD\ulaser2.51

Gross Alpha and Gross Beta Radioactivity in Water and Gross Beta Radioactivity in Air Filters by Proportional Counting

| | |
|------------------------------|--|
| Working Linear Range: | Infinite with dilution |
| Reporting Limit: | To be determined. |
| Reporting Units: | Water, pCi/L; Air filter, pCi/air filter |
| Matricies: | Water, air filters |

1.0 Scope and Application

- 1.1 The method establishes a procedure for monitoring water for gross alpha and gross beta activity and air filters for gross beta activity. The method can measure alpha particles with energies above 3.9 million-electron-volts (MeV) and beta particles with maximum energies above 0.1 MeV.
- 1.2 The minimum detectable concentration for the method depends on sample size, counting system characteristics, background, and counting time. For water with extremely high solids content (> 500 mg/L), EPA Method 900.1 is recommended.
- 1.3 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 An aliquot of a dissolved air filter or water sample is evaporated to a small volume and transferred quantitatively to a tared 2-inch stainless steel counting planchet. The sample residue is dried to constant weight and counted for alpha and/or beta radioactivity.
- 2.2 Counting efficiencies for both alpha and beta particle activities are selected from graphs (or best fit equations) of counting efficiency versus sample weight.
- 2.3 The radioactive constituents of the sample are not separated from the solids of the sample; therefore, the solids concentration is a limiting factor in the sensitivity of the method for any given (water) sample. For samples with very low radioactivity, it is essential to analyze as large a sample aliquot as possible to give reasonable counting times in meeting the required sensitivity (minimum detectable concentration).

- 2.4 The largest sample aliquot to be counted for gross alpha activity is the volume that gives a solids density thickness of 5 mg/cm^2 in the counting planchet. For a 2-inch-diameter counting planchet (20 cm^2), an aliquot containing 100 mg of solids is the maximum sample size to be evaporated and counted for gross alpha activity.
- 2.5 Sample density thickness on the planchet shall not be more than 5 mg/cm^2 for gross alpha and not more than 10 mg/cm^2 for gross beta.
- 2.6 The concentration of total dissolved solids is not as limiting for determining gross beta activity because beta particles are not stopped in solids as easily as alpha particles. Very often a single sample aliquot is evaporated and counted for both gross alpha and gross beta activity. In that case, the sample aliquot size would be dictated by the solids limitation for alpha particles. For beta counting only, the solids on the planchet shall be limited to 200 mg (for 2" planchet).
- 2.7 Radionuclides that are volatile under the sample preparation conditions of the method will not be measured. The sample is evaporated after nitric acid is added, and the nitrated solids that form will not remain at a constant weight after being dried and if exposed to high atmospheric humidity. Therefore, the samples need to be heated to a dull red glow for a few minutes to convert the nitrate salts to oxides. Sample weights are then usually stable enough to give consistent counting rates, and a correct counting efficiency can then be determined.
- 3.0 Interferences**
- 3.1 Moisture absorbed by the sample solids on the counting planchet alters counting and self-absorption characteristics.
- 3.2 Nonuniformity of sample residue in the counting planchet interferes with the accuracy and precision of the method.
- 3.3 When counting alpha and beta particles by a gas flow proportional counting system, counting at the alpha plateau discriminates against beta particles, whereas, counting at the beta plateau is sensitive to alpha particle activity present in the sample. This latter effect should be determined and compensated for during the calibration of the specific instrument being used.
- 3.4 Inaccuracies in the analyses of samples are mainly due to beta emitters with energies different than the calibration standards or collected matter flaking off of air filters.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA Regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous materials are used during the method, procedures for handling low level radioactive materials, acids and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Beakers, pipettes, funnels, volumetric flasks. Class A volumetric glassware is used for standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.
- 6.2 Stainless steel counting planchets: Planchets shall be fabricated from uniform density stainless steel and be capable of withstanding nitric acid and heat treatment. Planchets shall be ringed and have a raised wall to contain the sample being evaporated. Their size is dictated by the inside dimensions of the detector chamber. Planchets shall be nitric acid washed and flamed to a dull red glow prior to use.
- 6.3 Magnetic stirrer/electric hot plate: The apparatus should have a built-in stirrer and stepless temperature controls that can be changed as heating requirements demand.
- 6.4 Analytical balance: scale readability ± 0.1 mg.
- 6.5 Desiccator: Large enough to hold dried planchets until ready for counting.
- 6.6 Scissors, reserved for cutting only air filters.

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- 6.7 Platinum dishes, 125 mL.
- 6.8 Muffle furnace, able to reach at least 500°C and able to maintain temperatures within $\pm 15^\circ\text{C}$.
- 6.9 Teflon stirring rods.
- 6.10 Ash free filter paper, Whatman No. 42, or equivalent.
- 6.11 Gas-flow proportional counting system: Tennelec low background (LB5100 Model II or III) gas-flow proportional counting system, or equivalent. The detector must be a "thin window" type, e.g., $100 \mu\text{g}/\text{cm}^2$ or less. The detector must have a rigid sample positioning device that has accurate and reproducible geometry.
- 7.0 Routine Preventive Maintenance**
- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks and replace as necessary.
- 8.0 Reagents**
- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. All radionuclide standards must be corrected for decay. In all cases, acids or bases are added to water.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Nitric acid (HNO_3), 3 M: dilute 187.5 mL of 16 M HNO_3 to 1 L with water.
- 8.4 Nitric acid (HNO_3), 16 M: concentrated, reagent.

- 8.5 NIST, or NIST traceable, or another nationally recognized agency, standard sources or solutions of ^{239}Pu and $^{90}\text{Sr}/^{90}\text{Y}$ for detector efficiency calibrations.
- 8.6 Hydrofluoric acid (HF), 29 M: concentrated, reagent.

9.0 Calibration Procedure

- 9.1 The counting system is calibrated (e.g., plateau determination, operating voltages) according to the manufacturer's instructions at least annually and after every significant change to the detector system.
- 9.2 Plateau checks are made after every gas bottle change by counting a check source at the operating voltage. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.3 Detectors are calibrated annually to obtain the ratio of count rate to disintegration rate, i.e., efficiency. Plutonium-239 is used for alpha activity calibration of the method. (^{239}Pu has a higher alpha particle energy (5.16 MeV) than those emitted by naturally occurring uranium and ^{226}Ra radionuclides but is close to the energy of the alpha particles emitted by naturally occurring ^{228}Th and ^{224}Ra .) It is, therefore, the prescribed radionuclide for gross alpha calibration. Standards are prepared in the standard geometry for the weight ranges to be encountered in analyses.
- 9.4 Strontium-90 in equilibrium with its daughter ^{90}Y is the prescribed radionuclide for gross beta efficiency calibrations. The beta efficiency calibration is also performed annually and after significant changes in the detector system.
- 9.5 For each counting instrument to be used, the analyst shall prepare separate alpha and beta particle self-absorption graphs showing water sample residue weight (mg) versus efficiency factor (cpm/dpm) using standard alpha and beta emitter solutions and water. Activity is added to varying size aliquots of water so that aliquot residue weight is varied between 0 to 100 mg for alpha and 0 to 200 mg for beta (for a 2-inch counting planchet). The self-absorption curve shall have at least 5 points evenly spaced over the range of weights. Alternatively, $\text{Ca}(\text{NO}_3)_2$ may be substituted for water solids to achieve sufficient residue weights on the planchets.

- 9.6 Varying size water aliquots with a constant amount of added ^{239}Pu or ^{90}Sr standard must be acidified with a few milliliters of 16 M HNO_3 , then evaporated to a small volume in a beaker on a hot plate, transferred quantitatively in small portions to a flamed and tared counting planchet, evaporated to dryness, and then carefully flamed to a red glow. Cool and weigh, and record weight. Sample weight stability is essential to gross alpha and gross beta measurements to ensure the accuracy of the self-absorption counting efficiency factor to be used for samples. Weight-stable aliquot residues must then be alpha or beta counted to achieve less than or equal to 3% uncertainty at the 1 sigma level. A single set of reference standards prepared in this way can be used for each counting instrument for separate graph preparations and can be stored for reverification whenever needed.
- 9.7 When counting beta particles in the presence of alpha radioactivity by gas-flow proportional counting systems, alpha particles are also counted. Since alpha particles are more readily absorbed by the sample than beta particles, the alpha/beta count ratios vary with increasing sample thickness. Therefore, it is necessary to prepare an amplification factor curve by counting several ^{239}Pu standards that have varying density thickness of solids on the alpha plateau and then on the beta plateau, plotting the ratios of the two counts versus density thickness. The alpha amplification factor (E) from that curve is used to correct the alpha count on the beta plateau.
- 9.8 A background count of sufficient length to meet the required uncertainty and lower limit of detection is performed weekly. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 9.9 Daily, or before use, a check source is counted to verify detector efficiency. The results must be within the established limits, e.g., ± 3 sigma before commencing analyses.
- 10.0 Sample Preparation**
- 10.1 Water
- 10.1.1 Transfer to a beaker an appropriate volume of a water sample that will result in a solids content of 100 mg or less (for alpha only or alpha/beta determination) or 200 mg or less (for beta only). Record volume of sample transferred.
- 10.1.2 Evaporate aliquot to near dryness on a hot plate. Add 5 mL of 16 M HNO_3 to the sample residue and evaporate to near dryness. Repeat.

- 10.1.3 Add 10 mL 3 M HNO₃ to beaker and swirl to dissolve residue.
- 10.1.4 Quantitatively transfer aliquot concentrate in small portions (not more than a few mL at a time to avoid overflowing) to a new, washed, flamed, and tared planchet. Being careful to avoid spattering, evaporate each portion to near dryness. After adding the last portion, evaporate to dryness.
- 10.1.5 Carefully flame samples to a dull red glow for a few minutes to convert nitrate salts to oxides, cool in desiccator, and weigh. Record weight and divide net weight by the area of planchet to determine the density thickness. Store sample residue in desiccator until ready for counting.
- 10.1.6 Continue with Sample Analysis, Section 11.0.
- 10.2 Glass Fiber Filters
- 10.2.1 Remove the filter from the shipping envelope or bag and hold the filter over a 125-ml platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside the bag to the platinum dish.
- 10.2.2 Place the dish with sample in a muffle furnace. Ash the sample for about 16 hours at 500°C ± 15°C.
- 10.2.3 Remove the dish and allow to cool.
- 10.2.4 Completely dampen the sample with a minimum amount but no more than 10 mL of concentrated HNO₃.
- 10.2.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on a hot plate until a moist residue remains. Remove the dish and allow to cool. (**Caution:** Hydrofluoric acid is extremely hazardous. Wear rubber gloves, safety glasses or goggles and a laboratory coat. Clean up all spills and wash thoroughly after using HF. Perform operations in a hood and avoid breathing any HF fumes.)
- 10.2.6 Add 10 mL of concentrated HF and evaporate until the residue is almost completely dry. Remove the dish and allow to cool.
- 10.2.7 Add 10 mL of concentrated HNO₃ and evaporate until the sample is lightly fuming and just moist. Remove the dish and allow to cool.

- 10.2.8 Repeat above step (Step 10.2.7).
- 10.2.9 Moisten the residue on the sides and bottom of the dish with 3 M HNO₃. Scrape the residue from the sides and bottom of the dish and break it up with a Teflon rod. Wash down the sides of the dish and the Teflon rod thoroughly using 3 M HNO₃.
- 10.2.10 Return the dish to the hot plate and evaporate until about 5 mL of solution remains. Remove the dish and allow to cool.
- 10.2.11 Filter the sample using a funnel and Whatman No. 42 filter paper into a 50-mL volumetric flask.
- 10.2.12 Wash out the dish using 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.2.13 Wash down the filter and residue with 3 small portions (less than 5 mL each) of 3 M HNO₃.
- 10.2.14 Make up the contents of the volumetric flask to 50 mL with 3 M HNO₃, stopper, and mix thoroughly.
- 10.2.15 Using a volumetric pipette transfer an appropriate volume of sample to a new, washed, flamed, and tared planchet and evaporate to dryness.
- 10.2.16 Carefully flame samples to a dull red glow for a few minutes to convert nitrate salts to oxides, cool in desiccator, weigh, and count. Record weight and divide net weight by the area of the planchet to determine the density thickness. Store sample residue in desiccator until ready for counting.
- 10.2.17 Continue with Sample Analysis, Section 11.0 (beta count only).

11.0 Sample Analysis

Count for alpha and beta activity. If sample is to be recounted for verification, store it in a desiccator.

Note: As long as counting chambers are capable of handling the same size planchet, alpha and beta activity can be determined at their respective operating voltages in the designated counting instruments. Samples may be counted for beta activity immediately after drying, but alpha counting should be delayed at least 72 hours to allow decay of short half-life radon progeny. If the gas-flow internal proportional counter does not discriminate for higher energy alpha pulses at the beta plateau, alpha activity must be subtracted from the beta plus alpha activity. This is particularly important for samples with high alpha activity.

12.0 Calculations

12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

A = activity at mid-point of counting interval, in dpm, or pCi as appropriate,

A_0 = activity at time of standardization in same units as A,

λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,

t = time elapsed from standardization to mid-point of counting interval.

12.2 Calculate alpha radioactivity in pCi/L using the equation:

$$\text{alpha} = \frac{R}{(2.22) (C) (V)}$$

Where:

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- R = net alpha count rate (gross alpha count rate minus background count rate) at alpha operating voltage
- C = alpha efficiency factor from graph (or best fit equation) of efficiency versus weight of solids in planchet (cpm/dpm)
- V = volume of sample aliquot (L)
- 2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the following multiplicative factor: 3.667E-02 Bq/pCi. Final sample results shall be corrected for reagent blank contribution.

- 12.3 The beta activity of the sample can be determined by counting the sample at the beta operating voltage and using the following equation:

$$\text{beta} = \frac{B - (R)(E)}{(2.22) (D) (V)} \quad \text{pCi/L (or per air filter)}$$

Where:

- B = net beta count rate (gross count rate minus background count rate at beta operating voltage)
- D = beta efficiency factor from graph (or best fit equation) of efficiency versus weight of solids in planchet (cpm/dpm)
- R = net alpha count rate (gross alpha count rate minus background count rate)
- E = alpha amplification factor from the graph (or best fit equation) of the ratio of alpha counted at the beta voltage/alpha counted at the alpha voltage versus sample density thickness

V = volume of sample aliquot (L) (V for air filter is fraction of total filter)

2.22 = dpm per pCi

12.4 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical service contract(s). The minimum detectable concentration (MDC) in pCi/L (or air filter) shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s).

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP QAPjP or specified in the project specific Sampling Analysis Plan, or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Level and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|------------------------------|-----------|------------------|-------------------|
| Reagent Blank ^{***} | 1/20* | To Be Determined | Qualify Data |
| LCS | 1/20* | To Be Determined | Qualify Data |
| Duplicate ^{***} | 1/20* | To Be Determined | Qualify Data |

* or per batch or fraction thereof

*** per matrix

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15.0 References

- 15.1 *Prescribed Procedures for Measurement of Radioactivity on Drinking Water.* U.S. EPA Environmental Monitoring and Support Laboratory. Cincinnati, OH, EPA-600/4-80-032. 1980.
- 15.2 *Detector Calibration and Analysis of Radionuclides.* ASTM E181-82. 1982.
- 15.3 U.S. Environmental Protection Agency. Method 9310: Gross Alpha and Gross Beta. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.* SW-846, Office of Solid Waste, Washington DC. 1986.
- 15.4 *Radiochemical Analytical Procedures for Analysis of Environmental Samples.* U.S. EPA Environmental Monitoring and Support Laboratory. Las Vegas, NV, EMSL-LV-0539-17. 1979.

Radioanalysis of Soil/Sediment, Air Filters, Milk, and Water by Gamma Spectrometry

Working Linear Range: Infinite with dilution
Reporting Limit: To be determined
Reporting Units: Milk, Water, pCi/L; Solids, pCi/g; Air filters, pCi/air filter
Matricies: Water, soil/sediment, air filters, milk

1.0 Scope and Application

- 1.1 The method applies to determination of gamma ray emitting radionuclides in samples of soil/sediment, air filters, milk, water, and aqueous solutions (i.e., air filter solutions). Radionuclides covered by the method include $^{137}\text{Cs}/^{137}\text{Ba}$, $^{106}\text{Ru}/^{106}\text{Rh}$, ^{40}K . The minimum detectable concentration for this method depends on sample size and characteristics, counting system characteristics, background, and counting time.
- 1.2 This analytical method applies to Analytical Support Levels C and D.

2.0 Method Summary

- 2.1 The entire sample or a homogeneous aliquot of the liquid or solid sample is put into a standard geometry for gamma counting. The counting efficiency for the geometry must have been determined with standards of known radionuclide activity. Sample aliquots are counted long enough to meet the required sensitivity. The gamma spectrum is printed out or stored in an appropriate computer-compatible device for data processing (calculation of sample radionuclide concentrations).
- 2.2 Gamma ray spectra are typically measured with a modular equipment system consisting of a detector, analyzer, memory, printer, and permanent data storage device. Germanium (Ge) detectors are used because of their excellent energy resolution.

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3.0 Interferences

- 3.1 Sample homogeneity is important to gamma count reproducibility and counting efficiency validity. When sample radionuclides are adsorbed on the walls of the counting container, the sample is no longer homogeneous.
- 3.2 High count rates (i.e., greater than 1,000 cps unless high count rate electronics are utilized) should be avoided because of electronic dead time limitations. High count rates may be reduced by dilution or moving the sample farther from the detector.
- 3.3 Variations in the physical geometry from sample to sample in the positioning of samples on the detector will produce variation in the gamma ray spectrum. Calibrations must be designed to duplicate all conditions including sample shape, size, matrix (density), and distance between detector and sample.
- 3.4 Unique gamma photon signatures are employed, where possible, to quantify radionuclide emission rates. Associated minor photopeaks are used to confirm the presence of potential candidate radionuclides.

4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA Regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous materials are used during the method, procedures for handling low level radioactive materials, acids and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP QAPjP.

6.0 Apparatus

- 6.1 Large volume ($> 50 \text{ cm}^3$) Ge detector with full width at one-half the peak maximum (FWHM) less than 2.5 keV at 1,332 keV, and associated electronics.
- 6.2 Multichannel analyzer with at least 2,048 channels, or equivalent computer and software.
- 6.3 Standard geometry sample counting containers for detector (e.g., 1-pint cylindrical container or 1-liter Marinelli polyethylene beaker). Sample mounts and containers must have a reproducible geometry.
- 6.4 Drying oven: The gravity convection type oven is recommended, having thermostatic controls to maintain desired temperature within $\pm 5^\circ\text{C}$ and able to reach at least 125°C .
- 6.5 Sieves: 2-mm and 15 mesh
- 6.6 Grinder or Ball mill: Sufficient to reduce sample to pass 15 mesh sieve.
- 6.7 Data storage device.
- 6.8 System printer capable of graphics output, or plotter.
- 6.9 Class A volumetric glassware: For standard preparation, unless otherwise specified. Unless otherwise noted, all glassware shall be nitric acid washed before use.

7.0 Preventive Maintenance

- 7.1 Routine preventive maintenance for the instruments is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance will be documented in the instrument specific maintenance logbook as specified in Section 13 of the FEMP QAPjP.
- 7.3 Examine class A glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

- 8.1 Chemicals are reagent grade, meeting American Chemical Society (ACS) specifications. All radionuclide standards must be corrected for decay.
- 8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.
- 8.3 Nitric acid (HNO₃), 16 M: concentrated, reagent.
- 8.4 Resolution, efficiency, and energy calibration check sources (e.g., ¹³⁷Cs and ⁶⁰Co).
- 8.5 Nitric acid (HNO₃), 1 M: Mix 62 mL of 16 M HNO₃ (concentrated) with water, and dilute to 1 L.
- 8.6 NIST, or NIST-traceable, or another nationally recognized agency's standard preparations or solutions of gamma emitting radionuclides that approximately cover the gamma energy range of 0.06 to 2.0 MeV.

9.0 Calibration Procedures

- 9.1 Each Ge detector-gamma spectrometer shall be calibrated as described in ANSI Standard N42.14-1991 (reference 15.5). The general requirements are outlined below.
- 9.2 The instrumentation and detector are set up according to the manufacturer's instructions. The gain, zero-level, high voltage, pole zero, etc. must be adjusted to produce the desired energy calibration, usually 0.5 or 1.0 keV per channel.
- 9.3 Energy calibration should be done with certified sources that span the entire range of interest (typically approximately 0.06 to 2.0 MeV).

- 9.4 Efficiency calibrations are performed by placing on the Ge detector appropriate radionuclide standards in the same geometry that the samples will have. The standards must have as close as possible to the same characteristics (matrix) as the samples to be counted. NIST or NIST-traceable standards are prescribed for this calibration. The efficiency (cpm/dpm) of the Ge spectrometer is measured for the particular gamma ray of interest. Alternatively, the efficiency can be measured at a minimum of seven different energies and the data can be used to develop a best fit equation to calculate detector efficiency at any energy within the applicable range. This is done automatically on most computer-based gamma spectrometry systems.
- 9.5 A counting efficiency versus gamma energy curve must be determined for each container geometry and for each detector to be used for sample analysis.
- 9.6 Detector efficiency at a given photopeak energy for a given geometry is determined by using a known quantity or concentration (for a volume geometry) of a gamma emitting radionuclide as follows:

$$E = \frac{S-D}{A \times B}$$

Where:

- E = detector efficiency
- S = standard count rate (cpm; integrated counts in photopeak above base line continuum divided by counting time, in minutes)
- D = background count rate in cpm in the region of interest
- A = standard activity (dpm) corrected for decay to date/time of counting
- B = gamma ray abundance of the particular photon being measured (gammas/disintegration)

- 9.7 The energy and efficiency calibrations shall be done after a major component change in the gamma spectrometer system or at least annually.
- 9.8 A resolution, efficiency, and energy calibration check shall be done daily or before use.
- 9.9 Once per week a background spectrum must be acquired for each gamma spectrometer for a time that is appropriate to meet required sensitivities.

10.0 Sample Preparation

- 10.1 Soil/sediment samples are dried at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 12 hours or overnight, sieved (2 mm screen size), and ground or milled to pass 15-mesh screen, and blended until thoroughly mixed.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

- 10.2 A water sample is transferred into the standard geometry container. Larger sample aliquots may be evaporated to the standard geometry container volume to achieve to the required MDC.
- 10.3 Air filters are handled carefully to keep material from being rubbed or flaked off. Air filters are placed in an appropriate container before counting.
- 10.4 Measure an amount of the sample appropriate to meet the required sensitivity into a standard geometry container (one that has been calibrated). Record the weight or volume of the sample or sample aliquot. For air filters the entire filter is used.

11.0 Sample Analysis

- 11.1 Place standard geometry container (with sample or aliquot) on a shielded Ge detector, and gamma count for a period of time that will meet the required sensitivity of measurement.
- 11.2 Print the gamma spectrum, or store the spectrum on the appropriate computer-compatible data storage device.
- 11.3 Print out a hard copy of the measurement results on the system printer.

12.0 Calculations

- 12.1 All radionuclide standards must be corrected for decay from time of standardization to time of sample count using the following equation:

$$A = A_0 e^{-\lambda t}$$

where

- A = activity at mid-point of counting interval, in dpm, γ/s , or pCi as appropriate
- A_0 = activity at time of standardization in same units as A,
- λ = decay constant of radionuclide of interest ($\ln 2/T_{1/2}$), in same time units as t,
- t = time elapsed from standardization to mid-point of counting interval.

- 12.2 Radionuclide photopeaks in the gamma spectrum are indicated and quantified as follows.
- 12.2.1 Locate all significant photopeak areas requiring identification and quantification.
- 12.2.2 Integrate the photopeak regions of the spectrum, and subtract the area under the base line continuum to determine the true photopeak area.
- 12.3 Identify each radionuclide by its characteristic energies and emission intensities (when more than one gamma photon is emitted by a radionuclide in the sample).

12.4 Calculate sample radionuclide concentrations as follows:

$$X = \frac{U-R}{2.22 \times B \times E \times V}$$

Where:

- X = sample radionuclide concentrations (pCi/L, pCi/g, or pCi/air filter)
- U = sample count rate in peak area above base line continuum (cpm)
- R = detector background count rate in cpm in the region of interest
- B = gamma-ray abundance of particular photopeak being measured (gammas/disintegration)
- E = detector efficiency (counts/disintegration) for radionuclide photopeak energy being considered
- V = volume (L) or weight (g) of sample aliquot analyzed. V for air filter is 1.0.
- 2.22 = dpm per pCi

Note: pCi may be converted to Bq by using the following multiplicative factor: 3.667E-02 Bq/pCi.

12.5 The total propagated uncertainty is determined using the same parameters as the activity concentration calculation. Specific equations are contained in the analytical service contact(s). The minimum detectable concentration (MDC) in pCi/L (g or air filter) shall be calculated *a posteriori* as specified in the analytical laboratory service contract(s). Final sample results shall be corrected for differences in density between samples and standards. Final sample results shall also be corrected for activity contributions from the sample container.

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13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels and are outlined in the FEMP QAPjP or specified in the project specific Sampling Analysis Plan, or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Levels and the project specific QAPjP. A specific discussion of each type of QC sample is presented in the QAPjP.

Analytical Support Levels C and D

| Requirement | Frequency | Acceptance Range | Corrective Action |
|------------------------|-----------|------------------|-------------------|
| LCS | 1/20* | To be determined | Qualify Data |
| Duplicate [™] | 1/20* | To be determined | Qualify Data |

* or per batch or fraction thereof

[™] per matrix

15.0 References

- 15.1 *Radiochemical Analytical Procedures for Analysis of Environmental Samples.* U.S. EPA Environmental Monitoring and Support Laboratory. Las Vegas, NV, EMSL-LV-0539-17. 1979.
- 15.2 *High-Resolution Gamma-Ray Spectrometry of Water.* ASTM D3649-85. 1985.
- 15.3 *Detector Calibration and Analysis of Radionuclides.* ASTM E181-82. 1982.
- 15.4 *Prescribed Procedures for Measurement of Radioactivity on Drinking Water.* U.S. EPA Environmental Monitoring and Support Laboratory. Cincinnati, OH, EPA-600/4-80-032. 1980.

- 15.5 *American National Standard Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides. ANSI N42.14-1991.*

EM-GTT-0011

Soil Classification (Lab)

Applicable Standard: ASTM D 2487, Standard Test Method for Classification of Soils for Engineering Purposes

Exceptions

1.0 ASTM D 2487 Test Options

- 1.1 Separate samples into two fractions for preparation. The dry method of preparation of soil samples shall be used to determine grain size of one fraction and the wet method of preparation of soil samples to determine Atterberg limits of the other fraction.
- 1.2 Determine grain size analysis, including hydrometer analysis in accordance with Method No. FM-GTT-0031 (ASTM D 422) using dry method of preparation in accordance with Method No. FM-GTT-0015 (ASTM D 421).
- 1.3 Determine Atterberg limits in accordance with Method No. FM-GTT-0032 (ASTM D 4318) using wet method of preparation in accordance with Method No. FM-GTT-0014 (ASTM D 2217).

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A, B, and C: Report all information specified in ASTM D 2487.
- 2.2 ASL D: Report all information specified in ASTM D 2487, and provide:
 - Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers
 - Copies of all grain size calculations, including tare weights of sieves and total weight of material retained on each sieve
 - Plot of percentage passing each sieve versus grain size, in millimeters, showing D_{10} , D_{30} , and D_{60} grain sizes
 - Copies of all liquid limit, plastic limit, and plasticity index calculations

- Plot of moisture content versus number of blows of the liquid limit device
- Copies of calculations for coefficient of curvature (C_c) and coefficient of uniformity (C_u), where applicable
- Certification of calibration of Atterberg limit apparatus (Section 9 of ASTM D 4318) and apparatus used for grain size analyses (ASTM D 422)
- Demonstration of laboratory precision, as specified in Section 21.1 of ASTM D 4318

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct grain size analysis, including percent passing the No. 200 sieve, but do not conduct hydrometer analysis. Conduct minimum three-point liquid limit test and at least one plastic limit trial for each Atterberg limit determination.
- 3.2 ASLs C and D: Conduct grain size analysis, including percent passing the No. 200 sieve, but do not conduct hydrometer analysis. Conduct minimum five-point liquid limit test and at least two plastic limit trials for each Atterberg limit determination.

4.0 Method Validation

- 4.1 The laboratory precision of the Atterberg Limit results of tests performed by different operators at one laboratory on two soils shall conform to Section 21.2 of ASTM D 4318.
- 4.2 All test results shall be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

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5.0 Safety Precautions

In addition to Section 1.3 of ASTM D 2487, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/soil-lab.51

FM-GTT-0012

Soil Classification (Visual)

Applicable Standard: ASTM D 2488, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)

Exceptions

1.0 Data Package Deliverables

- 1.1 Analytical Support Levels (ASLs) A and B: Report all information specified in ASTM D 2488.
- 1.2 ASLs C and D: The method provides qualitative information only and is not considered applicable for ASLs C and D.

2.0 Quality Control Requirements

- 2.1 ASL A: Provide visual field classification at the time of sample collection before placing sample in container or before sealing ends of Shelby tube samples.
- 2.2 ASL B: Verify visual field classification in the laboratory by a second visual classification by a technically qualified person.

3.0 Method Validation

Changes to the field classifications must be initialled by the analyst who revised the classification and documented on an applicable nonconformance report.

4.0 Safety Precautions

In addition to Section 1.4 of ASTM D 2488, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

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5.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/soil-vis.51

FM-GTT-0013

Transporting Samples

Applicable Standard: ASTM D 4220, Standard Practices for Preserving and Transporting Soil Samples

Exceptions

1.0 ASTM D 4220 Method Options

- 1.1 Section 4.1.2: Group B samples are not to include thin-walled tubes. Thin-walled Shelby tube samples shall be Group C samples.
- 1.2 Section 8.3: Group B samples for moisture content and classification tests must be stored in glass jars with rubber-ringed lids or lids lined with a wax-coated paper seal.
- 1.3 Section 8.3: Group B samples for proctor tests and other bulk samples that will be remolded or compacted into sample molds are to be stored and transported in polyethylene inner bags with woven polypropylene outer bags.
- 1.4 Section 8.3.6: Thin-walled tubes are to be Group C samples and are to be sealed with plastic expandable packers and plastic end caps. Tubes stored for longer than 7 days shall have the end caps sealed in wax.

2.0 Data Package Deliverables

- 2.1 Analytical Support Level (ASL) A: Report as a minimum the project number, sampling date, sample number, boring/sample location number, and sampling depth.
- 2.2 ASLs B, C, and D: Report all information specified in ASTM D 2487, plus the following:
 - Description of packaging containers, shipping containers, and type of insulation, as well as a dimensioned sketch of the shipping container
 - Sample identification/traceability record (controlled document) as in Figure 1 of ASTM D 4220 and chain-of-custody form

3.0 Quality Control Requirements

- 3.1 All ASLs: All samples must include labels and accompanying traceability record and chain of custody. Group C samples must include labels showing the orientation in which they were sampled.
- 3.2 ASLs C and D: All shipping containers must be approved by the project geotechnical engineer before samples leave the FEMP site.

4.0 Safety Precautions

In addition to Section 1.3 of ASTM D 4220, the method may involve radioactive materials, operations, and equipment. The user must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to handling samples.

5.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/transport.51

FM-GTT-0014

Wet Preparation of Samples

Applicable Standard: ASTM D 2217, Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants

Exceptions

1.0 ASTM D 2217 Method Options

Section 1.2: Use Procedure B only.

2.0 Data Package Deliverables

2.1 Analytical Support Level (ASL) A: No data package deliverable.

2.2 ASLs B, C, and D: Record sample preparation procedure on accompanying traceability record (Method No. FM-GTT-0013; ASTM D 4220). The laboratory report of subsequent analyses must include a brief description of sample preparation procedure and a copy of the traceability record.

3.0 Safety Precautions

In addition to Section 1.3 of ASTM D 2217, the method may involve radioactive materials, operations, and equipment. The user must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to handling samples.

4.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

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Dry Preparation of Samples

Applicable Standard: ASTM D 421, Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants

Exceptions

1.0 Data Package Deliverables

- 1.1 Analytical Support Level (ASL) A: No data package deliverable.
- 1.2 ASLs B, C, and D: Record sample preparation procedure on accompanying traceability record (Method No. FM-GTT-0013; ASTM D 4220). The laboratory report of subsequent analyses must include a brief description of sample preparation procedure and a copy of the traceability record.

3.0 Safety Precautions

In addition to Section 1.2 of ASTM D 421, the method may involve radioactive materials, operations, and equipment. The user must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to handling samples.

4.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0021

Moisture Content

Applicable Standard: ASTM D 2216, Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures

Exceptions

1.0 ASTM D 2216 Test Options

- 1.1 Section 6.3, Note 2: Remove any large coarse-grained particle from test specimen when working with small, fine-grained soil sample.
- 1.2 Section 7.3, Note 4: Keep test specimens in drying oven for at least 16 hours.
- 1.3 Section 7.3, Note 5: Maintain oven-drying at $110^{\circ} \pm 5^{\circ}\text{C}$.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: Report sample identifying information and moisture content of specimen to nearest 0.1%.
- 2.2 ASL C: Report all information specified in ASTM D 2216, including moisture content of specimen to nearest 0.1%.
- 2.3 Analytical Support Level D: Report all information specified in ASTM D 2216, including moisture content of specimen to nearest 0.1%. Provide copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers.

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct at least one moisture content per sample.
- 3.2 ASLs C and D: Conduct at least two moisture contents per sample.

4.0 Method Validation

All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0022

Moisture Content (Microwave)

Applicable Standard: ASTM D 4643, Standard Test Method for Determination of Water (Moisture) Content of Soil by the Microwave Oven Method

Exceptions

1.0 ASTM D 4643 Test Options

- 1.1 Section 5.4: The method must not be used when the specimen contains more than 10% material coarser than the No. 4 sieve.
- 1.2 Section 5.6: Specimens used in the test must not be used for other tests subsequent to drying.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A, and B: Report sample identifying information and moisture content of specimen to nearest 0.1%.
- 2.2 ASL C: Report all information specified in ASTM D 4643.
- 2.3 ASL D: The method is not considered appropriate for Level D analytical support.

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct at least two moisture content tests per sample.
- 3.2 ASL C: Conduct at least two moisture content tests per sample and verify test results in accordance with ASTM D 2216.

4.0 Method Validation

- 4.1 The laboratory must demonstrate that the recommended microwave time increments and microwave energy settings are suitable for most specimens

having particles smaller than a No. 4 sieve and with a mass of approximately 200 grams.

- 4.2 The laboratory must demonstrate that the use of this method for each microwave results in moisture contents within 0.5% of those determined using ASTM D 2216 for each type of soil tested.
- 4.3 All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.6 of ASTM D 4643, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/mois-mic.51

FM-GTT-0023

Moisture Correction (Oversize)

Applicable Standard: ASTM D 4718, Standard Practice for Correction of Unit Weight and Water Content for Soils Containing Oversized Particles

Exceptions

1.0 ASTM D 4718 Method Options

Section 1.5: This practice shall be applied to samples containing a minimum of 5% of oversized particles.

2.0 Data Package Deliverables

2.1 Analytical Support Level (ASL) B and C: Report all information specified in ASTM D 4718.

2.2 ASLs C and D: Report all information specified in ASTM D 4718, and provide copies of all calculations.

3.0 Quality Control Requirements

3.1 ASLs A: The method is not considered appropriate for Level A analytical support.

3.2 ASLs B, C, and D: Determine the bulk specific gravity for the oversized particles using ASTM C 127.

4.0 Method Validation

All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

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5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/mois-cor.51

FM-GTT-0024

Specific Gravity

Applicable Standard: ASTM D 854, Standard Test Method for Specific Gravity of Soils

Exceptions

1.0 ASTM D 854 Test Options

- 1.1 Section 5.1: The pycnometer should consist of a volumetric flask having a capacity of at least 100 mL.
- 1.2 Section 6.1, Note 3: Use distilled water as the wetting agent.
- 1.3 Section 7.1: The sample should consist of at least 25 grams of material on the basis of oven-dried weight.
- 1.4 Section 8.2: Remove trapped air from sample in pycnometer by boiling for 10 minutes.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) B and C: Report all information specified in ASTM D 854.
- 2.2 ASL D: Report all information specified in ASTM D 854, and provide copies of all calculations.

3.0 Quality Control Requirements

- 3.1 ASL A: The method is not considered appropriate for Level A analytical support.
- 3.2 ASLs B and C: Conduct a specific gravity test on at least one specimen.
- 3.3 ASL D: Conduct a specific gravity test on at least two specimens. Determine bulk specific gravity for oversized particles using method ASTM C 127.

4.0 Method Validation

- 4.1 The laboratory precision of the results of the tests performed by different operators must conform to Section 10 of ASTM D 854.
- 4.2 All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.3 of ASTM D 854, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/specgrav.51

3204

Volume-Weight Relationships

Applicable Standard: COE Manual EM 1110-2-1906, Appendix II, Unit Weights, Void Ratio, Porosity, and Degree of Saturation

Exceptions

1.0 EM 1110-2-1906, Appendix II, Test Options

1.1 Section 3: The volumetric method shall be used. The following methods for obtaining a regularly shaped mass may be used:

- Calibrated ring-shaped specimen cutter (cylinder)
- Cylindrical carving or trimming device (vertical lathe)
- Thin-walled tube specimens, with saw-cut square ends
- Cylindrical compaction mold (compacted specimen)

Prepare samples that contain gravel, shells, or foreign materials by carving or trimming, removing the foreign matter, and carefully filling voids on the surface of the specimen with remolded soil from the trimmings. The diameter of the trimmed specimen must be at least four times the largest dimension of the pebble or shell.

1.2 Section 3.c.2: Make at least three height measurements and nine diameter measurements to determine the average height and diameter of the cylinder for each sample.

2.0 Data Package Deliverables

2.1 Analytical Support Levels (ASLs) A and B: Report all identifying information and unit weight, void ratio, porosity, and degree of saturation for the sample.

2.2 ASL C: Report all information specified in paragraph 2.1 above and all sample identifying information, and provide copies of original data logs (ENG Form No. 3836, Plate II-1, or equivalent).

2.3 ASL D: Submit all information specified in Paragraph 2.1 above and all sample identifying information, and provide copies of original data logs (ENG

Form No. 3836, Plate II-1, or equivalent), all calculations, all tare weights, wet weights, and dry weights of all containers, and certification of calibration for all scales and calipers.

3.0 Quality Control Requirements

3.1 ASL A: Conduct one volumetric test per sample. Volumetric error (Section 3.c.2) must be less than 1%.

3.2 ASLs B, C, and D: Conduct one volumetric test per sample. Volumetric error (Section 3.c.2) must be less than 0.5%.

4.0 Method Validation

All test results, data sheets and calculations must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 References

6.1 American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

6.2 U.S. Army Corps of Engineers. *Engineering and Design Laboratory Soils Testing Manual*, (EM-1110-2-1906). November 30, 1970.

Grain Size Analysis

Applicable Standard: ASTM D 422, Standard Method for Particle Size Analysis of Soils

Exceptions

1.0 ASTM D 422 Test Options

1.1 Section 3.2: Stirring Apparatus A must be used.

1.2 Section 3.6: A full set of sieves must be used. A No. 100 sieve may be substituted for the No. 140 sieve.

2.0 Data Package Deliverables

2.1 Analytical Support Levels (ASL) A and B: Report sample identifying information and results of grain size distribution in tabular form (grain size and corresponding percent passing) and graphic form (grain size versus percent passing).

2.2 Analytical Support Level C and D: Report all information specified in ASTM D 422, with results presented in both tabular and graphic form.

2.3 ASL D: Report all information specified in ASTM D 422, and provide:

- Results in both tabular and graphic form
- Tabular summary of moisture data, sieve analysis data (wash sieve analysis, tare weights, soil weights, etc.), and hydrometer analysis data
- Copies of laboratory data sheets and other calculations not included in the tabular summary, including hygroscopic moisture correction, percentage passing each fraction, percentages in suspension, diameters of soil particles, and other calculations
- Copies of all scale, hydrometer, and sieve calibration

3204

3.0 Quality Control Requirements

- 3.1 Sieves damaged during testing must not be used until they are satisfactorily repaired and recalibrated. Hydrometers damaged during testing shall be replaced.
- 3.2 Sieve calibration shall be in accordance with ASTM E11, *Standard Specification for Wire-Cloth Sieves for Testing Purposes, Appendix X2*. Scale calibration shall be in accordance with ASTM D 4753, *Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing*.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 19 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0032

Atterberg Limits

Applicable Standard: ASTM D 4318, Standard Test Method for Liquid Limit, Plastic Limit, and Plasticity Index of Soils

Exceptions

1.0 ASTM D 4318 Test Options

Section 1.1.1: The test procedure for performing the liquid limit must be in accordance with Procedure A, multipoint test using a wet preparation procedure, as described in Sections 10.1, 11, and 12 of ASTM D 4318.

2.0 Data Package Deliverables

2.1 Analytical Support Levels (ASLs) A and B: Report sample identifying information, and liquid limit, plastic limit, and plasticity index rounded to the nearest whole number.

2.2 ASL C: Report all information specified in ASTM D 4318.

2.3 ASL D: Report all information specified in ASTM D 4318, and provide:

- Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers
- Plot of moisture content versus number of blows of liquid limit device
- Certification of calibration of apparatus as specified in Section 9 of ASTM D 4318
- Demonstration of laboratory precision as specified in Section 21.2 of ASTM D 4318

3.0 Quality Control Requirements

3.1 ASLs A and B: Conduct at least three-point liquid limit test and one plastic limit trial.

3.2 ASLs C and D: Conduct at least five-point liquid limit test and two plastic limit trials.

4.0 Method Validation

4.1 The laboratory precision of the results of tests performed by different operators at one laboratory on two soils must conform to Section 21.2 of ASTM D 4318.

4.2 All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.10 of ASTM D 4318, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 19 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GT1-0033

Shrinkage Limit

Applicable Standard: ASTM D 427, Standard Test Method for Shrinkage Factors of Soils

Exceptions

1.0 Data Package Deliverables

- 1.1 Analytical Support Levels (ASLs) A, B, and C: Report sample identifying information and calculated shrinkage factors. Report moisture content, shrinkage limit, volumetric shrinkage, and linear shrinkage rounded to the nearest whole number. Report shrinkage ratio and specific gravity rounded to the nearest hundredth of a unit.
- 1.2 ASL D: Report the information required in paragraph 1.1, and provide:
 - Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers
 - Copies of all other calculations
 - Certification of calibration of applicable apparatus (balance, graduates, etc.)

2.0 Quality Control Requirements

- 2.1 ASLs A and B: Conduct one test per sample (single soil pat).
- 2.2 ASLs C and D: Conduct two tests per sample (two soil pats).

3.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

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4.0 Safety Precautions

In addition to Section 1.3 of ASTM D 427, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 19 CFR Part 1910.1450 and NRC regulations, prior to analysis.

5.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/shrink.51

3204

Standard Proctor

Applicable Standard: ASTM D 698, Standard Test Methods for Moisture Density Relations of Soils and Soil-Aggregate Mixtures Using 5.5-lb (2.49-kg) Rammer and 12-in. (305-mm) Drop

Exceptions

1.0 ASTM D 698 Test Options

- 1.1 Section 1.1: Method D shall be used.
- 1.2 Section 3.2: The mechanical rammer must be used and must be calibrated before each use.
- 1.3 Section 4.1: The dry preparation procedure must be used unless otherwise specified.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information and all information specified in ASTM D 698, Section 8.
- 2.2 ASL C: Report the information specified in paragraph 2.1, and provide a graph of the moisture-density relationship per ASTM D 698, Section 7.
- 2.3 ASL D: Report all information specified in paragraph 2.1, and provide:
 - Graph of the moisture-density relationship per ASTM D 698, Section 7, showing the location of the optimum moisture content and maximum density and including the zero air voids curve. Report specific gravity as determined in accordance with Method No. FM-GTT-0024 (ASTM D 854).
 - Calibration of mold volume in accordance with Section 3.1.3 of ASTM D 698.
 - Calibration of rammer weight, diameter, and fall distance in accordance with Section 3.2.3 of ASTM D 698.

- Copies of all moisture calculations (including tare weights, wet weights, and dry weights of all materials), density calculations (including weights and volumes), and correction factors.
- Demonstration of laboratory precision in accordance with Section 9 of ASTM D 698.

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct minimum four-point test (four specimens at different moisture contents). The four points shall bracket the optimum moisture content.
- 3.2 ASL C: Conduct minimum six-point test (six specimens at different moisture contents). The middle four points shall bracket the optimum moisture content.
- 3.3 ASL D: Conduct minimum six-point test (six specimens at different moisture contents). The middle four points shall bracket the optimum moisture content. In addition, determine the specific gravity in accordance with Method No. 24 (ASTM D 854).

4.0 Method Validation

- 4.1 Calculate laboratory precision of the maximum density and optimum moisture content results in accordance with Section 9 of ASTM D 698. Criteria for acceptance shall be a standard deviation less than 1 unit for each.
- 4.2 All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

3204

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/proc-std.51

Modified Proctor

Applicable Standard: ASTM D 1557, Standard Test Methods for Moisture Density Relations of Soils and Soil-Aggregate Mixtures Using 10-lb (4.54-kg) Rammer and 18-in. (457-mm) Drop

Exceptions

1.0 ASTM D 1557 Test Options

- 1.1 Section 1.1: Method D shall be used.
- 1.2 Section 3.2: The mechanical rammer shall be used, and shall be calibrated prior to each use.
- 1.3 Section 4.1: The dry preparation procedure shall be used unless otherwise specified.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information and all information specified in ASTM D 1557, Section 8.
- 2.2 ASL C: Report the information specified in paragraph 2.1, and provide a graph of the moisture-density relationship per ASTM D 1557, Section 7.
- 2.3 ASL D: Report all information specified in paragraph 2.1, and provide:
 - Graph of the moisture-density relationship per ASTM D 1557, Section 7, showing the location of the optimum moisture content and maximum density, and including the zero air voids curve. Report also the specific gravity, as determined in accordance with Method No. FM-GTT-0024 (ASTM D 854).
 - Calibration of mold volume, in accordance with Section 3.1.3 of ASTM D 1557.
 - Calibration of rammer weight, diameter, and fall distance, in accordance with Section 3.2.3 of ASTM D 1557.

- Copies of all moisture calculations (including tare weights, wet weights, and dry weights of all materials), density calculations (including weights and volumes), and correction factors.
- Demonstration of laboratory precision, in accordance with Section 9 of ASTM D 1557.

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct minimum four-point test (four specimens at different moisture contents). The four points shall bracket the optimum moisture content.
- 3.2 ASL C: Conduct minimum six-point test (six specimens at different moisture contents). The middle four points shall bracket the optimum moisture content.
- 3.3 ASL D: Conduct minimum six-point test (six specimens at different moisture contents). The middle four points shall bracket the optimum moisture content. In addition, determine the specific gravity in accordance with Method No. FM-GTT-0024 (ASTM D 854).

4.0 Method Validation

- 4.1 The laboratory precision of the maximum density and optimum moisture content results shall be calculated in accordance with Section 9 of ASTM D 1557. Criteria for acceptance shall be a standard deviation less than 1 unit for each.
- 4.2 All test results shall be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.3 of ASTM D 1557, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/proc-mod.51

Maximum (Relative) Density

Applicable Standard: ASTM D 4253, Standard Test Methods for Maximum Index Density of Soils Using a Vibratory Table

Exceptions

1.0 ASTM D 4253 Test Options

- 1.1 Section 1.3.2: Use the dry preparation (Method A) procedure unless otherwise specified.
- 1.2 Section 4.4: Double amplitudes of vibration other than 0.013 ± 0.002 inch @ 60 Hz or 0.019 ± 0.003 inch @ 50 Hz must not be used unless otherwise specified.
- 1.3 Section 6: Standard molds must be used.
- 1.4 Section 8.4: The moisture content of the field sample must be determined in accordance with Method No. FM-GTT-0021 (ASTM D 2216).

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A, B, and C: Report sample identifying information, all information specified in ASTM D 4253 Section 13, and the minimum void ratio and moisture content of the sample.
- 2.2 ASL D: Report the items described in paragraph 2.1, and provide:
 - Copies of laboratory data sheets showing calculations per ASTM D 4253, Section 12
 - Copies of laboratory data sheets showing moisture content calculations
 - Certification of calibration of apparatus used to perform the test per ASTM D 4253, Section 10
 - Certification of calibration of other test equipment used to perform the test (sieves, scales, etc.)

- Demonstration of laboratory precision, as specified in Section 14 of ASTM D 4253

3.0 Quality Control Requirements

- 3.1 ASLs A, B, or C: Conduct at least one test at one selected frequency.
- 3.2 ASL D: Conduct at least two tests at two different frequencies. Determine calibration of test apparatus per ASTM D 4253 Section 10 before use in Level D testing and at intervals not exceeding 100 tests.
- 3.3 Sieve calibration shall be in accordance with ASTM E11, *Standard Specification for Wire-Cloth Sieves for Testing Purposes, Appendix X2*. Scale calibration shall be in accordance with ASTM D 4753, *Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing*.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0044

Minimum (Relative) Density

Applicable Standard: ASTM D 4254, Standard Test Methods for Minimum Index Density of Soils and Calculation of Relative Density

Exceptions

1.0 ASTM D 4254 Test Options

- 1.1 Section 1.3: Method A, using a funnel pouring device or hand scoop to place material in a mold, must be used.
- 1.2 Section 6.3: Standard molds must be used.
- 1.3 Section 7.5: Determine moisture content of the field sample in accordance with Method No. FM-GTT-0021 (ASTM D 2216).

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A, B, and C: Report the sample identifying information all information specified in ASTM D 4254 Section 11, and the maximum void ratio and moisture content of the sample.
- 2.2 ASL D: Report the items described in paragraph 2.1, and provide:
 - Copies of laboratory data sheets showing calculations per ASTM D 4254, Section 10
 - Copies of laboratory data sheets showing moisture content calculations
 - Certification of calibration of apparatus used to perform the test per ASTM D 4254 Section 8
 - Certification of calibration of other test equipment used to perform the test (sieves, scales, etc.)
 - Demonstration of laboratory precision, as specified in Section 12 of ASTM D 4254

3.0 Quality Control Requirements

- 3.1 ASLs A, B, or C: Conduct at least three tests. Consistent values of minimum index density, within 1%, must be obtained.
- 3.2 ASL D: Conduct at least five tests. Consistent values of minimum index density, within 1%, shall be obtained. Determine calibration of test apparatus per ASTM D 4254 Section 8 before use in Level D testing and at intervals not exceeding 100 tests.
- 3.3 Sieve calibration shall be in accordance with ASTM E11, *Standard Specification for Wire-Cloth Sieves for Testing Purposes, Appendix X2*. Scale calibration shall be in accordance with ASTM D 4753, *Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing*.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The method does not purport to address all of the safety problems associated with its use. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0051

3204

Consolidation

Applicable Standard: ASTM D 2435, Standard Test Methods for One-dimensional Consolidation Properties of Soils

Exceptions

1.0 ASTM D 4235 Test Options

- 1.1 Section 1: Method B shall be used. Successive load increments must be not be applied in time increments less than 24 hours.
- 1.2 Section 11.4: The test must include one unload-reload cycle; the unload-reload cycle must not be initiated until at least two load increments after the preconsolidation pressure have been applied. The final load following the unload-reload cycle must be greater than eight times the preconsolidation pressure. Specific loading and unloading increments must be at the direction of the project geotechnical engineer.
- 1.3 Section 11.4.2: The unloading load increments must be equal to those used in loading but in reverse order.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) B and C: Report the sample identifying information and all information specified in ASTM D 2435 Section 13. Provide both a graph of deformation versus log time and a graph of deformation versus square root of time. Provide both a graph of void ratio versus log of pressure and a graph of percent compression versus log of pressure.
- 2.2 Analytical Support Level D: Report the items described in paragraph 2.1, and provide:
 - Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers
 - Copies of calculations for coefficient of consolidation, void ratio, and vertical stress for each load increment

- Graphical derivation of t_{100} from the plot of deformation versus log of time and graphical derivation of t_{90} from the plot of deformation versus square root of time
- Graphical derivation of preconsolidation pressure, consolidation index, C_c , and reconsolidation index, C_r , from the plot of void ratio versus log of pressure
- Certification of calibration of apparatus used to perform the test per ASTM D 4235 Section 7
- Certification of calibration of other test equipment used to perform the test (sieves, scales, etc.)

3.0 Quality Control Requirements

3.1 This procedure is not considered appropriate for ASL A support.

3.2 Sieve calibration shall be in accordance with ASTM E11, *Standard Specification for Wire-Cloth Sieves for Testing Purposes, Appendix X2*. Scale calibration shall be in accordance with ASTM D 4753, *Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing*.

4.0 Method Validation

All tests must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/consolid.51

FM-GTT-0061

Unconfined Compression

Applicable Standard: ASTM D 2166, Standard Test Method for Unconfined Compressive Strength of Cohesive Soil

Exceptions

1.0 ASTM D 2166 Test Options

- 1.1 Section 1.3 and Section 6.4, Note 5: This test method is applicable only to cohesive soils with a degree of saturation less than 90%.
- 1.2 Section 4.3, Note 2: Soils that cannot retain their shape shall not be tested.
- 1.3 Section 6.1: Take three height measurements 120° apart, and take three width measurements at the quarter points of the height.
- 1.4 Section 6.2: Trim and square the ends of all tube samples.
- 1.5 Section 7.1: All specimens must be tested to failure. If failure occurs in less than 5 minutes or after 15 minutes, the unconfined compression test results shall be rejected and the sample retested.

2.0 Data Package Deliverables

- 2.1 Analytical Support Level (ASL) A: Report all sample identifying information and unconfined compressive strength and shear strength.
- 2.2 ASL B: Report all sample identifying information, unconfined compressive strength, shear strength, and a plot of stress versus strain.
- 2.3 ASL C: Report all sample identifying information and all information specified in ASTM D 2166, including a plot of stress versus strain.
- 2.4 Analytical Support Level D: Report all sample identifying information and all information specified in ASTM D 2166, and provide:
 - Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers

- Copies of all measurements made, including laboratory logs and curves
- Copies of all axial strain calculations, including length measurements and cross-sectional area measurements
- Copies of all unconfined compressive strength calculations
- Copies of all degree of saturation calculations, including all information specified in (ASTM D 854) for specific gravity
- Copies of all sensitivity calculations, including data on remolded strength determination
- Certification of calibration of compression device

3.0 Quality Control Requirements

- 3.1 ASLs A, B, and C: Conduct unconfined compression test on one undisturbed specimen.
- 3.2 ASL D: Conduct unconfined compression test on both undisturbed and remolded specimens, and determine sensitivity and specific gravity.

4.0 Method of Validation

All test results and data sheets must be initialed by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.6 of ASTM D 2166, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/unconfm.51

Direct Shear (Controlled-Displacement Method)

Applicable Standard: ASTM D 3080, Direct Shear Test of Soils under Consolidated Drained Conditions (Controlled-Displacement Method)

Exceptions

1.0 ASTM D 3080 Test Options

- 1.1 This procedure applies to the controlled-displacement method only, where both ultimate stress and maximum stress can be determined.
- 1.2 Section 1.1: The direct shear test must be conducted in single shear only.
- 1.3 Section 4.1: The shear device must be round. Square devices may be used only when the soil material type is too large to be compatible with the standard shear device and only when special approval has been obtained from the project geotechnical engineer.
- 1.4 Section 4.3.2: The load-indicating device must be a proving ring only.
- 1.5 Section 5.2: Prepare remolded samples as follows:
 - Compact cohesive samples in at least three equivalent layers in an oversized mold and trim to inside dimension of direct shear device.
 - Compact noncohesive samples in at least three equivalent layers directly in the direct shear device.
 - The dry density of all compacted specimens must be within 1% of the target dry density specified in the sampling and analysis plan.
- 1.6 Section 5.3: The sample must be at least 2 inches wide and at least 1 inch thick, and the ratio of width to thickness must be at least 2:1 and no more than 3:1.
- 1.7 Section 7.1, Note 4: The porous stone shall be dampened only for saturated, undisturbed samples taken from below the water table.

- 1.8 Section 7.2: The final normal force for each test specimen must be as specified in the sampling and analysis plan. Normal force must be applied in four increments so that the respectively applied loads are equal to $\frac{1}{8}$ the final load, $\frac{1}{4}$ the final load, $\frac{1}{2}$ the final load, and the final load.
- 1.9 Section 7.3: The rate of shear must be held constant throughout the test. The proposed rate must be determined approximately by dividing the estimated shear deformation at maximum shear stress by the computed time to failure. The estimated shear deformation at maximum shear stress must be estimated by the project geotechnical engineer based on consideration of grain size, plasticity, moisture content, stiffness, and other factors. The actual time to failure must be no less than $25t_{50}$ and no greater than $100t_{50}$. If actual time to failure exceeds these limits, the test shall be repeated for that normal stress specimen.
- 2.0 Data Package Deliverables**
- 2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information, and provide a plot of shear stress versus displacement for each normal stress increment (test specimen) and a plot of shear stress versus normal stress showing both maximum and ultimate shear stress.
- 2.2 ASL C: Report all information specified in ASTM D 3080, and provide plot of ultimate shear stress versus normal stress and plots of consolidation (normal displacement over time under each normal stress increment).
- 2.3 ASL D: Report all information specified in ASTM D 3080, and provide:
- Copies of all moisture calculations, including tare weights, wet weights, and dry weights of all containers, and including void ratio before and after consolidation and after shear for each test specimen, showing initial and final degrees of saturation for each test specimen
 - Copies of all stress data calculations, including normal stress and shear stress, and calculation of t_{50} , time to failure, and constant rate of shear
 - Plot of shear stress versus normal stress, showing both maximum and ultimate shear stress and estimated slope angle
 - Plot of consolidation under each normal stress increment (normal displacement versus time) and showing the applicable t_{50} times

- Certification of calibration of the single shear direct-shear device as specified in ASTM D 3080 Section 6, and certification of proving ring calibration
- Description of the type of shear device, including the porous stone size, permeability, and dampening process
- Demonstration of technician training and experience for method validation

3.0 Quality Control Requirements

3.1 ASLs A and B: Conduct minimum three-point test; that is, using three identical specimens for each normal stress increment.

3.2 ASLs C and D: Conduct minimum five-point test; that is, using five identical specimens for each normal stress increment.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

Direct Shear (Controlled-Stress Method)

3204

Applicable Standard: ASTM D 3080, Direct Shear Test of Soils under Consolidated Drained Conditions (Controlled-Stress Method)

Exceptions

1.0 ASTM D 3080 Test Options

1.1 The procedure applies to the controlled-stress method, where the maximum shear stress can be approximately determined.

1.2 The analyst must comply with all test options specified for Method No. FM-GTT-0062, except that the shear-force load-indicating device and constant rate of shear are not required.

1.3 Section 7.3: The initial shearing force increments must be approximately 10% of the estimated maximum shear force and reduced as specified in ASTM D 3080. The project geotechnical engineer must estimate maximum shear force (failure force) based on consideration of applied normal load, grain size, plasticity, moisture content, stiffness, and other factors. The shearing force increment applied just prior to the failure load must be less than 2.5% of the maximum shear force. If the actual increment exceeds these limits, the test must be repeated for that normal stress specimen.

2.0 Data Package Deliverables

2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information, and provide a plot of shear stress versus displacement for each normal stress increment (test specimen) and a plot of maximum shear stress versus normal stress.

2.2 ASL C: Report all information specified in ASTM D 3080, including plots of consolidation (normal displacement over time under each normal stress increment) and plots of consolidation under each shear stress increment (shear displacement over time).

2.3 ASL D: The procedure is not considered appropriate for Level D analytical support.

3.0 Quality Control Requirements

3.1 ASLs A and B: Conduct minimum three-point test; that is, using three identical specimens for each normal stress increment.

3.2 ASL C: Conduct minimum five-point test; that is, using five identical specimens for each normal stress increment.

4.0 Method Validation

All test results shall be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0064

3204

Triaxial Compression (UU)

Applicable Standard: ASTM D 2850, Standard Test Method for Unconsolidated, Undrained Compressive Strength of Cohesive Soils in Triaxial Compression

Exceptions**1.0 ASTM D 2850 Test Options**

- 1.1 Section 6.3: The dry density of any remolded specimen must be within 1% of the dry density determined for the original, undisturbed specimen.
- 1.2 Section 6.4: The dry density of all compacted specimens must be within 1% of the target dry density as specified in the Sampling and Analysis Plan.
- 1.3 Section 8.5: Latex membranes shall be used. The effect of the membrane on the lateral stress may be assumed to be negligible.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information, the initial dry unit weight and moisture content of the sample, the value of the deviator stress, and the value of the minor and major principal total stresses at failure.
- 2.2 ASL C: Report all information specified in ASTM D 2850.
- 2.3 ASL D: Report all information specified in ASTM D 2850 and provide:
 - Copies of all moisture calculations, stress calculations, strain calculations, and other calculations, including measurements of all dimensions, weights, volumes, or other units
 - Copies of all logs and notes taken during testing
 - Plots of the stress-strain curve (deviator stress versus axial strain) for each specimen showing maximum deviator stress and axial strain at failure and tangential and secant Young's moduli

- A single plot of the Mohr stress circles for all specimens of the one sample based on total stresses, showing minor and major principal stresses and maximum deviator stress

3.0 Quality Control Requirements

3.1 ASLs A, B, and C: Test at least one specimen at the chamber pressure specified in the Sampling and Analysis Plan.

3.2 ASL D: Test at least three specimens at the chamber pressures specified in the Sampling and Analysis Plan.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FM-GTT-0065

Triaxial Compression (CU)

Applicable Standard: ASTM D 4767, Standard Test Method for Consolidated-Undrained Triaxial Compression Test on Cohesive Soils

Exceptions

1.0 ASTM D 4767 Test Options

- 1.1 Section 6.3: The dry density of all compacted specimens must be within 1% of the target dry density as specified in the Sampling and Analysis Plan.
- 1.2 Section 7.2, Note 12: The wet mounting method must be used for all test specimens. Record latex membrane thickness and combined height of cap, base, porous discs, and filter discs, and determine specimen dimensions after the specimen has been mounted.
- 1.3 Section 8.2.3: Back pressure increments shall be at the judgment of the analyst in consultation with the project geotechnical engineer.
- 1.4 Section 10.2.2: Calculate the cross-sectional area of the specimen after consolidation using both Method A and Method B. The average of both methods shall be used in subsequent calculations. If the value calculated by both methods differs by more than 5%, the error must be noted in the data package.
- 1.5 Section 5.3: Filter paper discs may be used, but filter paper strips must not be used.
- 1.6 Section 10.7.1: Latex membranes must be used. The effect of the membrane on the lateral stress may be assumed to be negligible.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: The procedure is not considered appropriate for Levels A and B analytical support.
- 2.2 ASL C: Report all information specified in ASTM D 4767.

2.3 ASL D: Report all information specified in ASTM D 4767 and provide:

- Copies of all moisture calculations, stress calculations, strain calculations, back pressure calculations, and other calculations including measurements of all dimensions, weights, volumes, or other units
- Copies of all logs and notes taken during testing
- Plots of consolidation (volume change versus time) for each specimen

3.0 Quality Control Requirements

3.1 ASL C: Test at least one specimen at the consolidation pressure specified in the Sampling and Analysis Plan.

3.2 ASL D: Test at least three specimens at the consolidation pressures specified in the Sampling and Analysis Plan.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.6 of ASTM D 4767, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

California Bearing Ratio

Applicable Standard: ASTM D 1883, Standard Test Method for CBR
(California Bearing Ratio) of Laboratory-Compacted Soils

Exceptions

1.0 ASTM D 1883 Test Options

- 1.1 Section 1.6: All specimens shall be soaked before penetration.
- 1.2 Section 7.2.4: Allow all specimens to soak for 96 hours.
- 1.3 Section 8.2, Note 4: Do not attach strain gauge to testing machine support bars.

2.0 Data Package Deliverables

- 2.1 Analytical Support Level (ASL) A: Report the sample identifying information, calculated California Bearing Ratio, and the density at which the test was performed.
- 2.2 ASL B: Report the sample identifying information plus:
 - Dry density of sample before and after soaking
 - Moisture content of sample in percent before and after compaction
 - Bearing ratio of sample
- 2.3 ASL C: Report the sample identifying information and all information specified in ASTM D 1883, Section 10.
- 2.4 ASL D: Report the information specified in paragraph 2.3, and provide:
 - Percent shrink/swell change during soaking
 - Copies of all calculations
 - Copies of all tare weights, wet weights, and dry weights

- Copies of all curve plots for each specimen
- Certification of calibration of apparatus used to perform the test per ASTM D 1883 Sections 7 and 8
- Certification of calibration of other test equipment used to perform the test (i.e., sieves, scales, etc.)

3.0 Quality Control Requirements

- 3.1 ASL A: Conduct at least one California Bearing Ratio test at the water content and density specified by the project geotechnical engineer.
- 3.2 ASLs B and C: Conduct California Bearing Ratio tests on at least four specimens at the water contents and densities specified by the project geotechnical engineer.
- 3.3 Analytical Support Level D: Conduct California Bearing Ratio tests on at least six specimens at the water contents and densities specified by the project geotechnical engineer.
- 3.4 Sieve calibration shall be in accordance with ASTM E11, *Standard Specification for Wire-Cloth Sieves for Testing Purposes, Appendix X2*. Scale calibration shall be in accordance with ASTM D 4753, *Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing*.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.9 of ASTM D 1883, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/cbr.51

3204

Permeability (Constant Head)

Applicable Standard: ASTM D 2434, Standard Test Method for Permeability of Granular Soils (Constant Head)

Exceptions**1.0 ASTM D 2434 Test Options**

- 1.1 Section 4.2, Note 1: Do not use tap water as permeant. Use de-ionized, de-mineralized, and de-aired water.
- 1.2 Section 6.5: "Minimum" and "maximum" densities are to be reported as "loose" and "compact" densities and are not to be confused with Method Nos. FM-GTT-0043 and FM-GTT-0044 (ASTM D 4253 and D 4254) to determine relative density. The dry density of compacted specimens for each run must be within 10% of the targeted dry density.
- 1.3 Section 7.2: Begin the initial test run at a head difference of 0.5 cm, and increase by 0.5 cm for subsequent runs in the laminar flow range and 1.0 cm for subsequent runs in the turbulent flow range. The test shall be stopped after making 10 successive runs in the turbulent flow range.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASLs) A and B: Report the sample identifying information, the dry unit weight and moisture content of each run specimen, and the value of the coefficient of permeability in the laminar flow range of each run.
- 2.2 ASL C: Report all information specified in ASTM D 2434. Include plots of velocity versus hydraulic gradient for each run and a plot of the coefficient of permeability versus dry density.
- 2.3 ASL D: Report all information specified in ASTM D 2434, and provide:
- Copies of all moisture calculations and other calculations used to determine temperature correction, velocity, gradient, and permeability (include measurements of all dimensions, weights, volumes, temperature, or other units)

- Copies of all logs and notes taken during testing
- Plots of velocity versus hydraulic gradient for each run, and coefficient of permeability versus hydraulic gradient for each run
- A plot of the coefficient of permeability versus dry unit weight and a plot of permeability versus void ratio, indicating "loose" and "compact" relative compaction

3.0 Quality Control Requirements

- 3.1 ASL A: Test at least one run specimen at the dry density specified in the Sampling and Analysis Plan.
- 3.2 ASLs B and C: Test at least three specimens. For a three-run test, the targeted densities shall be 0%, 50%, and 100% relative compaction.
- 3.3 "Relative compaction" refers to the "loose" and "compact" densities discussed in paragraph 1.2 above, and is defined as:

$$\text{Relative Compaction} = \frac{(\gamma_s - \gamma_l)}{(\gamma_c - \gamma_l)} \times (100)$$

Where

- γ_s = dry density of the specimen
- γ_l = dry density of the "loose" specimen
- γ_c = dry density of the "compact" specimen

- 3.4 ASL D: Test at least five specimens. For a five-run test, the targeted densities shall be 0%, 25%, 50%, 75%, and 100% relative compaction.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/perm-ch.51

Permeability (Triaxial)

Applicable Standard: ASTM D 5084, Standard Test Method for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter

Exceptions

1.0 ASTM D 5084 Test Options

- 1.1 Section 5.1: Constant head test (Method A) shall be used.
- 1.2 Section 6.1.2, Note 4: Permeant solution shall be 0.005 N CaSO₄, prepared by dissolving CaSO₄ in de-aired, distilled water.
- 1.3 Section 8.3.3: Verify back-pressure saturation by measuring the B coefficient in accordance with Section 8.3.3.1.
- 1.4 Section 8.4: Consolidate the specimen to the effective stress specified by the project geotechnical engineer.
- 1.5 Section 8.5.1: The hydraulic gradient shall not exceed 10.
- 1.6 Section 8.5.3: Continue permeation until at least two pore volumes of permeant have flowed through the sample.

2.0 Data Package Deliverables

- 2.1 Analytical Support Level (ASL) B: Report the sample identifying information, the dry unit weight and moisture content of each run specimen, and the average hydraulic conductivity of the last four determinations.
- 2.2 ASL C: Report all information specified in ASTM D 5084, including plots of hydraulic conductivity versus time and hydraulic conductivity versus pore volume, and measurement of inflow and outflow rates throughout the test.

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2.3 ASL D: Report all information specified in ASTM D 5084, and provide:

- Copies of all moisture calculations, stress calculations, back pressure calculations, and other calculations used to determine gradient and hydraulic conductivity, including measurements of all dimensions, weights, volumes, or other units
- Copies of all logs and notes taken during testing
- Plots of hydraulic conductivity versus time and hydraulic conductivity versus pore volume
- Certification of calibration of all equipment, gauges, scales, etc.

3.0 Quality Control Requirements

3.1 ASL A: The procedure is not considered appropriate for Level A analytical support.

3.2 ASLs B, C, and D: Conduct tests on at least one undisturbed specimen. Measure inflow and outflow rates, and record any changes in specimen height throughout the test.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

The method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FERNALD/perm-tri.51

FM-GTT-0082

Btu Content (Solids)

3204

Applicable Standard: ASTM D 2015, Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter

Exceptions

1.0 ASTM D 2015 Test Options

- 1.1 Section 1.1: The method may also be applied to determine the gross calorific value of organic soils and organically contaminated soils.
- 1.2 Section 8.1: The sample must not be pulverized nor screened to pass the No. 40 sieve. Keep sample sealed to avoid loss or volatilization of organics until inserted into the calorimeter.
- 1.3 Section 8.2: Moisture content shall be determined in accordance with Method No. FM-GTT-0021 (ASTM D 2216).
- 1.4 Section 8.3: Sulfur analysis shall not be performed.
- 1.5 Section 11.1: It will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the sample.
- 1.6 Section 12.1: Do not mix the sample. Take special precaution to avoid loss or volatilization of organics within the soil sample.
- 1.7 Section 12.2, Note 8: Do not use asbestos lining method. Increase the mass of the sample or add benzoic acid as specified.
- 1.8 Section 13.2: Do not correct for difference between heat of formation of sulfuric acid and nitric acid, but include correction for the heat of combustion of benzoic acid if used to obtain a complete burn.

2.0 Data Package Deliverables

2.1 Analytical Support Levels (ASLs) A, B, and C: Report the sample identifying information and gross calorific value per dry weight basis (Btu/lb).

2.2 ASL D: Provide:

- Sample identifying information
- Gross calorific value per dry weight basis (Btu/lb)
- Demonstration of equipment calibration, including calorimeter heat rise during mixing, thermometer accuracy, and pressure gauge accuracy
- Demonstration of reagent purity, including water and oxygen purity
- Demonstration of restandardization procedure, including dates of restandardization, latest oxygen supply change, and latest change to calorimeter
- Oxygen pressure measured for all tests
- Copies of all calculations, including correction of water volumes for density changes due to temperature, correction for combustion of benzoic acid if used to obtain complete combustion, other thermochemical or thermometric corrections, and calculation of gross calorific value

3.0 Quality Control Requirements

3.1 ASLs A, and B: Conduct at least one test per sample.

3.2 ASL C: Conduct at least two tests per sample. Results shall not vary by more than 50 Btu/lb.

3.3 ASL D: Conduct at least three tests per sample. Results shall not vary by more than 50 Btu/lb.

4.0 Method Validation

All test results must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.3 of ASTM D 2015, the method may involve hazardous or radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*.
Volume 04.02, latest edition.

FM-GTI-0083

3204

Ash Content

Applicable Standard: ASTM D 3174, Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal

Exceptions

1.0 ASTM D 3174 Test Options

- 1.1 Section 7.2: The alternative method of drying shall not be used.
- 1.2 Section 7.3, Note 3: All samples will remain in the incinerator for at least 3 hours and until a constant weight (± 0.001 gram) has been maintained.

2.0 Data Package Deliverables

- 2.1 Analytical Support Levels (ASL) A, B, and C: Report all sample identifying information and the percentage of ash content, rounded to the nearest 1%.
- 2.2 ASL D: Report all sample identifying information, and provide:
 - Copies of all calculations, including measurements of tare weights, wet weights and dry weights
 - Copies of all laboratory logs and notes, including temperature readings over time
 - Certification of calibration of furnace temperature, scales, sieve, etc.

3.0 Quality Control Requirements

- 3.1 ASLs A and B: Conduct at least one ash content test per sample.
- 3.2 ASLs C and D: Conduct at least two ash content tests per sample.

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4.0 Method Validation

All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and the test results.

5.0 Safety Precautions

In addition to Section 1.2 of ASTM D 3174, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.

FERNALD/ash-cnt.51

FM-GTT-0084

Organic Content

3204

Applicable Standard: ASTM D 2974, Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils

Exceptions

1.0 ASTM D 2974 Test Options

- 1.1 Section 2.3: Method C, igniting the oven-dried sample from the moisture content determination in a muffle furnace, shall be used.
- 1.2 Section 3.2: The muffle furnace must be capable of producing a constant temperature of 440°C.
- 1.3 Section 9.3: Hold the furnace temperature for at least 4 hours, or until there is no change of mass after further heating.

2.0 Data Package Deliverables

- 2.1 ASL A: Report the sample identifying information and moisture content, ash content, and organic matter content, rounded to the nearest 1%.
- 2.2 ASLs B and C: Report the sample identifying information and all information specified in ASTM D 2974.
- 2.3 ASL D: Report all sample identifying information and all information specified in ASTM D 2974, and provide:
 - Copies of all calculations, including measurements of tare weights, dry weights, and wet weights
 - Copies of all laboratory logs and notes, including temperature readings over time
 - Certification of calibration of furnace temperature and scales

3.0 Quality Control Requirements

3.1 ASLs A and B: Conduct at least one organic content test per sample.

3.2 ASLs C and D: Conduct at least two organic content tests per sample.

4.0 Method Validation

All test results and data sheets must be initialled by the analyst who performed the test and signed by the person in responsible charge who checked the calculations and test results.

5.0 Safety Precautions

In addition to Section 1.3 of ASTM D 2974, the method may involve radioactive materials, operations, and equipment. The analyst must practice appropriate safety and health procedures and determine applicability of regulatory limitations, including OSHA regulations 29 CFR Part 1910.1450 and NRC regulations, prior to analysis.

6.0 Reference

American Society for Testing and Materials. *Annual Book of ASTM Standards*. Volume 04.02, latest edition.