Method for the Determination of Radium-228 and Radium-226 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors

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I-1. Introduction

To lower the cancer risks of the consumers of drinking water provided by Public Water Supplies (PWSs), the Safe Drinking Water Act (SDWA) requires PWSs to measure, at a minimum, the gross alpha particle activity of their finished water at specific intervals appropriate to the specific local conditions of each water supply. Additionally, concern related to the radium-228 (Ra-228) content of drinking waters has resulted in the requirement finished waters intended for public consumption from PWSs be analyzed for this carcinogen, in addition to the gross alpha particle activity, beginning with the compliance monitoring period starting on December 8, 2003. If the gross alpha radioactivity measured for a PWS is above 5 pCi/L, then the measurement of the regulated contaminant, radium-226 (Ra-226) is also required. These requirements will have the consequence of a tremendous increase of the number Ra-228 measurements that must be made, as well as the likelihood both Ra-226 and Ra-228 must be measured in the same sample, increasing the number of measurements required.

While other EPA-approved radium methods can provide sufficient accuracy and precision for the purposes of the SDWA monitoring program, they all share the general assessment by radiochemists after using them that they are labor intensive and time consuming. They all require several isolation and purification steps involving sequential precipitations from analytically large volumes, then possibly liquid-liquid extractions (depending on the particular method). They all end with a final preparation step for measurement either by gas proportional counting (EPA 903.0, EPA 904.0, etc), or by evolving a gaseous daughter product from the radionuclide of interest from the sample, then measuring it with an alpha scintillation detection system (EPA 903.1, etc). Additionally, training periods for technicians performing these methods are long because of the numerous steps and the time involved in performing these analyses, increasing their overall cost.

This draft method has been developed in an effort to provide a more cost-effective alternative that reduces the labor and time required for processing samples for these analyses. It utilizes the initial precipitation steps found in the approved methods, but utilizes gamma-ray spectrometry techniques for detection and quantitation using High Purity Germanium (HpGe) detectors. Lithium-drifted Germanium (Ge(Li)) detectors may also be used, but will require larger volumes of sample since they have lower detection efficiencies than the HpGe detectors. Unlike sodium iodide gamma-ray detectors, these solid state detectors have sufficient spectral resolution so that peaks unique to the daughter progeny of Ra-226 and Ra-228 can be quantitatively measured in shorter count times typically used for gas proportional measurements of these regulated contaminants.

1.0 Scope and Application

1.1 This method describes the measurement of Radium-226 (Ra-226, CAS Registry No.13982-63-3) and Radium-228 (Ra-228, CAS Registry No. 15262-20-1) in finished drinking water matrices in the same compliance monitoring sample. This method can also be used to measure them separately if only one of these analyses is required. These data may be used in the Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Safe Drinking Water Act. It utilizes the initial precipitation steps for these analytes found in methods 903.0, 904.0, Ra-05, and other similar methods, but uses gamma-ray spectrometry techniques for detection and quantitation instead of gas proportional counting. Analytical test conditions are selected to ensure the required detection limit of 1 pCi/L can be achieved routinely according to the capabilities of each laboratory that chooses to utilize this method. Since the method of detection's calibration efficiency is linear with respect to intensity, it has a quantitative analytical range of several orders of magnitude.

1.2 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1 An aliquant from a sample (whose volume is appropriate for the efficiency of the detector and projected count time so that a detection limit of 1 pCi/L can be achieved) is poured into a borosilicate beaker sufficiently large to hold the entire sample. A solution of barium chloride is added to the aliquant of sample to serve as carrier. The sample is then stirred and heated to boiling. Concentrated sulfuric acid is added to the heated sample and radium is collected by coprecipitating it as a sulfate.

2.2 The precipitate is collected on preweighed filter paper, then dried and reweighed to obtain a net weight of precipitate to assess the chemical efficiency of the coprecipitation. The filter paper holding the precipitate is placed into containers whose geometry is appropriate for the type of gamma-ray detector being used.

2.3 The prepared samples can either be directly measured for their Ra-228 content, or set aside for a minimum ingrowth period appropriate for each measurement (from 5 days to 2 weeks for Ra-226, or both measurements). After the necessary ingrowth period, the sample is counted with a gamma-ray spectrometry system to determine the content of the regulated contaminants for a count time previously determined to achieve the required detection limit.

2.4 Quality is assured by repeated testing of the precipitation, counting, and gravimetric systems.

3.0 Definitions

3.1 Definitions for terms used in this method are given in section 18, Glossary of Definitions and Purposes.

4.0 Interferences

4.1 Reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents is required to ensure no traces of the analytes are present. The glassware and sample processing hardware is cleaned by washing in hot water and a detergent designed to remove radioactive compounds, then rinsing them in tap water, and a final rinse in deionized water. All glassware must also receive an acid rinse to ensure contaminant removal and to hydrate the outer layers of silica, making them more resistant to contamination. This is followed by a final rinse in deionized water.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory blanks as described in Section 9.4.

4.3 Excess barium and strontium in the drinking water sample can result in high chemical yields, sometimes exceeding 100 percent recovery. Since their concentrations are restricted in finished drinking water to low

levels, the related bias would only be a concern if this method is used to measure source or waste waters.

4.4 Interferences separated from samples will vary considerably from source to source, depending upon the diversity of the site being sampled.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent and radioactive standards used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals and radioactive standards should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method, and all analysts should wear radiation dosimetry badges while performing this method to monitor their exposure to ionizing radiation. The results of this monitoring must be made available to the analyst.

5.2 Sample containers should be opened in a restricted area with caution and handled with gloves to prevent exposure.

5.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.4–16.6.

5.4 Diethyl ether (also referred to as "ethyl ether") is an extremely flammable solvent, and may form explosive peroxides during storage. Diethyl ether also is considered a skin, eye, and respiratory irritant. This reagent should be used in a well ventilated area (e.g., a fume hood), kept away from ignition sources, and handled by analysts wearing appropriate protective-wear (e.g., safety glasses or goggles). For additional information on this substance please consult the Material Safety Data Sheet (MSDS) for diethyl ether.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Sampling equipment.

6.1.1 Sample collection bottles—Plastic, with screw cap. Sample collection bottles should be of an appropriate volume to minimize the number of containers required per sample. Each sample must have a minimum of 4 aliquants of volume available so they may be available to be used as a batch QC sample and have at least one aliquant available in the event retesting becomes necessary.

6.1.2 Bottles and lids must be lot-certified to be free of artifacts by running laboratory blanks according to this method (per Section 9.4).

6.2 Equipment for glassware cleaning.

6.2.1 Laboratory dishwasher. If one is not available, then the laboratory must have a dishwashing station set up consisting of the minimum of a sink for washing and rinsing glassware, and a drying rack.

6.2.2 A nonmetallic tub or vat with a minimum volume of 30 L to hold the acidic solutions used for acid rinsing. It must also have a cover that can be placed over it when it is not in use.

6.2.3 A source of ASTM Type 2 reagent water to use for a final rinse for glassware.

6.3 Equipment for calibration.

6.3.1 Analytical balance—a readability of 0.01 mg is required.

6.3.2 Volumetric flasks—Glass, 100 mL, 500 mL, 1000 mL and 2000 mL

6.3.3 Bottles—Assorted sizes, with PTFE-lined screw caps reagent storage

6.3.4 Volumetric pipettes—Glass, 1 mL, 5 mL

6.3.5 Gamma-ray spectrometry system utilizing either High Purity Germanium (HPGe) or lithium drifted germanium (Ge (Li))detectors.

6.4 Equipment for sample precipitation.

6.4.1 Beaker—must be made of a heat resistant borosilicate glass and capable of holding the volume of sample necessary to reach the required detection limit.

6.4.2 Heated magnetic stirrer

6.4.3 PTFE-coated magnetic stirring bars

6.4.4 Volumetric flasks 2000 mL

6.5 Equipment for collecting precipitate.

6.5.1 Filtering apparatus— 25 mm or 47 mm diameter filter funnel that is mounted on either a manifold connected to a vacuum source or to a vacuum flask that is connected to a vacuum source.

6.5.2 Filter paper— Membrane, 0.45 μm porosity, 25 mm or 47 mm diameter, whichever is appropriate for the filter funnel.

6.5.3 Sample containers for the selected geometry, such as stainless steel planchets, plastic Petri dishes or vials of the appropriate size to fit into the well of a deep well gamma-ray detector

6.5.4 Drying lamp

6.6 Equipment for yield determination.

6.6.1 Analytical Balance— a readability of 0.01 mg is required.

6.7 Equipment for counting gamma rays from analytes.

6.7.1 Gamma-ray spectrometry system utilizing either High Purity Germanium (HPGe) or lithium-drifted germanium (Ge(Li))detectors.

7.0 Reagents and Standards

7.1 Reagent water—Standard Methods (see reference 16.2) requires reagent water for radiochemistry methods meet the requirement specified as ASTM Type 2 reagent water. Distilled water, deionized water or water prepared by passage of tap water through activated carbon have been shown to be acceptable sources of reagent water. The reagent water's resistivity must be checked prior to its use to prepare samples or standards to ensure it is of adequate quality for use with this method.

7.2 Hydrochloric acid, HCl (12 N)

7.3 Sulfuric acid, H_2SO_4 (18 N) : cautiously add, with stirring, 500 mL 36 N H_2SO_4 to 400 mL water and dilute to 1 L.

7.4 Ethanol—ACS, residue less than 1 mg/L.

7.5 Diethyl ether.

7.6 Nitric Acid, HNO_3 (16 N)

7.7 Barium carrier Ba^{++} - 9 mg/mL. Dissolve 16.01 grams of Ba Cl_2 – 2 H_2O in water, add 5 mL 16 N HNO_3, and dilute to 1 L with reagent water.

7.8 Ra-226 spiking standard solution; for matrix spikes and matrix spike duplicates.

7.8.1 Use a NIST traceable Ra-226 standard when available that is from a different source than the one used to prepare the efficiency calibration standard

7.8.2 The calibration certificates for these standardized solutions most often report their concentrations as an activity per volume weight. When extracting the standard solution from the container it arrives in, the total net weight of solution should be measured to ensure the reported total activity is accurate.

7.8.3 Before diluting it, calculate a final dilution volume that will provide an activity between 5 and 10 pCi/mL.

7.8.4 Use a Class a volumetric flask that will contain all the calculated final volume.

7.8.5 Use a diluent that has the same molar concentration and is of the same type of acid used to produce the original standardized solution.

7.8.6 Pour approximately 75 percent of the diluent into the volumetric flask.

7.8.7 Weigh the standard in its original container.

7.8.8 Remove the standardized solution from the balance and pour its contents into the volumetric flask. Wash the original container three times with some of the remaining diluent, and pour these washings into the volumetric flask.

7.8.9 Wash the original container with ethanol to remove any remaining rinse solution and discard it since it should not have any activity. Set aside to dry. Once dry, record its weight.

7.8.10 Slowly bring the volume of diluted solution in the volumetric flask up to the white line that represents its calibrated volume. Ensure the final volume is not above this line.

7.8.11 Subtract the weight of the empty original container from the weight of the container and original solution. Compare this to the weight reported on the calibration certificate.

7.8.12 If different, use the determined net total weight of the standardized solution and multiply it by the activity per gram reported on the calibration certificate, then divide it by the volume of diluent in the final working solution. Use this result when using a final activity per mL for the standard.

7.9 Ra-228 Standard spiking solution. Use the same steps as in section 7.8 used to prepare the Ra-226 standard spiking solution.

7.10 Alternate Carrier: Pb^{2+} Carrier – 20 mg/mL. Dissolve 32 g of $Pb(NO_3)_2$ in water. Add 5 mL 16N HNO_3 and dilute to 1 L with reagent water.

8.0 Sample Collection, Preservation, and Storage

8.1 Collect a sufficient volume of sample so that a minimum of 4 aliquants of sample can be prepared from it. This provides sufficient volume that a sample, a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) pair may be prepared from each collected sample, with one aliquant volume left for reserve in case the sample must be remeasured. Plastic bottles or cubitainers may be used to collect the sample following conventional sampling procedures.

8.2 Once collected, samples for these analyses must be preserved within 5 days of collection by adding sufficient concentrated nitric acid so that the collected sample has a pH of less than 2 as specified in Table 17.2.

8.3 All samples must be analyzed within prescribed maximum holding time after collection in Table 17.2.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.8). For each method the laboratory uses to report compliance monitoring results, the minimum requirements of this program consist of an initial demonstration of analyst capability, ongoing analyses of

standards and reagent blanks as a test of continued accuracy and freedom from interferences, and analyses of matrix spike (MS) and matrix spike duplicate (MSD) samples to assess precision and provide an additional metric of accuracy. Laboratory analyst performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of ability to generate acceptable accuracy and precision with this method. This ability is established as described below.

9.1.2 Each sample analytical batch must include Quality Control (QC) samples to demonstrate the overall accuracy, precision and freedom from interferences for the analyses. Analysis of a Matrix Spike (MS) is done to demonstrate accuracy. Precision can be demonstrated by using a second aliquant of the sample selected to produce the MS to produce a Matrix Spike Duplicate (MSD). The criteria for spiking samples are described in Section 9.3.

9.1.3 Alternatively, the MSD may be replaced by using a second aliquant of a sample to duplicate the measurement (DUP), then comparing their results to assess precision. The criteria for duplicating samples are described in Section 9.4.

9.1.4 An analysis of a Reagent Blank (RB) is required to demonstrate the reagents, sample processing glassware, and workspace are free from contamination that will interfere with the measurements of the samples in each analytical batch. The results of RBs shall be recorded and monitored to ensure interferences in the analysis system remain in control. The criteria for RBs are described in Section 9.5.

9.1.5 The laboratory shall demonstrate calibration verification for each analytical batch of samples by measuring a Laboratory Fortified Blank (LFB). The results of the LFBs shall be recorded and monitored to ensure the analysis system remains in control. These procedures are described in Section 9.6.

9.1.6 The laboratory must maintain records to define the quality of data that is generated. Development of accuracy statements should be completed as described in Sections 9.3.7 and 9.6.3.

9.1.7 For this procedure, a sample preparation batch is a set of samples precipitated at the same time, and must not exceed 20 samples. Each sample preparation batch must also include the four Quality Control samples described in sections 9.1.2. though 9.2.5 for a maximum number of samples in each sample preparation batch of 24. If greater than 20 samples are to be precipitated at one time, the samples must be separated into two sample preparation batches of 20 or fewer samples.

9.2 Initial Demonstration of Laboratory Capability

9.2.1 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.1.1 Prepare four samples by using 4 to 8 L of ASTM type I or II deionized water and add a sufficient volume of Ra-226 and Ra-228 standard spiking solutions so that both radioanalyte concentrations are between 5 and 10 times their required detection limits. Divide the volumes equally into four aliquants.

9.2.1.2 Using the results of the set of four analyses, compute the average percent recovery (P_{av}) and the standard deviation of the percent recovery (s) for Ra-226 and for Ra-228 (if determined). Use the following equation for calculation of the standard deviation of the percent recovery:

$$P_{av} = \frac{1}{n}\sum_{i=1}^{n} P_i \quad \text{and} \quad s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(P_i - P_{av})^2} \tag{1}$$

where:

n = number of samples
P_i = percent recovery for each sample
P_{av} = average percent recovery for all samples
s = standard deviation of the percent recovery

9.2.1.3 Compare s and P_{av} with the corresponding limits for initial precision and recovery in Table 17.1. If s and P_{av} meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or P_{av} falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

9.3 Matrix Spikes

9.3.1 The laboratory must spike, in duplicate, a minimum of 5 percent of all samples (one sample in each batch of twenty samples. The two sample aliquants shall be spiked with the Ra-226 and Ra-228 spiking solutions.

9.3.1.1 Prepare a spiking solution that will produce an activity concentration between 3 and 5 pCi/L (between 3 times the required detection limit and the combined MCL for these radioanalytes) when added to each aliquant selected for spiking.

9.3.1.2 Analyze the first sample aliquant according to the procedure beginning in Section 11 to determine the background concentration of Ra-226 and Ra-228.

9.3.1.3 Spike the two aliquants selected for spiking, then also measure them according to the procedure beginning in Section 11.

9.3.1.4 Calculate the percent recovery (P) of Ra-226 and Ra-228 in each aliquant using the following equation:

$$P = \frac{(A - B) \times 100\,\%}{T} \qquad (2)$$

where:

A is the total activity concentration of the analyte of interest
B is the background concentration of the analyte of interest
T is the activity concentration of the analyte added to the sample

9.3.1.5 Compare the percent recovery of the Ra-226 and Ra-228 with the corresponding QC acceptance criteria in Table 17.1.

9.3.1.6 If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Table 17.1, an interference is present. In this case, the result may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS/MSD.

9.3.1.7 If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, the problem shall be identified and corrected, and the sample shall be reanalyzed.

9.4 Precision Assessments

Compute the relative percent difference (RPD) between the two results of either the sample and its duplicate measurement or between the Matrix Spike and the Matrix Spike Duplicate (not between the two recoveries) using the following equation:

$$RPD = \frac{|A_1 - A_2|}{(A_1 + A_2)/2} \times 100\,\% \tag{3}$$

where:

A_1 is the concentration of Ra-226 or Ra-228 in the sample

A_2 is the concentration of Ra-226 or Ra-228 in the second (duplicate) sample

9.4.2 The relative percent difference for the duplicate measurements shall meet the acceptance criteria in Table 17.1. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.4.3 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if $P_a = 90$ % and $s_p = 10$ % for five analyses of Ra-226 and for Ra-228, the accuracy interval is expressed as 70 %–110 %. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.5 Reagent Blanks for Contamination Checks

9.5.1 Reagent water blanks are analyzed to demonstrate freedom from contamination.

9.5.2 Precipitate a sample prepared with laboratory reagent water using the same volume as samples with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.5.3 If material is detected in the blank at a concentration greater than the Minimum Level required by EPA of 1 pCi/L, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.6 Laboratory Fortified Blanks for Ongoing Precision and Recovery Assessments

9.6.1 One sample shall be prepared with reagent water that is spiked with a known amount of analyte to assess the Ongoing Precision and Recovery method performance that is independent of matrix effects.

9.6.1.1 Precipitate a spiked aliquant of laboratory reagent water at the same volume as samples with each analytical batch. This Laboratory Fortified Blank (LFB) must be subjected to the same procedural steps as the samples.

9.6.1.2 Spike the LFB with enough Ra-226 and Ra-228 so the activity concentration is approximately 5 pCi/L .

9.6.1.3 Evaluate using Equation 2 where $B = 0$.

9.6.2 Compare the concentration with the limits for ongoing precision and recovery in Table 17.1. If the concentration is in the range specified, the analytical processes are in control and the analysis of

samples are acceptable. If, however, the concentration is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-extract the analytical batch, and reevaluate the ongoing precision and recovery sample for acceptability.

9.6.3 The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if R = 95 % and s_r = 5 %, the accuracy is 85 % to 105 %.

9.7 The specifications contained in this method can be met if the apparatus used is scrupulously cleaned and dedicated for the determination of Ra-226 and Ra-228. The standards used for initial precision and recovery (IPR, Section 9.2.2), matrix spikes (MS/MSD, Section 9.3), and ongoing precision and recovery (OPR, Section 9.6) should be identical, so that the most precise results will be obtained. However, they musty not be from the same source used for calibration standards.

9.8 Depending upon specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1 Analytical balance calibration

10.1.1 The analytical balance must be calibrated annually using NIST –traceable weights.

10.1.2 Prior to use for this method the calibration for the balance must be checked with 1mg and 1000 mg weights from a Class S set.

10.1.3 Calibration shall be within ± 10 % (i.e. ±0.1 mg) at 1 mg and ± 0.5 % (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

10.2 Carrier standardization

10.2.1 In triplicate in a 100 mL beaker to 20 mL DI H_2O pipet 5 mL of barium carrier. Add 5 drops of concentrated HCl. If the laboratory prefers to use a lead carrier, substitute 10 mL of lead carrier in place of the barium carrier.

10.2.2 Heat to boiling and add 20 mL 18 N H_2SO_4 with stirring.

10.2.3 Digest 5–10 minutes and then let solution cool.

10.2.4 Slurry precipitate and transfer to a 100 mL centrifuge tube using 0.1 N H_2SO_4 as a wash.

10.2.5 Wash precipitate twice with 10 mL 0.1 N H_2SO_4 and discard washes.

10.2.6 Transfer precipitate to a preweighed sintered glass crucible and dry at 110°C for two hours.

10.2.7 Place in desiccator to cool.

10.2.8 Weigh, Record gross and net weight for use in calculating barium (or lead) weight per mL.

10.3 Gamma-ray Detector Calibration

10.3.1 Laboratories may choose to follow the energy and efficiency calibration procedures for gamma-ray detectors as described in EPA method 901.1. Provisions must be made to ensure calculations in data reduction spreadsheets and software are able to adjust sample measurements for systematic interferences to gamma-ray measurements. Specifically software must correct for the summation effect observed for the 609 keV photopeak from Bi-214. If not, then the following steps must be followed to calibrate the gamma-ray detector for energy and efficiency.

10.3.2 Energy Calibration

10.3.2.1 Follow the instrument manufacturer's instructions for powering up and adjusting the electronics of the gamma-ray detector system. A gamma-ray spectral window extending to a minimum of 2000 keV is required for this method.

10.3.2.2 Obtain and measure a NIST-traceable source that contains a minimum of 6 photopeaks that extend throughout the spectral range selected for use by the laboratory. Since the energy response for gamma-ray detectors is not affected by geometry, this energy calibration source need not be in the same geometry used for sample measurements. Count time used for energy calibrations only need to be long enough so the lowest activity peaks used for calibration are distinct and well defined from the Compton background.

10.3.2.3 From the acquired spectra, determine the channel number where the maximum (i.e. the peak centroid) for each peak occurs either by manual inspection and calculation, or manufacturer supplied data reduction software. Record each peak centroid and channel number pair.

10.3.2.4 Using a calculation spreadsheet or manufacturer supplied software, determine the relationship for the peak energy/centroid pairs by plotting them or fitting a mathematical formula to them.

10.3.3 Efficiency Calibration with a prepared efficiency source. Measuring a source prepared in the same way as the samples and measured in the same geometrical orientation distance from the detector as the samples produce the most accurate measurement of the efficiency for the peaks originating from the Ra-226 and Ra-228 progeny.

10.3.4 Efficiency calibration source preparation.

10.3.4.1 Obtain NIST traceable solutions of Ra-226 and Ra-228.

10.3.4.2 Pipet 5 mL of barium carrier into a small beaker, then add 5 drops of concentrated HCl and 20 mL of deionized water.

10.3.4.3 Add appropriate amounts of NIST traceable solutions of Ra-226 and Ra-228 with a calibrated autopipette or glassware so that source count times will be no longer than the count times for samples, but not so high that instrument dead time will exceed 5 percent. Calculate the decays per minute for each radioanalyte.

10.3.4.4 Heat the contents of the beaker to boiling, then add 20 mL 18 N H_2SO_4 while stirring the contents of the beaker.

10.3.4.5 Digest 5- 10 minutes and then let solution cool.

10.3.4.6 Slurry precipitate and transfer to a centrifuge tube using 0.1 N H_2SO_4 as a wash.

10.3.4.7 Wash precipitate twice with 10 mL 0.1 N H_2SO_4 . Centrifuge between washes and discard the washes.

10.3.4.8 Obtain a filter of the same type and size to fit inside the sample containers selected for use to make sample measurements. Tare the filter by weighing it to an accuracy of 0.01 mg.

10.3.4.9 Place the filter in an appropriate sized filtering funnel mounted on a vacuum manifold.

10.3.4.10 Filter with suction through the tared filter. Quantitatively transfer precipitate to the filter by rinsing the remaining particles from the beaker with a jet of reagent water.

10.3.4.11 Dry the precipitate on the filter with 10 mL ethanol, followed by 10 mL

diethyl ether.

10.3.4.12 Weigh filter and precipitate to determine yield.

10.3.4.13 Place filter in the same type of sample container that will be used for samples.

10.3.4.14 Hold for a minimum of 4 weeks so the radium progeny can approach full ingrowth prior to gamma-ray spectral analysis with a germanium detector.

10.3.5 Efficiency Source Measurement

10.3.5.1 This calibration is performed with the same counting geometry as the samples. After ingrowth, place the prepared efficiency source into the sample cave in the same orientation and distance from the germanium detector as will be used for sample measurement.

10.3.5.2 Count the efficiency source for a long enough count time so that the peaks selected to use for sample measurements (the 338, 352, 609 and 911 keV photopeaks) will have accumulated at least 10,000 net counts above the Compton background.

10.3.5.3 After the measurement count time is complete, obtain the net counts for the peaks referenced in the previous step using commercially available gamma-ray data analysis software or a calculation spreadsheet.

10.3.5.4 Calculate the efficiency (ε) individually for each photopeak using the following calculation;

$$\varepsilon = \frac{C}{D \times T \times R \times F}$$

where:

C = Net counts

D = Calibrated decays per minute (DPM) for the photopeak from step 10.3.3.1.3.

R = Fractional chemical yield of barium carrier from step 10.3.1.12.

T = Count time (in minutes)

F = Fractional intensity of the photopeak

10.4 Detector Background Characterization. The laboratory must determine the background activity that occurs in the regions of interest for each photopeak used to measure the radium isotopes in each gamma-ray detector used to make measurements for the method before it can be implemented on a routine basis.

10.4.1 Place a sample container containing a clean filter of the same type and size that will be used for sample measurements into the gamma-ray detector cave. Ensure it is in the same orientation and distance from the detector as will be used for sample measurements.

10.4.2 Measure the sample container and filter for a sufficiently long count time to determine if there is any activity in the regions of interest for the photopeaks used to measure the radium isotopes. A minimum count time of 36000 seconds is recommended.

10.4.3 Examine the regions of interest used for the radium measurements to see if there is a net activity noted in them. If net activities are noted, use them in Step 11.2 in the next section to determine if they are sufficiently low so that reasonable count times and sample volumes can be used to reach the required sensitivities for each radium isotope measured with this method.

10.4.4 If the background is determined to be excessive, see if this background can be reduced by cleaning the interior of the gamma-ray detector cave, removing samples from the count room, venting the liquid nitrogen exhaust into the sample cave to displace any radon present, or adding additional shielding to the gamma-ray detector cave, then repeat steps 10.4.1 though 10.4.3

10.4.5 If the background is determined not to be excessive, store the background measurement

electronically for later use in data reduction.

10.4.6 At least monthly, repeat steps 10.4.1 through 10.4.5 and record the activities for each region of interest used to measure the radium isotopes. The laboratory should then control chart the results and set control limits for the backgrounds in each region of interest to ensure their background activities remain in control for sample measurements.

11.0 Procedure

This method is entirely empirical. Precise and accurate results can be obtained only by strict adherence to all details.

Note: *The procedure below is based on the preparation, precipitation, and analysis of a 2 L sample volume and a nominal 40 % efficiency high purity germanium detector. If a different detector is used for analysis, the laboratory may need to adjust the volume of sample and counting time required to reach the desired detection limit.*

11.1 Determine the sample volume, ingrowth period and count time required to meet the required detection limits.

11.1.1 The sensitivity of these measurements must comply with the required detection limits for these radioanalytes specified at 40 CFR part 141.25(c), Table 1 as 1 pCi/L for both radium isotopes.

11.1.2 A minimum ingrowth period of 14 days is recommended for Ra-226 measurements.

11.2 Radium purification.

11.2.1 Measure the volume of preserved drinking water sample (Note 1), determined in step 11.1 in a volumetric flask or graduated cylinder, then pour the measured volume into a borosilicate beaker large enough to contain it.

11.2.2 Add 10 mL of 12 N hydrochloric acid for every liter of sample used and stir.

11.2.3 Using a volumetric pipet add 5.0 mL barium carrier (9 mg/mL). If the lead carrier is being used instead, add 10.0 mL lead carrier (20 mg/mL) in place of the barium carrier.

11.2.4 Stir and heat to boiling.

11.2.5 Precipitate barium sulfate by adding 10 mL of 18 N H_2SO_4 for every liter of sample used, stirring frequently. Boil for 30 min.

11.2.6 Store overnight to let the precipitate settle, or for fast settling cool 30 min in an ice bath.

11.2.7 Obtain a filter of the size appropriate for the filtering funnel (Note 2) used at the laboratory. Tare the filter by weighing it to the nearest 0.01 mg.

11.2.8 Place the tared filter into a filter funnel that is attached to a vacuum manifold or to a vacuum flask that is connected to a vacuum source.

11.2.9 Filter with suction through the tared filter. Quantitatively transfer precipitate to the filter by rinsing the remaining particles from the beaker with a jet of water.

11.2.10 Dry the precipitate on the filter with 10 mL ethanol, followed by 10 mL diethyl ether.

11.2.11 Weigh filter and precipitate. Record the weight.

11.2.12 Subtract the tared filter weight from the combined weight of the filter and precipitate to determine the net weight of the precipitate. Divide this net weight of the precipitate by the maximum theoretical weight of the precipitate based on the amount of barium carrier that is used for the precipitation. The ratio is the Fractional Chemical Yield (Y) for the sample precipitation.

11.2.13 Place the filter in the same type of sample container as the efficiency calibration standard.

11.2.14 Repeat steps 11.2.1 for each sample in the preparation batch.

11.2.15 Hold the prepared samples for Ra-226 progeny ingrowth before proceeding to the next step. If only Ra-228 measurements are to be made for the prepared samples, then proceed directly to the next step. Calculate the ingrowth by the following equation:

Ra-226 progeny ingrowth = $1 - e^{-\lambda t}$

Where;

t is time in days and λ is ln(2) divided by the half-life in days of 3.825 = 0.18112 d^{-1} (or one can interpolate from Table 17.3)

Note 1: At the time of sample collection, add 4 mL 16 N HNO_3 for each gallon (3.7 L) of water.

Note 2: A 47 mm filter is used with a steel planchet or plastic Petri dish (step 11.1.8) but other filters can be substituted, subject to step 11.2.1, such as a 25 mm filter for placement in ring and disk or filters of various sizes for placement in vial to be counted in well type detector.

11.3 Sample Measurement

11.3.1 Place the sample container and filter assembly in the same geometry as was used for measuring the efficiency source in step 10.3.5. Collect the gamma-ray spectra for the count time determined in step 11.1.

11.3.2 Use either manufacturer supplied software or a calculation spreadsheet to determine the net activity in the regions of interest for each photopeak used to measure the radium isotopes. Ensure it will:

11.3.2.1 Subtract the Compton background under each peak properly.

11.3.2.2 Subtract the net background adjusted for the sample count time for each region of interest. To adjust the background measured for each region of interest used to measure the radium isotopes, multiply each region's count rate (cpm) obtained from the background measurement by the number of minutes the sample was counted. The software or calculation spreadsheet must then subtract this net background activity from the net counts in each photopeak's region of interest that is above the Compton background in the sample spectra to obtain the final net counts used in calculating the activity and uncertainty for the samples.

12.0 Data Analysis and Calculations

12.1 Sample activity concentration, the combined standard uncertainty of measurements of sample activity concentration made using this method, and method sensitivity are determined using the equations given below.

12.2 Calculate the concentration, A_S of Ra-228 and Ra-226 in picocuries per liter (pCi/L) as follows:

Assumptions:

- The detector is calibrated with a prepared radium source, not a mixed-gamma source.
- There is negligible uncertainty associated with the calibration.
- The uncertainties of times, volumes, and masses are negligible.
- There is negligible variability in replicate determinations of the carrier mass.
- There is negligible variability in the ratio of the radium and barium recoveries.

Given these assumptions, the only significant sources of uncertainty are counting statistics and the determination of net photopeak areas in the gamma-ray spectrum.

For both Ra-228 and Ra-226, the activity equation can be written as

$$A_S = \frac{W_1 \frac{R_1}{\varepsilon_1 F_1} + \cdots + W_n \frac{R_n}{\varepsilon_n F_n}}{2.22 \times V_S \times Y_S \times D_S} \tag{4}$$

where

A_S	is the sample activity concentration (pCi/L)
n	is the number of peaks used (typically $n = 2$)
R_i	(for $i = 1, 2, \ldots, n$) is the net count rate in counts per minute (min^{-1}) for peak i, corrected for baseline, background, and interferences
V_S	is the volume of the sample aliquant analyzed (L)
Y_S	is the chemical yield, or recovery, for the sample (fraction)
D_S	is the correction factor for decay/ingrowth (fraction)
ε_i	is the detection efficiency for peak i (fraction)
F_i	is the branching fraction for peak i (fraction)
W_i	is the weighting factor for peak i (fraction); $W_1 + W_2 + \cdots + W_n = 1$; e.g., W_i might be $\varepsilon_i F_i / (\varepsilon_1 F_1 + \cdots + \varepsilon_n F_n)$

Other unit conversions can be handled by including a constant factor in the denominator of the expression for A_S.

12.4 The equation for the combined standard uncertainty of A_S is shown below.

$$u_c(A_S) = \frac{\sqrt{W_1^2 \frac{u^2(R_1)}{\varepsilon_1^2 F_1^2} + \cdots + W_n^2 \frac{u^2(R_n)}{\varepsilon_n^2 F_n^2}}}{2.22 \times V_S \times Y_S \times D_S} \tag{5}$$

The values and uncertainties for R_i for $i = 1$ to n, should be provided by the gamma-analysis software. Note that the uncertainties of V_S, Y_S, D_S, and ε_i are assumed to be negligible, and the uncertainty of F_i does not affect the combined standard uncertainty of A_S when a radium source is used for efficiency calibration at each of the gamma-ray energies.

Any additional uncertainties for V_S, Y_S, D_S, or for the calibration standard or the yield obtained during the calibration can be included by adding terms to $u_c^2(A_S)$ that look like:

$$A_S^2 \frac{u^2(\text{Some quantity})}{(\text{Some quantity})^2}$$

12.5 Method Sensitivity

Since this method utilizes multiple photopeaks for quantitation, the sensitivity depends on the Compton baseline and on the background activity for each photopeak above the baseline. When Equation 4 is used for the activity concentration of a sample, the following equation may be used to estimate the SDWA detection limit:

$$\text{DL} = \frac{1.96^2}{2t_S} \sum_{i=1}^{n} \frac{W_i^2}{\varepsilon_i F_i} \left[1 + \sqrt{1 + \frac{4t_S^2}{1.96^2} \frac{\sum_{i=1}^{n} \frac{W_i^2 V(R_i)_{R_i=0}}{\varepsilon_i^2 F_i^2}}{\left(\sum_{i=1}^{n} \frac{W_i^2}{\varepsilon_i F_i} \right)^2}} \right] \times \frac{1}{2.22 \times V_S \times Y_S \times D_S} \tag{6}$$

where:

DL	is the SDWA detection limit, in picocuries per liter (pCi/L)
t_S	is the sample count time (min)
$V(R_i)_{R_i=0}$	is the variance of the observed net count rate, R_i, when the sample activity is zero

Each variance $V(R_i)_{R_i=0}$ may be estimated as follows:

$$V(R_i)_{R_i=0} = \frac{C_{S,Comp,i} + (C_{B,i} - C_{B,Comp,i}) \times t_S / t_B + u^2(C_{S,Comp,i})}{t_S^2} + \frac{C_{B,i} + u^2(C_{B,Comp,i})}{t_B^2} \quad (7)$$

where:

$C_{S,Comp,i}$	is the number of counts in sample peak *i* due to the Compton baseline of the sample spectrum
$u(C_{S,Comp,i})$	is the standard uncertainty of the estimated number of counts in sample peak *i* due to the Compton baseline (depends on the model used to estimate the baseline under the peak)
$C_{B,i}$	is the total count in the background peak (if any) for peak *i*, before correction for the Compton baseline of the background spectrum
$C_{B,Comp,i}$	is the number of counts in the background peak (if any) for sample peak *i* due to the Compton baseline of the background spectrum
$u(C_{B,Comp,i})$	is the standard uncertainty of the estimated number of counts in the background peak for sample peak *i* due to the Compton baseline
t_S	the sample count time (min)
t_B	is the background count time (min)

Note: If there is no background peak, omit the background terms in the equation above.

13.0 Method Performance

This method was validated through an inter-laboratory method validation study. There were 9 method ruggedness samples with known concentrations in these studies (n = 9). Table 13.1 below demonstrates the method has comparable or better performance when compared to EPA approved methods to measure these radioanalytes in drinking water.

Table 13.1. The accuracy and precision results derived from matrix spike and duplicated samples in the method ruggedness studies

Ra226	Percent Recovery	RPD	Ra228	Percent Recovery	RPD
Avg	99	7		101	6
Std. Dev.	7	6		9	6
Limit		19			18
Lower Limit	85			83	
Upper Limit	113			119	

One laboratory also conducted a study to document the equivalency of using lead as the carrier instead of barium. Table 13.2 below demonstrates the accuracy and precision for the 10 samples that were spiked with known amounts of the radioanalytes of interest.

Table 13.2. The accuracy and precision results derived from the matrix spike and duplicated samples in the lead carrier equivalency study.

	Percent			Percent	
Ra226	**Recovery**	**RPD**	**Ra228**	**Recovery**	**RPD**
Average	102	4		95	6
Std. Dev.	2	2		3	2

14.0 Pollution Prevention

14.1 The solvents used in this method pose little threat to the environment when recycled and managed properly.

14.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 Samples preserved with HCl or H_2SO_4 to pH < 2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

15.3 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.4 Use of this method may result in the generation of mixed waste (MW). MW contains both hazardous waste (as defined by RCRA and its amendments) and radioactive waste (as defined by AEA and its amendments). It is jointly regulated by NRC or NRC's Agreement States and EPA or EPA's RCRA Authorized States. The fundamental and most comprehensive statutory definition is found in the Federal Facilities Compliance Act (FFCA) where Section 1004(41) was added to RCRA: "The term 'mixed waste' means waste that contains both hazardous waste and source, special nuclear, or byproduct material subject to the Atomic Energy Act of 1954." For more information on the handling and treatment of MW, please see http://www.epa.gov/radiation/mixed-waste/

16.0 References

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17.0 Tables

Table 17.1. Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial precision and recovery	9.2.2	
Ra-226 Precision (s)	9.2.2.2	12
Ra-226 Recovery (X)	9.2.2.2	76–125
Ra-228 Precision (s)	9.2.2.2	10
Ra-228 Recovery (X)	9.2.2.2	77–115
Matrix spike/matrix spike duplicate	9.3	
Ra-226 Recovery	9.3.4	85-113
Ra-226 RPD	9.3.5	12
Ra-228 Recovery	9.3.4	84-118
Ra-228 RPD	9.3.5	18
Ongoing precision and recovery	9.6	
Ra-226 Recovery	9.6	76–125
Ra-228 Recovery	9.6	77–115

Table 17.2: Sample Handling, Preservation, and Instrumentation

Parameter	Preservative[1]	Container[2]	Maximum Holding Time[3]
Radium-226	Conc. HCl or HNO_3 to pH <2	P or G	6 mo
Radium-228	Conc. HCl or HNO_3 to pH <2	P or G	6 mo

[1]It is recommended that the preservative be added to the sample at the time of collection. However, if the sample has to be shipped to a laboratory or storage area, acidification of the sample (in its original container) may be delayed for a period not to exceed 5 days. A minimum of 16 hours must elapse between acidification and analysis.
[2]P = Plastic, hard or soft; G = Glass, hard or soft.
[3]Holding time is defined as the period from time of sampling to time of analysis. In all cases, samples should be analyzed as soon after collection as possible. If a composite sample is prepared, a holding time cannot exceed 12 months.

Table 17.3. Ingrowth Factors for Short –lived Radium-226 Progeny y

	% Ingrowth		% Ingrowth		% Ingrowth
Day1	0.165	Day2	0.304	Day3	0.419
Day4	0.515	Day5	0.595	Day6	0.662
Day7	0.718	Day8	0.765	Day9	0.804
Day10	0.836	Day11	0.863	Day12	0.886
Day13	0.905	Day14	0.920	Day15	0.933
Day16	0.944	Day17	0.954	Day18	0.961
Day19	0.968	Day20	0.973	Day21	0.977
Day22	0.981	Day23	0.984	Day24	0.987
Day25	0.989	Day26	0.991	Day27	0.992

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols

°C	degrees Celsius
<	less than
%	percent
±	plus or minus

18.1.2 Alphabetical characters

g	gram
h	hour
L	liter
mg	milligram
mg/L	milligram per liter
mg/mL	milligram per milliliter
mL	milliliter
No.	number

18.2 Definitions, acronyms, and abbreviations

18.2.1 Analyte: The Ra-226 or Ra-228 tested for by this method.

18.2.2 Analytical batch: The set of samples extracted at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an ongoing precision and recovery sample (OPR, Section 9.6), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 OPR, 1 MS, and 1 MSD) and a maximum of 14 analyses (10 samples, 1 blank, 1 OPR, 1 MS, and 1 MSD) in the batch. If greater than 10 samples are to be extracted at one time, the samples must be separated into analytical batches of 10 or fewer samples.

18.2.3 Field blank: An aliquant of reagent water that is placed in a sample container in the laboratory or in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

18.2.4 IPR: See initial precision and recovery.

18.2.5 Initial precision and recovery (IPR): Four aliquants of the diluted PAR analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrumentation is modified.

18.2.6 Laboratory blank (method blank): An aliquant of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

18.2.7 Laboratory control sample (LCS): See Ongoing precision and recovery standard (OPR).

18.2.8 Matrix spike (MS) and matrix spike duplicate (MSD): Aliquants of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are prepared and/or analyzed exactly like a

field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquant and the measured values in the MS and MSD corrected for background concentrations.

18.2.9 May: This action, activity, or procedural step is neither required nor prohibited.

18.2.10 May not: This action, activity, or procedural step is prohibited.

18.2.11 Method Detection Limit: The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

18.2.12 Minimum Level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

18.2.13 Must: This action, activity, or procedural step is required.

18.2.14 Ongoing precision and recovery standard (OPR, also called a laboratory control sample): A laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and accuracy.

18.2.15 OPR: See Ongoing precision and recovery standard.

18.2.16 PAR: See Precision and recovery standard.

18.2.17 Precision and recovery standard: Secondary standard that is diluted and spiked to form the IPR and OPR.

18.2.18 Quality control sample (QCS): A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

18.2.19 Reagent water: Water demonstrated to be free from Ra-226, Ra-228 and potentially interfering substances at or above the Minimum Level of this method.

18.2.20 Should: This action, activity, or procedural step is suggested but not required.

18.2.21 Stock solution: A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.