Method 904.0, Revision 1.0: Radium-228 in Drinking Water

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Office of Water (MS-140)
EPA 815-B-22-003
March 2022

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Acknowledgements

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1 Scope and Application

1.1 Background

Method 904.0, Revision 1.0 is a method for the determination of radium-228 in drinking water. In this method the beta activity emitted from actinium-228, which is the decay progeny of radium-228, is determined and correlated to the radium-228 in a sample. When secular equilibrium is established, the activity of actinium-228 will be equal to the activity of radium-228.

1.2 Drinking Water Regulatory Requirements

The Code of Federal Regulations (CFR) at 40 CFR 141.66(b) specifies a maximum contaminant level (MCL) for combined radium-226 and radium-228 of 5 pCi/L. As specified at 40 CFR 141.25(c)(1), the required detection limit for radium-228 is 1 pCi/L.

1.3 Sensitivity

The sensitivity of the method is a function of sample size, instrument background, counting efficiency, yield, and counting time.

2 Summary of the Method

The radium isotopes in a drinking water sample are collected by coprecipitation with barium and lead sulfate and purified by re-precipitation from a basic EDTA solution. After a 36-hour ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and counted for beta activity. If determination of radium-226 is also desired, the supernatant can be reserved for analysis by an alternate procedure.

NOTE: This method contains options for carrier standardization, calibration and yield determination. The laboratory is expected to select an option and incorporate it into their procedure consistently. Switching options among analytical batches can result in possible QC failures.

3 Definitions

3.1 Activity

Rate of nuclear decay occurring in a body of material, equal to the number of nuclear disintegrations per unit time.

3.2 Batch, Preparation

A set of up to 20 environmental field samples of the same matrix that are prepared and/or analyzed together with the same instrumentation and personnel, using the same lot(s) of reagents, with a maximum time between the start of preparation of the first and last sample in the batch being 24 hours.

3.3 Detection Limit (DL)

The DL for radionuclides in drinking water is defined in 40 CFR 141.25(c) as the radionuclide concentration that can be counted with a precision of plus or minus 100% at the 95% confidence level (1.96σ, where σ is the standard deviation of the net counting rate of the sample).

3.4 Duplicate (DUP)

A second aliquot of a field sample that is processed in the same manner as the samples in the preparation batch. Analysis of the DUP provides a measure of the precision associated with batch preparation.

3.5 Field Blank

Samples preserved with reagents that are **not** provided by the laboratory should be accompanied by a field blank sample that is preserved in the same manner as the submitted samples. The field blank is a volume of blank matrix that is placed in a clean sample container, preserved in the field, shipped along with the samples and subjected to the same analytical procedures as the samples. A sample of the preservative should also accompany the field samples to determine whether it contributes any contamination.

3.6 Laboratory Fortified Blank (LFB)

The LFB consists of a volume of a blank matrix to which a known activity of a radioisotope has been added. The LFB is processed in the same manner as the samples in the preparation batch, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements. The drinking water LFB activity should be at a level between the required detection limit and the MCL.

3.7 Laboratory Reagent Blank (LRB)

The LRB consists of an aliquot of a blank matrix that is processed in the same manner as the samples in the preparation batch, including exposure to all glassware and equipment that are used in the preparation batch. The LRB is used to assess the process of handling, preparation and analysis for cross-contamination and for low-level analytical bias.

3.8 Laboratory Fortified Sample Matrix (LFSM)

An aliquot of a field sample to which a known activity of the radionuclide(s) being measured has been added. The LFSM is processed in the same manner as the samples in the preparation batch. Its purpose is to determine whether the sample matrix contributes bias to the results. The native level of the radionuclide(s) must be determined in an unspiked field sample aliquot in order to correct for levels already present in a sample that could contribute to the LFSM response. Spike drinking water LFSMs with a known activity of radium-228 standard that is approximately 10 times the anticipated level in the samples or approximately 10 times the DL (i.e. 10 pCi/L).

3.9 Laboratory Fortified Sample Matrix Duplicate (LFSMD)

An additional aliquot of a field sample that has the same quantity of radionuclide(s) added to it as the LFSM. The LFSMD is processed in the same manner as the samples in the preparation batch. It may be used in place of the DUP to assess preparation batch precision.

3.10 Picocurie (pCi)

The pCi is the quantity of radioactive material producing 2.22 nuclear disintegrations per minute.

3.11 Uncertainty, Counting

The component of measurement uncertainty attributable to the random nature of radioactive decay and radiation counting.

3.12 Uncertainty, Standard
An estimate of the measurement uncertainty expressed as one standard deviation.

3.13 Uncertainty, Expanded
An estimate of the uncertainty U of a measurement result y that provides a high level of confidence that the interval $y \pm U$ includes the actual value of the quantity being measured. The expanded uncertainty is typically obtained by multiplying the standard uncertainty by a coverage factor. A coverage factor of 1.96 is routinely used for drinking water analysis and the coverage factor (or confidence level) should be specified on the sample report.

4 Interferences

4.1 Naturally occurring barium
A significant natural barium content in a sample may bias the barium sulfate chemical yield high resulting in lower sample activity results.

4.2 Strontium-90
The presence of strontium-90 in the water sample will give a positive bias to the radium-228 activity measured.

4.3 Group IIA elements
High levels of the Group IIA elements (e.g. calcium, strontium) can be a potential problem since the chemical behavior of these elements mimic that of radium.

5 Safety

The specific toxicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining a chemical hygiene plan (CHP) with an awareness of the appropriate regulations regarding safe handling of chemicals used in this method. A reference file of safety data sheets (SDSs) should be made available to all personnel involved in the preparation of samples and their analyses.

6 Equipment and Supplies

6.1 Gas-flow proportional counter
The detector may be either a windowless (internal proportional counter) or a thin window type. The system should be capable of accommodating counting planchets and be sufficiently free from background so that required detection levels can be met within a reasonable counting time.

6.2 Stainless steel counting planchets
A planchet should be flat-bottomed, or with concentric rings, with a raised wall to contain the sample being evaporated.
NOTE: Always use the same type planchet (to maintain the same geometric configuration) for calibration and sample determinations.

6.3 Electric hot plate or hot water bath

6.4 Drying oven/heat lamp

Drying oven capable of maintaining a temperature of 105 °C ± 2 °C. Alternately, infrared heat lamps may be used if a drying oven is not available.

6.5 Desiccator

6.6 Centrifuge/Centrifuge tubes

6.7 Glassware

Beakers and graduated cylinders of various sizes as appropriate for sample preparation as described in the method. Vacuum flasks of sufficient capacity to hold filtered sample volumes. Glass or ceramic filter funnels.

6.8 Pipettes

Pipettes of various sizes.

6.9 Volumetric glassware

Volumetric flasks, class A, 100-mL to 2-L

6.10 Analytical balance

The analytical balance should have a readability of 0.1 mg.

6.11 Membrane filters and filter funnel assemblies

Vacuum filter funnel assemblies and membrane filters with 0.45 µm pore diameter. Membrane filters must be capable of being dissolved in concentrated nitric acid.

6.12 Additional filters and filter papers (as appropriate for procedural options)

Ashless filter paper. Diameter as appropriate for glass or ceramic filter funnels, including sintered glass crucibles.

6.13 *Optional*: Equipment for pH determination

6.13.1 pH meter

Potentiometer with glass electrode, reference electrode, and temperature compensation capability.

6.13.2 pH paper

Short range and wide range.

7 Reagents and Standards

Analytical reagent grade or better chemicals should be used. Commercial reagents are often not tested for trace radioactivity. Therefore, analysts need to carefully monitor their laboratory reagent blank (LRB) control charts to identify situations where levels of radioactivity may be present in reagents that could compromise results.

NOTE: Laboratories can adjust reagent and solution volumes as appropriate to meet testing needs provided the molar ratios are maintained.

7.1 Distilled/deionized water

Distilled or deionized water meeting the requirements of ASTM Type 1, 2, or 3 reagent water.

7.2 Acetic acid

Acetic acid, 17.4 M: glacial CH_3COOH (conc.), sp.gr. 1.05, 99.8%.

7.3 Acetone

Acetone, reagent grade or better

7.4 Ammonium hydroxide

Ammonium hydroxide, NH_4OH (conc.), sp.gr. 0.90, 56.5%

7.5 Ammonium hydroxide (6M)

Prepare by adding about 40.5 mL concentrated NH_4OH to 50 mL distilled/deionized water and dilute to 100 mL.

7.6 Ammonium oxalate, saturated

Prepare by adding 10 g $(NH_4)_2C_2O_4 \cdot H_2O$ to 100 mL boiling distilled/deionized water. Cool.

7.7 Ammonium oxalate, 5% (m/v)

Prepare by dissolving 5 g $(NH_4)_2C_2O_4 \cdot H_2O$ in distilled/deionized water and diluting to 100 mL.

7.8 Ammonium sulfate (200 mg/mL)

Prepare by dissolving 20 g $(NH_4)_2SO_4$ in a minimum of distilled/deionized water and dilute to 100 mL.

7.9 Ammonium sulfide, 2% (v/v)

Prepare by diluting 10 mL $(NH_4)_2S$ (20-24%) to 100 mL with distilled/deionized water.

7.10 Barium carrier (16 mg Ba^{2+}/mL)

Prepare carrier by dissolving about 2.8 g $BaCl_2 \cdot 2H_2O$ in distilled/deionized water, adding 0.5 mL 16 M HNO_3, and diluting to 100 mL with distilled/deionized water. Alternatively, purchase a high purity commercial barium standard solution and dilute appropriately. Standardize ***in triplicate*** using one of the options described below.

Note: Use the appropriate calculations in Section 12.1 to determine yield.

7.10.1 Standardize according to approach used to determine yield (Section 11.15)

7.10.1.1 Standardize barium based on chemical yield as $BaSO_4$

Pipette 2.00 mL carrier solution into a centrifuge tube containing 15 mL water. Add 1 mL 9 M H_2SO_4 (Section 7.28) with stirring and digest precipitate in a hot water bath for 10 minutes. Cool, centrifuge, and decant supernatant. Wash precipitate with 15 mL water. Centrifuge and decant supernatant. Transfer the precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp or in a 105°C ± 2 °C oven, cool in a desiccator and weigh as $BaSO_4$. Verify the average mass is within ± 5% of the expected mass with a relative standard deviation among the replicates of < 5%. Calculate the barium content:

$$Ba^{2+}\ in\ mg/mL = \frac{(mg\ BaSO_4) \times \left({mg\ Ba^{2+}}/{mg\ BaSO_4}\right)}{Volume\ Ba^{2+}}$$

Substituting (137.34 g/mole Ba^{2+}/233.404 g/mole $BaSO_4$) = 0.5884, and 2.00 mL carrier volume yields:

$$Ba^{2+}\ in\ mg/mL = \frac{(mg\ BaSO_4) \times (0.5884)}{2.00\ mL}$$

NOTE: If barium-133 will be used as a tracer for radiochemical analysis, the barium carrier prepared in Section 7.10 does not need to be separately standardized.

7.10.1.2 Standardize using barium-133 tracer for radiochemical yield

Add barium-133 tracer solution to the prepared barium carrier (Section 7.10) at a level that will yield at least 6000 – 8000 pCi/100 mL. Pipette 2.00 mL carrier solution into a beaker or centrifuge tube containing 20 mL basic EDTA reagent (Section 7.13). Add 1 mL ammonium sulfate (200 mg, Section 7.8) and mix well. Add acetic acid (17.4 M, Section 7.2) until barium sulfate precipitates, then add 2 mL in excess. Digest precipitate in a hot (near boiling) water bath for about 15 minutes until precipitate settles. Cool, centrifuge, and decant the supernatant. Wash precipitate with 10 mL distilled/deionized water. Centrifuge and decant supernatant. Place a 0.45 µm membrane filter in a vacuum filter assembly, prewet with distilled/deionized water and start vacuum. Transfer the precipitate to the filter using distilled/deionized water to ensure the transfer is quantitative. Add a small volume of ethanol to the precipitate and maintain suction to fully dry the precipitate. The filter containing the precipitate should be mounted and counted in a geometry for which the gamma spectrometer has been properly calibrated. Ba-133 is counted long enough so about 10,000 counts above background are accumulated. Verify that the average Ba-133 activity is within ± 5% of the expected level with a relative standard deviation between the replicates of < 5%. This method does not discuss specifications related to analytical requirements for gamma spectrometers; however, laboratories incorporating barium-133 as a tracer will be expected to document energy and efficiency calibration as well as performance checks related to verifying detection efficiency, energy calibration, background, peak resolution, etc. Calculation of yield using the tracer is discussed in Section 12.1.2.

7.11 Bromocresol green indicator (*optional*)

Commercially available bromocresol green indicator solution to monitor pH

7.12 Citric acid (1 M)

Prepare by dissolving 21.0 g $C_6H_8O_7 \cdot H_2O$ in distilled/deionized water and dilute to 100 mL.

7.13 EDTA, basic reagent (0.25 M)

Prepare by dissolving 20 g NaOH in 750 mL distilled/deionized water, heat and slowly add 93 g ethylenediamine tetraacetic acid disodium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$). Heat and stir until dissolved, filter through coarse filter paper (Section 6.12) and dilute to 1 L.

7.14 Ethanol (*optional*)

Ethanol, 95%.

7.15 Lead carrier (15 mg/mL)

Prepare by dissolving 2.4 g $Pb(NO_3)_2$ in a minimum volume of distilled/deionized water, add 0.5 mL 16 N HNO_3 and dilute to 100 mL with distilled/deionized water.

7.16 Lead carrier (1.5 mg/mL)

Dilute 10 mL lead carrier (15 mg/mL) to 100 mL with distilled/deionized water.

7.17 Methyl orange indicator, 0.1% (m/v)

Prepare by dissolving 0.1 g methyl orange indicator in 100 mL distilled/deionized water.

7.18 Nitric acid (16 M)

Nitric acid, 16 M: HNO_3 (conc.), sp.gr. 1.42, 70.4%.

7.19 Nitric acid (6 M)

Prepare by carefully adding 187.5 mL 16 M HNO_3 to about 300 mL distilled/deionized water. Dilute to 500 mL.

7.20 Nitric acid (1 M)

Prepare by carefully adding 62.5 mL 16 M HNO_3 to about 800 mL distilled/deionized water. Dilute to 1-L.

7.21 Radium-228

Radium-228 standard traceable to a national metrology institute (such as the National Institute of Standards and Technology [NIST]). Prepare a standard working solution equivalent to about 50 pCi radium-228 per mL to use in preparing laboratory quality control checks.

NOTE: After making a working solution from the standard, verify the concentration by conducting at least three separate verification measurements to confirm that each individual measurement is within 5% of the expected value.

7.22 Sodium carbonate (1 M)

Prepare by dissolving 106 g Na_2CO_3 in distilled/deionized water and dilute to 1 liter.

7.23 Sodium hydroxide (18 M)

Prepare by dissolving 72 g NaOH in about 80 mL distilled/deionized water and dilute to 100 mL.

7.24 Sodium hydroxide (10 M)

Prepare by dissolving 40 g NaOH in about 80 mL distilled/deionized water and dilute to 100 mL.

7.25 Sodium hydroxide (6 M)

Prepare by dissolving 24 g NaOH in about 80 mL distilled/deionized water and dilute to 100 mL.

7.26 Strontium carrier (10 mg/mL)

Prepare by dissolving 24.16 g $Sr(NO_3)_2$ in a minimum volume of distilled/deionized water and dilute to 1 liter. When using strontium-89 as the calibrant, standardize the strontium carrier ***in triplicate*** by one of the following options:

7.26.1 Standardize by precipitation as strontium oxalate

Pipet 2-mL of 10 mg/mL strontium carrier into a beaker or centrifuge tube. Dilute with about 20 mL distilled/deionized water. Add 2 mL concentrated NH_4OH, heat to nearly boiling then slowly add 5 mL saturated ammonium oxalate solution (Section 7.6). Continue heating in a hot water bath near boiling for about 15 minutes. Cool, centrifuge, discard supernate. Rinse with a 20 mL volume of distilled/deionized water, centrifuge and discard supernate. Slurry the strontium oxalate precipitate with a few mLs distilled/deionized water and quantitatively transfer to a tared planchet. Dry under an infrared lamp or in a 105 °C $\pm$ 2 °C oven, cool in a desiccator and weigh. Verify that the average precipitate mass is within $\pm$ 5% of the expected level with a relative standard deviation between the replicates of < 5%.

7.27 Strontium-89 (calibrant)

Strontium-89 NIST-traceable standard solution for detector calibration. Prepare a standard working solution appropriate for meeting calibration requirements described in Section 10.

NOTE: After making the working solution from the NIST-traceable standard, verify the concentration by conducting at least three separate verification measurements to confirm that each individual measurement is within $\pm$ 5% of the expected value.

7.28 Sulfuric acid (9 M)

Cautiously mix 1 volume 18 M H_2SO_4 (conc.) with 1 volume of distilled/deionized water.

7.29 Yttrium carrier (18 mg/mL)

Add 22.85 g Y_2O_3 to an Erlenmeyer flask containing about 20 mL distilled/deionized water. Heat to boiling. Stir in small volumes of 16 M HNO_3 to dissolve the Y_2O_3. Small additions of water may be required to replace that lost through evaporation. After total dissolution, add about 70 mL 16 M HNO_3 and dilute to 1 liter with distilled/deionized water.

7.30 Yttrium carrier (9 mg/mL)

Dilute 50 mL yttrium carrier (18 mg/mL) to 100 mL with distilled/deionized water. There are two chemical yield options, either as yttrium oxalate or yttrium oxide. Standardize the yttrium carrier ***in triplicate*** based on the yield option selected:

7.30.1 Standardization based on yttrium oxalate yield

Yttrium oxalate can take the form of multiple hydrates. In order to achieve a uniform nonahydrate ($Y_2(C_2O_4)_3{\cdot}9H_5O$), the pH in the final precipitation step should ideally fall in the range of 1.7 - 1.9. Verify the pH and adjust if needed with HNO_3 or NaOH.

In triplicate: carefully pipet 10.0 mL portions of the yttrium carrier solution into separate centrifuge tubes. Add 30 mL saturated $(NH_4)_2C_2O_4{\cdot}H_2O$ (Section 7.6) to each centrifuge tube and stir. Digest in a hot water bath (near boiling) for 30 minutes. Cool in an ice bath. Centrifuge and discard supernate. Slurry the yttrium oxalate precipitate with a small volume of distilled/deionized water and transfer to a tared stainless steel planchet. Dry under an infrared lamp or in a 105 °C ± 2 °C oven, cool in a desiccator and weigh. Verify that the average precipitate mass is within ± 5% of the expected level with a relative standard deviation between the replicates of < 5%. Calculate the yttrium concentration:

$$Y^{3+},\ {}^{mg}/_{mL} = \frac{\left(mg\ \left(Y_2(C_2O_4)_3 \cdot (9H_2O)\right)\right)\left({}^{mg\ Y}/_{mg\ \left(Y_2(C_2O_4)_3 \cdot (9H_2O)\right)}\right)}{Volume}$$

$$= \frac{\left(mg\ \left(Y_2(C_2O_4)_3 \cdot (9H_2O)\right)\right)(0.29448)}{1\ mL}$$

7.30.2 Standardization based on yttrium oxide yield (in triplicate)

Follow the procedure described in Section 7.30.1, but instead of centrifuging the yttrium oxalate solution and transferring it to a planchet, allow the solution to cool. Filter the precipitate onto a quantitative ashless filter paper (e.g Whatman #42 (or equivalent)). Transfer the filter paper and precipitate to a previously ignited and tared porcelain crucible. Ignite at 800 °C in a muffle oven for one hour to convert the oxalate to the oxide. Cool and weigh. Verify that the average precipitate mass is within ± 5% of the expected level with a relative standard deviation between the replicates of < 5%. Calculate the yttrium concentration:

$$Y^{3+},\ {}^{mg}/_{mL} = \frac{(mg\ Y_2O_3)\left({}^{mg\ Y}/_{mg\ Y_2O_3}\right)}{Volume}$$

$$= \frac{(mg\ Y_2O_3)(0.78743)}{1\ mL}$$

7.31 Strontium-yttrium mixed carrier, 0.9 mg/mL Sr^{2+} and 0.9 mg/mL Y^{3+}

7.31.1 Solution A: yttrium carrier

Pipet a 10-mL aliquot of standardized yttrium carrier (18 mg/mL) into a 100-mL volumetric flask and dilute with distilled/deionized water.

7.31.2 Solution B: strontium carrier

Dissolve 0.435 g $Sr(NO_3)_2$ in a minimum amount of distilled/deionized water and dilute to 100 mL with distilled/deionized water.

7.31.3 Strontium-yttrium mixed carrier

Combine Solution A and Solution B.

8 Sample Collection, Preservation, and Storage

8.1 Containers

Collect samples in glass or plastic containers. A sample volume of 1 gallon (approximately 4 liters) is recommended for collection of drinking water samples, but collection volume is left to the discretion of the laboratory.

8.2 Sample Collection for Drinking Water

Open the cold water tap and allow the system to flush until the water temperature has stabilized (about 3 to 5 minutes). Collect samples from the flowing system. If the samples are preserved with reagents (i.e. nitric acid, Section 8.3) that are **not** provided by the laboratory, they should be accompanied by a Field Blank (Section 3.5) that is preserved in the same manner as the samples. A sample of the preservative used in the field should also accompany the samples and Field Blank to the laboratory to determine the contribution, if any, from the addition of the preservative.

NOTE: This section describes collection of drinking water samples at the entrance to the distribution system. Other guidance may apply for collection of water samples for other programs.

8.3 Preservation

It is preferred that samples be preserved at the time of collection by adding enough nitric acid to the sample to bring it to a pH < 2 (e.g. 1-2 mL 16 M HNO_3 per liter of sample will generally yield a pH < 2). Alternate concentrations of HNO_3 are permitted, although the volume added to achieve a pH < 2 should not exceed 30 mL/L. If the samples are preserved in the field using acid that has not been supplied by the laboratory, add the same level of acid to a Field Blank (Section 3.5). The pH of all samples must be verified upon receipt in the laboratory. If the pH is > 2, treat the sample as if it were collected without preservation as described in Section 8.4.

NOTE: Drinking water samples do not require thermal preservation.

8.4 Handling Unpreserved Samples and Storage

If samples are collected without preservation, they must be received by the laboratory within 5 days, then preserved with 16 M HNO_3 to a pH < 2 and held in their original containers for a minimum of 16 hours. The 16-hour waiting period helps solubilize finely suspended materials or surface adsorbed materials. Verify that the pH is < 2 before preparing the samples for analysis.

NOTE: Screen sample preservatives used by the laboratory (or by field samplers) for radioactive content by lot number prior to use, if possible, to verify that preservatives do not introduce radioactive contamination.

NOTE: Drinking water compliance samples must be prepared 'as received' (i.e. not filtered). Other programs/projects may have alternate requirements. If such programs/projects specify filtration, it must be performed prior to preservation.
NOTE: The requirement for pH < 2 adequately addresses radionuclides of concern for drinking water compliance samples; however, that may not be adequate for programs evaluating other radionuclides in non-drinking water matrices. Other programs should optimize sample preservation as appropriate to address such radionuclides of concern.
NOTE: The laboratory must have appropriate segregation procedures in place to prevent cross contamination of samples.

9 Quality Control

9.1 QC Requirements

QC requirements include an Initial Demonstration of Capability (IDC), ongoing Demonstration of Capability, and ongoing QC requirements that must be met when preparing and analyzing drinking water compliance samples. This section describes QC parameters, their required frequencies, and performance criteria that must be met in order to meet EPA quality objectives for drinking water analyses. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.1.1 Initial Demonstration of Capability

A successful IDC must be performed by each analyst prior to analyzing any field samples. Before conducting the IDC, set up and calibrate the instrument as described in Section 10. The IDC consists of the following: demonstration of low system contamination (Section 9.1.1.1), demonstration of accuracy (Section 9.1.1.2) and confirmation of method sensitivity through a DL study (Section 9.1.1.3).
NOTE: The primary analyst is responsible for conducting a full DL study along with the demonstration of low system contamination and demonstration of accuracy. Other analysts/technicians that may also be responsible for performing the method can document their IDCs by either conducting a DL study *or* by evaluating four LRBs (Section 9.1.1.1) and four LFBs (Section 9.1.1.2) and successfully meeting the specified acceptance criteria.

9.1.1.1 Demonstration of Low System Contamination

Contamination due to sample processing is assessed by preparing and counting at least four LRBs (Section 3.7). For drinking water, the LRB volume should be the same as the volume used in establishing detection capability (Section 9.1.1.3) and representative of typical drinking water sample volumes. LRBs are prepared and handled like samples following the procedure described in Section 11. Each LRB result must be below the radium-228 detection limit of 1 pCi/L.

9.1.1.2 Demonstration of Accuracy

Initial demonstration of accuracy is verified by preparing and counting at least four LFBs (Section 3.6) according to the procedure in Section 11. The recommended LFB fortification with radium-228 standard is about 2.5 – 5 pCi/L. The average recovery for the LFBs must be within ± 20% of the known amount of added radium-228 activity.

9.1.1.3 Detection Limit Study

Laboratories testing drinking water samples for Safe Drinking Water Act compliance monitoring need to confirm detection capability by performing a Detection Limit (DL) study. After calibrating the instrument

as described in Section 10, fortify seven LFBs with the radium-228 standard at activity concentrations near the 1 pCi/L required detection limit. Prepare and analyze the LFBs following the procedure described in Section 11. Calculate the DLs as described in Section 12.5.
NOTE: Further discussion of the drinking water DL procedure along with derivation of the final DL equation from the 40 CFR 141.25(c) definition can be found in *Procedure for Safe Drinking Water Act Program Detection Limits for Radionuclides*, USEPA 815-B-17-003, April 2017.
NOTE: Programs that do not analyze drinking water compliance samples may have alternate detection capability requirements.

9.1.1.4 Exception for Experienced Analysts

If an analyst has at least one year of experience preparing and analyzing LRBs and LFBs for a coprecipitation Ra-228 method (such as a previous version of EPA Method 904.0), and there have been no changes to the instrumentation, previously documented data may be used to fulfill the IDC low system contamination and accuracy requirements. Ongoing demonstrations of capability (Section 9.1.2) will verify analyst conformance to the criteria described in this revised method.

9.1.2 Ongoing Demonstration of Capability

Ongoing demonstrations of capability may be fulfilled by repeating the IDC studies described in Sections 9.1.1.1 – 9.1.1.2 annually or by documenting batch QC LRBs and LFBs that an analyst has processed during the year since the last demonstration of capability. The data for at least four LRBs processed in different batches can be used to assess sample processing contamination and the data for at least four LFBs processed in different batches can be used to assess accuracy. The amount of the Ra-228 standard added to the sample batch LFBs should follow the guidance described in Section 9.1.1.2.

9.2 Ongoing QC Criteria

This section summarizes ongoing QC criteria that must be followed when processing and analyzing drinking water compliance samples.

9.2.1 Calibration Stability and Background Checks

The calibration stability and background of each detector used to count analytical samples is checked and recorded on control charts each day prior to use to verify the instrument response has not changed since it was calibrated. During periods when gas proportional counters are idle, check the detector calibration stability and the background weekly to confirm the ready status of the instrument for sample measurements.

9.2.1.1 Calibration Stability Check

To verify detector calibration stability, each day prior to sample counting, run a beta QC check source. The check source does not have to be NIST-traceable but must have a documented count rate. Count the check source long enough to obtain about 10,000 counts (1% counting uncertainty). Record and monitor the measurements on a control chart.

9.2.1.2 Background Check

Each day prior to sample counting, run a background check with only a clean planchet in the detector. Record and monitor background measurements on a control chart.

9.2.1.3 Post-run Calibration Stability and Background Checks

After completion of a sample counting batch, run the beta check source and a background check to verify that the calibration and background did not change significantly while the samples were being counted.

9.2.2 Control Charts

Analysts are responsible for preparing and maintaining control charts. After a sufficient number of checks have been obtained (usually at least 20 measurements), calculate the mean values on the control charts. Establish warning limits at ±2 standard deviations and control limits at ±3 standard deviations relative to the mean values. Monitor control charts to ensure measurements remain in statistical control relative to the control limits. Also, monitor control charts to ensure instrument performance does not change significantly (i.e., drifting or trending of responses) relative to the time of the initial calibration. **NOTE:** As opposed to manually plotting data and calculating control limits, most instrument software provides this capability. Analysts still have a responsibility to monitor the control charts as described above to ensure that measurements remain in statistical control.

9.2.3 Corrective Action

If instrument control measurements exceed their control limits or exhibit a significant change in performance, the proportional counter is placed out of service until stability of the system relative to the initial calibration can be demonstrated.

9.2.4 Laboratory Reagent Blank (LRB)

An LRB (Section 3.7) must be prepared with each preparation batch to confirm there is no significant contamination introduced in processing the batch which would contribute bias to the analytical results. Ensure that LRB activity does not exceed the regulatory DL as described in Section 9.1.1.1. Record LRB activities on control charts and monitor for trends that could indicate the need for corrective action.

9.2.5 Laboratory Fortified Blank (LFB)

An LFB (Section 3.6) must be prepared with each preparation batch to assess batch accuracy independent of compliance sample matrix effects. Fortify with radium-228 standard at a level between the required detection limit and the MCL, although it is recommended to keep the fortification level between 2.5 and 5.0 pCi/L since uncertainty at the DL is higher. Accuracy as percent recovery must be within ±20% of the amount of activity added. If the LFB fails to meet the recovery criterion, the batch is considered compromised which may be due to contamination, poor precipitation/preparation technique, etc. Re-prepare the sample batch with new QC checks provided sufficient volume is available. Otherwise, a new set of samples should be collected. Record and monitor LFB recoveries on control charts.

9.2.6 Laboratory Fortified Sample Matrix (LFSM)

Prepare one LFSM (Section 3.8) per preparation batch. Spike the LFSM with a known activity of radium-228 standard that is approximately 10 times the anticipated level in the samples or at least 10 times the DL (i.e. 10 pCi/L). Accuracy as percent recovery must be within ±30% of the amount of activity added. If the LFSM fails to meet the recovery criterion, re-prepare the sample batch with new QC checks provided sufficient volume is available. Otherwise, flag sample results in the batch as possibly biased low or high (as the LFSM result indicates) due to matrix effects. Record and monitor LFSM recoveries on control charts.

9.2.7 Duplicate (DUP) or Laboratory Fortified Sample Matrix Duplicate (LFSMD)

Batch precision is assessed through preparation of either a DUP (Section 3.4) or a LFSMD (Section 3.9) with every preparation batch. The LFSMD is spiked at the same level as the LFSM. Precision is assessed by calculating the relative percent difference (RPD). RPD must be < 20%. If the RPD exceeds 20%, and a duplicate sample measurement is < 5X the DL, calculate the normalized absolute difference (NAD). Calculations for the RPD and NAD are provided in Section 12.6. A sample/DUP or LFSM/LFSMD that fail the batch precision criteria may be an indication of a lack of sample homogeneity and the samples in the preparation batch should be reported with a qualifier indicating the measurement has questionable precision. If a client requires unqualified results, prepare a new sample batch with new QC checks provided sufficient volume is available. Otherwise, a new set of samples should be collected. Record and monitor RPD and NAD on control charts.

9.2.8 Field Blank (if needed)

If a Field Blank (Section 3.5) is provided with the samples, prepare and analyze it to confirm that field-supplied preservative does not contribute uncertainty to the analytical results.

10 Calibration

10.1 Instrument Setup

Establish voltage plateaus and appropriate operating conditions as recommended by the instrument manufacturer. Perform a calibration stability check and background check as described in Section 9.2.1 following instrument set-up, anytime operating voltage is changed, following instrument repairs, and after gas bottle changes. If QC checks fail, take corrective action (which may entail re-establishing instrumental operating conditions and recalibration).

10.2 Detector Background

Detector chamber background levels must be determined to provide for background subtraction in activity calculations and verification that the instrument is free of contamination. A clean, empty planchet is counted (for each detector in the counting system) for at least the same length of time that typical samples are expected to be counted.

10.2.1 Background Subtraction

For drinking water compliance samples, background subtraction measurements should be performed with each batch of samples, however a long weekly count as described in Section 10.2.2 is also acceptable. If desired, the background subtraction measurement can substitute as either the pre- or post-background check as described in Section 9.2.1.

NOTE: Other programs that do not analyze drinking water compliance samples may have alternate background subtraction counting frequencies, as appropriate.

10.2.2 Multiple Detector Systems

There are counting systems that have multiple single detectors and the batch is counted on several different detectors. For such systems, the laboratory may establish a control chart with a weekly long background count. On a daily basis, count a clean planchet before and after analyzing a drinking water compliance batch for a shorter time (at least ten minutes). Plot the short background measurements on the longer background control chart. If the short background measurements are in statistical control of the long background (i.e., within $\pm$ 3 standard deviations of the mean long background measurements), then the weekly long background count can be used for background subtraction.

10.3 Geometry Considerations

Initial calibration involves preparation of a mass-efficiency curve. There are two calibration options for Ra-228 determination as described in Section 10.4 – using Sr-89 as the calibration surrogate or using Ra-228 and calibrate relative to Ac-228. Either option is acceptable, however analysts must be cognizant of the short half-life of actinium-228 (6.15 hours) and the requirement to meet the regulatory detection limit. The geometry of the calibration sources prepared for the mass-efficiency curve needs to be the same as that of the prepared sample and QC planchets (i.e., prepare and mount calibration sources in the same manner as samples).

10.4 Calibration and Development of Mass-Efficiency Curve

The acceptable yttrium yield (as yttrium oxalate nonahydrate, $Y_2(C_2O_4)_3 \cdot 9H_2O$) is 70-110%. The target 100% yield is about 30.5 mg when 9 mg standardized yttrium carrier (Section 7.30) is used. Based on the recovery acceptance criterion, the relative yttrium oxalate mass range is approximately 21.4 mg (70%) to 33.6 mg (110%). Therefore, efficiency calibration sources should be prepared that bracket the mass range.

10.4.1 Sr-89 Calibrant

Standard Sr-89 can be used as a beta energy surrogate for calibration in place of Ac-228. Generate a strontium oxalate mass range that brackets the acceptable yttrium oxalate mass range.

10.4.1.1 Preparation of Sr-89 Efficiency Calibration Sources as Strontium Oxalate Monohydrate

Assuming 100% yield, 1.5 mL of 10 mg/mL strontium carrier will yield 33 mg strontium oxalate monohydrate. Prepare at least four centrifuge tubes that contain varying amounts of standardized strontium carrier (10 mg/ml, Section 7.26) that will bracket the mass range. To each tube, add approximately 1000 dpm Sr-89 standard and dilute with about 20 mL distilled/deionized water. Add 2 mL concentrated NH_4OH (Section 7.4), heat to nearly boiling then slowly add 5 mL saturated ammonium oxalate solution (Section 7.6) to each tube. Heat the tubes in a hot water bath for 15 minutes. Remove the tubes from the bath and allow to cool. Centrifuge and discard the supernates. Rinse each strontium oxalate precipitate with about 20 mL distilled/deionized water. Centrifuge and discard the supernate. Slurry each strontium oxalate precipitate with a few mLs distilled/deionized water and quantitatively transfer each precipitate to separate tared planchets. Dry under an infrared lamp or in a 105 ^{o}C $\pm$ 2 ^{o}C oven, cool in a desiccator and weigh to determine the mass of strontium oxalate recovered. Count as described in Section 10.5. Calculate efficiency standard yields as described in Section 12.1.5.

10.4.2 Ra-228 Calibrant (measured as Ac-228)

Standard Ra-228 is used as the calibrant to establish beta mass efficiencies over a range of precipitate weights as described in Section 10.4.2.1 below. After a 36-hour ingrowth of Ac-228, the Ac-228 is carried on yttrium oxalate. The final yield can be based on either yttrium oxalate or yttrium oxide; however, counting Ac-228 is performed using the yttrium oxalate precipitate. Therefore, prepare a set of at least four calibration sources that will bracket the minimum and maximum allowable masses for Ac-228 carried on yttrium oxalate based on a yield of 70-110% (21.4 mg to 33.6 mg yttrium oxalate nonahydrate).

10.4.2.1 Preparation of Ra-228 Calibration Standards

Pipet approximately 1500-2000 dpm Ra-228 standard into at least four separate 50-mL centrifuge tubes. Pipet variable volumes of 9 mg/mL standardized yttrium carrier (Section 7.30) covering the range of about 0.5 – 1.5 mL (to fully encompass the yield range) into the tubes. To each tube, add 5 mL 18 M

NaOH, stir well and digest the tubes in a hot water bath until yttrium hydroxide coagulates. Centrifuge and discard supernates. Note the time of the yttrium hydroxide precipitation – this marks the end of the Ac-228 ingrowth and beginning of Ac-228 decay. Move quickly from this point forward. Dissolve precipitate with 1 mL 1 M HNO_3 (Section 7.20). Put tubes in hot water bath for a few minutes to make sure samples are clear. Dilute the contents of each tube to a 5-mL volume with distilled/deionized water and add 2 ml 5% ammonium oxalate (Section 7.7) to each centrifuge tube and stir. Heat for just a few minutes to coagulate oxalate precipitate (excessive heating can cause dissolution of the precipitate back into solution). Centrifuge and discard the supernate. Slurry the yttrium oxalate precipitate with a small volume of distilled/deionized water and transfer to a tared stainless steel planchet. Dry under an infrared lamp or in a 105 °C ± 2 °C oven. Cool in a desiccator and weigh to determine the mass of yttrium oxalate recovered. Count as described in Section 10.5.

10.5 Counting

Count the prepared efficiency standards until at least 10,000 total counts greater than background (where the background should be less than 1-2% of the total counts above background) have been accumulated.

10.6 Generate Curve

Prepare the mass-efficiency curve and generate the best curve fit by plotting the efficiency of the radionuclide standard as calculated in Section 12.3 along the y-axis vs. the measured precipitate mass along the x-axis.

10.7 Annual Verification

Annual verification of efficiency calibration is required. Due to the half-lives associated with the calibrants, it is not appropriate to save the prepared calibration sources for reuse to verify the calibration. As a result, prepare new sources as described in either Section 10.4.1.1 or 10.4.2.1. For the calibration verification to be acceptable, the original measurements of each efficiency standard should lie within the range defined by the uncertainty of the new efficiency standards calculated at the 95% confidence level.

NOTE: Evaluate a beta check source standard after instrument repair and after gas bottle changes. If the check source indicates a change in instrument performance, verify with a recount. If the recount still indicates a problem, then corrective action is warranted. Re-establish instrument parameters and recalibrate.

11 Procedure

11.1 Citric Acid Addition

To a 1-L acid-preserved drinking water sample, add 5 mL 1 M citric acid (Section 7.12) and a few drops methyl orange indicator. The solution should be red.

11.2 Add Carriers

Add 10 mL lead carrier (150 mg, Section 7.15), 2 mL standardized strontium carrier (20 mg, Section 7.26), 2 mL standardized barium carrier (32 mg, Section 7.10) and 1 mL yttrium carrier (18 mg, Section 7.29). Stir well. Heat to a low boil and digest for 30 minutes.

NOTE: If barium-133 is used for yield determination, add the tracer to the barium carrier as described in Section 7.10.1.2.

11.3 Precipitate $PbSO_4$ and $BaSO_4$

Add concentrated NH_4OH (Section 7.4) until a definite yellow color is obtained (pH $\geq$ 4.4), then add a few drops in excess. Precipitate lead and barium sulfates by adding 9 M H_2SO_4 (Section 7.28) until the red color reappears, then add 0.25 mL excess. Add 5 mL $(NH_4)_2SO_4$ (1 g, Section 7.8). Stir frequently and maintain a sub-boiling temperature of about 90 °C for 30 minutes.

11.4 Isolate Precipitate

Allow precipitate to settle and cool slightly. Filter with suction through a metricel membrane filter (GA-6, 0.45 µm, or equivalent). Transfer any remaining precipitate in the container to the filter using a strong jet of distilled/deionized water. Place the filter in a glass beaker and add 10 mL 16 M HNO_3 (Section 7.18) to dissolve the filter. Heat gently until the filter completely dissolves. Transfer the precipitate to a centrifuge tube with a small amount of 16 M HNO_3. Centrifuge and discard the supernate. Wash the precipitate with about 15 mL 16 M HNO_3, centrifuge and discard the supernate. Wash the precipitate once more with 15 mL 16 M HNO_3, centrifuge and discard the supernate.

11.5 Dissolve Precipitate with Basic EDTA Solution

Dissolve the precipitate by adding 25 mL basic EDTA reagent (Section 7.13). Heat in a hot water bath and stir well. Add a few drops 10 M NaOH (Section 7.24) if precipitate does not readily dissolve.

11.6 Precipitate $BaSO_4$

Add 1 mL strontium-yttrium mixed carrier (Section 7.31) and stir thoroughly. Add a few drops of 10 M NaOH (Section 7.24) if any precipitate forms. Add 1 mL $(NH_4)_2SO_4$ (200 mg, Section 7.8) and stir thoroughly. Add 17.4 M CH_3COOH (Section 7.2) slowly until precipitation begins. If desired, add a few drops of bromocresol green indicator. Continue to add up to 2 mL additional acetic acid to ensure complete precipitation. Check the pH because this step is pH-dependent by either watching the bromocresol green indicator or using an appropriate pH paper strip. Acidification releases barium/radium from the EDTA complex, but if the pH drops below about 4.5, the lead that is bound within the EDTA complex will begin to be released. Digest in a hot water bath until the precipitate settles. Centrifuge and discard the supernate.

NOTE: If pH is monitored using the bromocresol green indicator, the appropriate endpoint is green. It is recommended that analysts become familiar with recognizing the appropriate color of a pH 4.5 solution by adjusting a solution of similar composition to pH 4.5 using a pH meter.

11.7 Isolate Precipitate

Add 20 mL basic EDTA reagent (Section 7.13), heat in a hot water bath and stir until precipitate dissolves. Repeat procedure described in Section 11.6. **Note the time of the final $BaSO_4$ precipitation; this is the beginning of Ac-228 ingrowth**.

11.8 Dissolve Precipitate, Add Carriers and Allow Ac-228 Ingrowth

Add 20 mL basic EDTA reagent (Section 7.13) to the precipitate, heat in a hot water bath and stir to dissolve the precipitate. Add 1.0 mL standardized yttrium carrier (9 mg, Section 7.30) and 1 mL lead carrier (1.5 mg, Section 7.16). If any precipitate forms, dissolve by adding a few drops of 10 M NaOH (Section 7.24). Cap the centrifuge tube and allow Ac-228 ingrowth for at least 36 hours.

11.9 Scavenge Ingrown ^{212}Pb

At the end of the ingrowth period, add 0.3 mL $(NH_4)_2S$ (Section 7.9) and stir well. Add 10 M NaOH (Section 7.24) dropwise with vigorous stirring until black lead sulfide precipitates, then add 10 drops

excess. Stir intermittently for about ten minutes. Centrifuge and decant the supernate (which contains barium, yttrium and Ac-228) into a clean centrifuge tube. Dispose of the PbS precipitate. To the supernate in the centrifuge tube, add 1 mL lead carrier (1.5 mg, Section 7.16), 0.1 mL $(NH_4)_2S$ (Section 7.9) and a few drops of 10 M NaOH (Section 7.24). Repeat lead sulfide precipitation as before. Centrifuge and filter the supernate through a Whatman #42 (or equivalent) filter paper into a clean centrifuge tube. Rinse the filter with a small amount of distilled/deionized water. Dispose of the PbS residue. *Proceed without delay to the final separation and count to minimize Ac-228 decay*.

11.10 Precipitate $Y(OH)_3$

Add 5 mL 18 M NaOH (Section 7.23) to the filtrate, stir well and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge, decant the supernate into a clean beaker or centrifuge tube, and save for barium yield determination and, if desired, radium-226 analysis. **Note the time of yttrium hydroxide precipitation; it marks the end of Ac-228 ingrowth and the beginning of Ac-228 decay.**

11.11 Purify Precipitate

Dissolve the precipitate in about 2 mL 6 M HNO_3 (Section 7.19). Heat and stir in a hot water bath about five minutes. Add 5 mL distilled/deionized water and reprecipitate yttrium hydroxide with 3 mL 10 M NaOH (Section 7.24). Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and add supernate to the beaker/centrifuge tube for barium yield determination (Section 11.10 above).

11.12 Precipitate $Y_2(C_2O_4)\cdot 9(H_2O)$

Dissolve yttrium hydroxide precipitate with 1 mL 1 M HNO_3 (Section 7.20). Heat in a hot water bath for a few minutes. Dilute to a 5-mL volume with distilled/deionized water. Add 2 mL 5% ammonium oxalate (Section 7.7). Heat in a hot water bath for a few minutes to coagulate the precipitate. Be careful in this step because prolonged heating can cause partial dissolution of the precipitated yttrium oxalate back into solution. Centrifuge and discard supernate.

NOTE: If yttrium yield is determined relative to yttrium oxalate (as opposed to optionally converting the yttrium oxalate to yttrium oxide), reproducibility and accuracy in the mass of the final oxalate precipitate depends upon carefully reproducing the acid and base amounts used in the procedural steps described in Sections 11.12 and 11.13. A pH of 1.7 – 1.9 in the solution from which yttrium oxalate is being precipitated is required in order to obtain a uniform 9-hydrate ($Y_2(C_2O_4)\cdot 9\ H_2O$) precipitate.

11.13 Purify Precipitate

Add 10 mL distilled/deionized water, 6 drops 1 M HNO_3 (Section 7.20) and 6 drops 5% ammonium oxalate (Section 7.7). Heat in a hot water bath for a few minutes. Centrifuge and discard supernate.

11.14 Prepare Planchet and Count

Preparation of the final precipitate for counting depends on the manner in which yield will be determined, either as the oxalate or the oxide:

11.14.1 Procedure based on determining yield as yttrium oxalate

Slurry the yttrium oxalate precipitate with a minimum of distilled/deionized water and transfer quantitatively to a tared stainless steel planchet. Dry under a heat lamp or in a 105 $^{o}C \pm 2\ ^{o}C$ oven until a constant weight is obtained. Count in a low-background gas flow proportional counter to determine beta activity. Determine yttrium recovery as described in Section 12.1.3.

11.14.2 Procedure based on determining yield as yttrium oxide

Place an ashless cellulose or glass fiber filter in a filter assembly and quantitatively transfer the yttrium oxalate precipitate to the filter using distilled/deionized water to ensure transfer is complete. Add a small volume of acetone to the precipitate to facilitate drying. Place the filter containing the precipitate in a gas flow proportional counter to determine beta activity of the Ac-228. After counting, transfer the filter to a tared crucible. Ignite at 800 °C for 1 hour in a muffle oven to convert the oxalate to the oxide. Cool completely and weigh the crucible. Determine the yttrium recovery as described in Section 12.1.4.

11.15 Barium Yield

Procedure followed is based on either gravimetric chemical yield of $BaSO_4$ or radiochemical yield of Ba-133 tracer:

11.15.1 Procedure based on gravimetric chemical yield determination

To the combined supernate collected in Sections 11.10 and 11.11, add 4 mL 16 M HNO_3 (Section 7.18) and 2 mL ammonium sulfate (400 mg, Section 7.8), stirring well after each addition. Add 17.4 M acetic acid (Section 7.2) slowly until barium sulfate precipitates, then add 2 mL in excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate. Add 20 mL basic EDTA reagent (Section 7.13), heat in hot water bath and stir until precipitate dissolves. Add a few drops of 10 M NaOH (Section 7.24) if needed to ensure dissolution of the precipitate. Add 1 mL ammonium sulfate (400 mg, Section 7.8) and stir well. Add 17.4 N acetic acid until barium sulfate precipitates, then add 2 mL in excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate. Wash precipitate with about 10 mL distilled/deionized water. Centrifuge and discard the supernate. Slurry the precipitate in a small volume of distilled/deionized water and transfer quantitatively to a tared stainless steel planchet. Dry under a heat lamp or in a 105 °C ± 2 °C oven until a constant weight is obtained. Determine barium recovery as described in Section 12.1.1.

11.15.2 Procedure based on radiochemical yield using Ba-133 tracer

Precipitate barium sulfate as described in Section 11.15.1 above. Instead of transferring precipitate to a planchet, place a 0.45 um membrane filter in a vacuum filter assembly, prewet with distilled/deionized water and start vacuum. Transfer the precipitate to the filter using distilled/deionized water to ensure transfer is quantitative. Add a small volume of ethanol to the precipitate and maintain suction to fully dry the precipitate. Place the filter containing the precipitate in a planchet and count in a gamma spectrometer detector. Determine barium recovery as described in Section 12.1.2.

12 Data Analysis and Calculations

12.1 Yield Calculations

12.1.1 Barium Chemical Yield (Precipitate)

The chemical yield for the barium carrier is calculated as follows:

$$Theoretical\ Yield, Std.\ Ba^{2+} in\ mg/mL = \frac{(mg\ BaSO_4)(0.5884)}{2.0\ mL}$$

Theoretical yield of barium sulfate must be determined based on the standardized concentration of the barium carrier (Section 7.10.1.1). If the standardized carrier concentration is 16 mg/mL, then the theoretical 100% yield of barium sulfate would be 54.38 mg.
The fractional yield would thus be:

$$Y = \frac{(m_s - m_p)}{54.38}$$

Where

m_s= mass of planchet with the dried barium sulfate precipitate, mg

m_p= mass of planchet, mg

54.38 = mass of barium sulfate precipitate if all the added barium carrier (32 mg) is recovered. If the standardized concentration of the barium carrier differs from the 16 mg/mL prepared in Section 7.10, adjust the theoretical Ba^{2+} concentration accordingly.

12.1.2 Barium Radiochemical Yield (Ba-133 Tracer)

Alternately to the chemical yield calculated in Section 12.1.1, radiochemical yield based on addition of barium-133 as a tracer is calculated using the following equation:

$$Y = \frac{A_m}{A_s}$$

Where

A_m= Activity of Ba-133 measured in the sample, pCi/mL

A_s= Activity of standardized Ba-133 solution, pCi/mL

12.1.3 Yttrium Yield (as Yttrium Oxalate Nonahydrate)

The yield for yttrium oxalate is calculated as follows:

$$Theoretical\ Yield\ for\ Std.\ Y^{3+}, in\ mg/mL = \frac{(mg\ Y_2(C_2O_4)_3 \cdot 9H_2O)(0.29948)}{1.0\ mL}$$

If the standardized yttrium carrier concentration is 9 mg/mL, then the theoretical 100% yield of yttrium oxalate nonahydrate would be 30.56 mg.

The fractional yield would be:

$$Y = \frac{(m_s - m_p)}{30.56}$$

Where

m_s= mass of planchet with the dried yttrium oxalate nonahydrate precipitate, mg

m_p= mass of planchet, mg

30.56 = mass of yttrium oxalate nonahydrate precipitate if all the added yttrium carrier (9 mg) is recovered. If the standardized concentration of the yttrium carrier differs from the 9 mg/mL prepared in Section 7.30, adjust the theoretical Y^{3+} concentration accordingly.

12.1.4 Yttrium Yield (as Yttrium Oxide)

The yield for yttrium oxide is calculated as follows:

$$Theoretical\ Yield\ for\ Std.\ Y^{3+}, in\ mg/mL = \frac{(mg\ Y_2O_3)(0.78743)}{1.0\ mL}$$

If the standardized yttrium carrier concentration is 9 mg/mL, then the theoretical 100% yield of yttrium oxide would be 11. 43 mg.

The fractional yield would be:

$$Y = \frac{(m_s - m_p)}{11.43}$$

Where

m_s= mass of planchet with the dried yttrium oxide precipitate, mg

m_p= mass of planchet, mg

11.43 = mass of yttrium oxide precipitate if all the added yttrium carrier (9 mg) is recovered. If the standardized concentration of the yttrium carrier differs from the 9 mg/mL prepared in Section 7.30, adjust the theoretical Y^{3+} concentration accordingly

12.1.5 Strontium Oxalate Monohydrate (Efficiency Calibration Yields)

Calibration with Sr-89 and determination of detector efficiency entails determination of strontium oxalate monohydrate yield. For any given mass of strontium carrier used in preparing efficiency standards (i.e., 1.0 mL of 10 mg/mL strontium carrier results in 10 mg Sr^{2+}), multiply by 2.211 in order to determine the theoretical yield of strontium oxalate monohydrate precipitate. Assess fractional yield for each standard and calculate efficiency as described in Section 12.3.1.

12.2 Count Rate

The net count rate, R_x, for any single count (sample, background, standard) is generically calculated as

$$R_x = \frac{N_x}{t_s} - \frac{B_x}{t_B}$$

where

R_x = Net count rate in counts per minute

N_x = Number of counts observed over the sample counting period

t_s = Duration of the sample counting period (i.e., live time) in minutes

B_x = Number of counts observed over the background counting period

t_B = Duration of the background counting period (i.e., live time) in minutes

The standard uncertainty ("one-sigma") of R_x is then given by

$$u(R_x) = \sqrt{\frac{N_x}{t_s^2} + \frac{B_x}{t_B^2}}$$

The square of the standard uncertainty is denoted by $u^2(R_x)$.

$$u^2(R_x) = \frac{N_x}{t_s^2} + \frac{B_x}{t_B^2}$$

12.3 Efficiency

The beta counting mass-efficiency (self-absorption) calibration is established as described in Section 10. Calculate efficiencies as based on calibrant as follows:

12.3.1 Sr-89

$$\varepsilon_{\beta m} = \left(\frac{R_\beta}{A_{\mathrm{Std}(\beta)}}\right)\left(\frac{1}{Y}\right)$$

where

$\varepsilon_{\beta m}$ = Beta Efficiency determined for mass m

R_β = Net count rate of the Sr-89 standard, counts per minute

$A_{\mathrm{Std}(\beta)}$ = Activity of the Sr-89 standard, disintegrations per minute, at midpoint of the count

Y = Strontium oxalate yield (as calculated in Section 12.1.5)

λ = Sr-89 decay constant, (0.0137 day^{-1})

12.3.2 Ra-228

$$\varepsilon_{\beta m} = \left(\frac{R_\beta}{A_{\mathrm{Std}(\beta)}}\right)\left(\frac{1}{Y_{Ba} \times Y_Y}\right)\left[\frac{1}{1 - e^{-\lambda_1(t_2 - t_1)}}\right]\left[\frac{1}{e^{-\lambda_1(t_3 - t_2)}}\right]\left[\frac{\lambda_1 t_s}{1 - e^{-\lambda_1 t_s}}\right]$$

where
$\varepsilon_{\beta m}$ = Beta Efficiency determined for mass m
R_β = Net count rate, counts per minute
$A_{\mathrm{Std}(\beta)}$ = Activity of the Ra-228 standard, disintegrations per minute
Y_{Ba} = Barium Yield (as calculated in Section 12.1)
Y_Y = Yttrium Yield (as calculated in Section 12.1)
λ_1 = Ac-228 decay constant, (0.1127 hr^{-1})
t_1 = Beginning of Ac-228 ingrowth
t_2 = Beginning of Ac-228 decay
t_3 = Beginning of sample count
t_s = Sample count time

12.4 Radium-228 Activity and Uncertainty

Calculate the radium-228 activity concentration for each sample.

$$^{228}Ra\ Activity,\ pCi/L = \frac{R_\beta}{\varepsilon_\beta \times V \times 2.22 \times Y_{Ba} \times Y_Y} \times \left[\frac{1}{1 - e^{-\lambda_1(t_2 - t_1)}}\right]\left[\frac{1}{e^{-\lambda_1(t_3 - t_2)}}\right]\left[\frac{\lambda_1 t_s}{1 - e^{-\lambda_1 t_s}}\right]\left[\frac{1}{e^{-\lambda_2(t_2 - t_0)}}\right]$$

where
R_β = Net beta count rate, counts per minute
ε_β = Beta efficiency, cpm/dpm
V = Volume of sample aliquot, in liters
2.22 = Conversion factor from dpm to pCi
Y_{Ba} = Barium Yield (as calculated in Section 12.1)
Y_Y = Yttrium Yield (as calculated in Section 12.1)
λ_1 = Ac-228 decay constant, (0.1127 hr^{-1})
λ_2 = Ra-228 decay constant, (0.1205 yr^{-1})
t_1 = Beginning of Ac-228 ingrowth
t_2 = Beginning of Ac-228 decay
t_3 = Beginning of sample count
t_s = Sample count time
t_0 = Time when sample was collected

The radium standard counting uncertainty and expanded counting uncertainty (95 % confidence) are calculated as:

$$u(c_\beta) = \frac{\sqrt{u^2(R_\beta)}}{\varepsilon_\beta \times V \times 2.22 \times Y_{Ba} \times Y_Y} \times \left[\frac{1}{1 - e^{-\lambda_1(t_2 - t_1)}}\right]\left[\frac{1}{e^{-\lambda_1(t_3 - t_2)}}\right]\left[\frac{\lambda_1 t_s}{1 - e^{-\lambda_1 t_s}}\right]\left[\frac{1}{e^{-\lambda_2(t_2 - t_0)}}\right]$$

$$U_{95\%} = 1.96 \times u(c_\beta)$$

where
$u(c_\beta)$ = Radium standard counting uncertainty ("one-sigma") in pCi/L
$U_{95\%}$ = Expanded counting uncertainty (95 % confidence) in pCi/L
1.96 = Coverage factor for 95 % level of confidence
R_β = Net beta count rate, counts per minute
ε_β = Beta efficiency, cpm/dpm
V = Volume of sample aliquot, in liters

2.22 = Conversion factor from dpm to pCi
Y_{Ba} = Barium Yield (as calculated in Section 12.1)
Y_Y = Yttrium Yield (as calculated in Section 12.1)
λ_1 = Ac-228 decay constant, (0.1127 hr^{-1})
λ_2 = Ra-228 decay constant, (0.1205 yr^{-1})
t_1 = Beginning of Ac-228 ingrowth
t_2 = Beginning of Ac-228 decay
t_3 = Beginning of sample count
t_s = Sample count time
t_0 = Time when sample was collected

12.5 Safe Drinking Water Act Detection Limit

The detection limit (DL) requirement for drinking water compliance samples is defined in Section 3.3 and determination of method detection capability is described in Section 9.1.1.3. From the definition, the equation in Section 12.5.1 can be derived (see reference 7 in Section 14).

12.5.1 DL Equation

The single sample drinking water detection limit is calculated as:

$$DL = \frac{\frac{1.96^2}{2t_s} \times \left[1 + \sqrt{1 + \frac{4t_s^2}{1.96^2} \times \frac{B}{t_B} \times \left(\frac{1}{t_s} + \frac{1}{t_B}\right)}\right]}{\varepsilon_\beta \times V \times 2.22 \times Y_{Ba} \times Y_Y} \times \left[\frac{1}{1 - e^{-\lambda_1(t_2 - t_1)}}\right]\left[\frac{1}{e^{-\lambda_1(t_3 - t_2)}}\right]\left[\frac{\lambda_1 t_s}{1 - e^{-\lambda_1 t_s}}\right]\left[\frac{1}{e^{-\lambda_2(t_2 - t_0)}}\right]$$

where
t_s = Sample count time
t_B = Background count time
B = Number of background counts
ε_β = Beta efficiency, cpm/dpm
V = Volume of sample aliquot, in liters
2.22 = conversion factor from dpm to pCi
Y_{Ba} = Barium Yield (as calculated in Section 12.1)
Y_Y = Yttrium Yield (as calculated in Section 12.1)
λ_1 = Ac-228 decay constant, (0.1127 hr^{-1})
λ_2 = Ra-228 decay constant, (0.1205 yr^{-1})
t_1 = Beginning of Ac-228 ingrowth
t_2 = Beginning of Ac-228 decay
t_3 = Beginning of sample count
t_s = Sample count time
t_0 = Time when sample was collected

12.5.2 DL Study

The DL study described in Section 9.1.1.3 consists of seven replicate laboratory fortified blanks that are prepared and counted as specified in the method. The replicate results are assessed using a chi-square statistic to test whether the relative standard deviation of the results exceeds the maximum value allowed at the required DL.
Calculate the mean of the measured values and the chi-square statistic as follows:

$$\bar{X}_i = \frac{1}{n}\sum_{j=1}^{n} X_{ij}$$

And

$$\chi_i^2 = \frac{1.96^2}{\mu^2}\sum_{j=1}^{n}\left(X_{ij} - \bar{X}_i\right)^2$$

Where

n = Number of replicate measurements

μ = Activity fortified in sample replicates

To be deemed acceptable, the value of χ^2 should be less than or equal to the 99th percentile of the χ^2 distribution with (n-1) degrees of freedom.

12.6 Relative Percent Difference Calculation

As described in Section 9.2.7, relative percent difference (RPD) is used to evaluate precision of duplicate measurements. The RPD is calculated as

$$RPD = \frac{|A_s - A_{dup}|}{(A_s + A_{dup})/2} \times 100\ \%$$

where

A_s = Net activity of the first aliquot of sample

A_{dup} = Net activity of the measurement obtained from a second aliquot of the same sample

If a duplicate sample measurement has an activity < 5x the detection limit and the calculated RPD > 20%, calculate the normalized absolute difference (NAD). The NAD of the two measurements made from the same sample assesses whether they are within 2 standard deviations of their aggregate measurement uncertainty of each other. Calculate the NAD as

$$NAD = \frac{|A_s - A_{dup}|}{\sqrt{u^2(A_s) + u^2(A_{dup})}}$$

where

A_s = Net activity of the first aliquot of sample

A_{dup} = Net activity of the measurement obtained from a second aliquot of the same sample

$u^2(A_s)$ = Square of the standard counting uncertainty ("one-sigma") associated with A_s

$u^2(A_{dup})$ = Square of the standard counting uncertainty ("one-sigma") associated with A_{dup}

If the NAD is less than or equal to 2, then the two measurements are within 2 standard deviations of each other and therefore acceptable. If, however, the NAD exceeds 2, it is unacceptable since it means there is > 2 standard deviations of difference between the two measurements drawn from the same sample. Recount the sample and duplicate. If RPD/NAD evaluation still fails, a new sample and duplicate should be prepared.

13 Pollution Prevention

The procedures described in this method generate relatively small amount of waste since only small amounts of reagents are used. The matrices of concern are finished drinking water or source water. Laboratory waste practices must be conducted consistent with the laboratory's radioactive materials license and all applicable rules and regulations, and that laboratories protect the air, water, and land by

minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

14 References

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3. *Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)*, NTIS PB2004-105421, July 2004.
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6. Sill, C. W., Determination of Radium-226 in Ores, Nuclear Wastes and Environmental Samples by High-Resolution Alpha Spectrometry, Nuclear and Chemical Waste Management, 7, 239-256 (1987).
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