Designation: D7283 – 17

Standard Test Method for Alpha and Beta Activity in Water By Liquid Scintillation Counting[1]

This standard is issued under the fixed designation D7283; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of gross alpha- and beta- activity concentrations in a homogeneous water sample. It is applicable to alpha emitters with activity concentration levels above 0.11 Bq/L (3 pCi/L) and beta emitters with activity concentration levels above 0.15 Bq/L (4 pCi/L). This test method is not applicable to samples containing radionuclides that are volatile under conditions of the analysis.

1.2 This test method may also be used for the direct measurement of gross alpha- and beta- activity concentrations in homogeneous water samples with alpha emitter activity concentration levels above 1.8 Bq/L (50 pCi/L) and beta emitter activity concentration levels above 3.7 Bq/L (100 pCi/L).

1.3 This test method was tested using single-operator tests.[2,3] A collaborative study following the U.S. EPA "Protocol for the Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water" was performed. The results of this study are on file at ASTM Headquarters.[4]

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to pCi/L that are provided for information only and are not considered standard. An exception is noted in Section 14.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[5]

D1129 Terminology Relating to Water
D1125 Test Methods for Electrical Conductivity and Resistivity of Water
D1193 Specification for Reagent Water
D1890 Test Method for Beta Particle Radioactivity of Water
D1943 Test Method for Alpha Particle Radioactivity of Water
D3370 Practices for Sampling Water from Closed Conduits
D3648 Practices for the Measurement of Radioactivity
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4448 Guide for Sampling Ground-Water Monitoring Wells
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6001 Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization
D7902 Terminology for Radiochemical Analyses
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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[2] Wong, C. T., Soliman, V. M., and Perera, S. K., *Journal of Radioanalytical and Nuclear Chemistry*, Vol 264, No. 2, 2005, pp. 357–363.

[3] Ruberu, S.R., Liu, Y.G., and Perera, S.K., *Health Physics*, Vol 95, No. 4, October 2008, pp. 397–406.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1195. Contact ASTM Customer Service at service@astm.org.

[5] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Standards and Publications:*

EPA 900.0 Gross Alpha and Gross Beta Radioactivity in Drinking Water, from *Prescribed Procedures for Measurement of Radioactivity in Drinking Water* (EPA-600/4-80-032)[6]

Standard Methods 7110C Coprecipitation Method for Gross Alpha Radioactivity in Drinking Water[7]

Standard Methods 8010E Table 8010: Recommended Composition for Reconstituted Fresh Water[7]

ISO 9696 Water Quality—Measurement of Gross Alpha Activity in Non-saline Water—Thick Source Method[8]

ISO 11704:2010 Water Quality—Measurement of Gross Alpha and Beta Activity Concentration in non-saline water – Liquid Scintillation Counting Method[8]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies D1129 or D7902. For terms not defined in this test method or in Terminology D1129, reference may be made to other published glossaries.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *alpha-to-beta spillover, n—in the measurement of radioactivity*, for a given emitting source, that fraction of alpha particles that are misclassified as beta particles by the counter.

3.2.2 *alpha particle detection efficiency, n—in the measurement of radioactivity*, for a given emitting source, that fraction of alpha particles that are identified as alpha particles by the counter.

3.2.3 *beta-to-alpha spillover, n—in the measurement of radioactivity*, for a given emitting source, that fraction of beta particles that are misclassified as alpha particles by the counter.

3.2.4 *beta energy, maximum, n*—the maximum energy of the beta particle energy spectrum produced during beta decay of a given radionuclide.

3.2.4.1 *Discussion*—Since a given beta emitter may decay to several different nuclear energy levels of the progeny, more than one maximum energy may be listed for a given radionuclide.

3.2.5 *beta particle detection efficiency, n—in the measurement of radioactivity*, for a given emitting source, that fraction of beta particles that are identified as beta particles by the counter.

3.2.6 *detector background, n—in the measurement of radioactivity*, the counting rate resulting from factors other than the radioactivity of the sample and reagents used.

3.2.6.1 *Discussion*—Detector background varies with the location, shielding of the detector, and the electronics; such background includes cosmic rays, contaminating radioactivity, and electronic noise.

3.2.7 *figure of merit, n*—a numerical quantity based on one or more characteristics of a system or device, representing a measure of efficiency or effectiveness; figure of merit is generally calculated as the square of the efficiency divided by the background.

3.2.8 *gross alpha, n*—in the measurement of radioactivity, a semi-quantitative estimate of the combined activity of alpha-emitting radionuclides in a test sample.

3.2.9 *gross beta, n*—in the measurement of radioactivity, a semi-quantitative estimate of the combined activity of beta-emitting radionuclides in a test sample.

3.2.10 *homogeneous water sample, n*—water in which the alpha and beta activity is uniformly dispersed throughout the volume of water sample and remains so until the measurement is completed or until the sample is evaporated or precipitating reagents are added to the sample.

3.2.11 *reagent background, n—in the measurement of radioactivity of water samples*, the counting rate observed when a sample is replaced by mock sample salts or by reagent chemicals used for chemical separations that contain no analyte.

3.2.11.1 *Discussion*—Reagent background varies with the reagent chemicals and analytical methods used and may vary with reagents from different manufacturers and from different processing lots.

4. Summary of Test Method

4.1 The test sample is reduced by evaporation, transferred to a scintillation vial and mixed with a suitable liquid scintillation cocktail. Gross alpha- and beta- activity concentrations are measured simultaneously by liquid scintillation using alpha/beta discrimination. By optimizing the alpha/beta discriminator, a high efficiency of alpha- and beta- particle detection can be achieved with acceptable misclassification of beta particles into the alpha multi-channel analyzer (MCA) and alpha particles into the beta MCA. The alpha- and beta- particle efficiency and spillover calibrations of the liquid scintillation system are determined by using known activities of established reference nuclides in test sources having cocktail-solvent ratios comparable to that of the test samples. Some commonly employed reference standards include ^{241}Am, ^{239}Pu, ^{230}Th, natural isotopic abundance uranium (^{234}U, ^{235}U, and ^{238}U), for gross alpha, and ^{90}Sr/^{90}Y, and ^{137}Cs/^{137m}Ba for gross beta. Results are reported in activity units equivalent along with the reference radionuclide (for example, Bq/L gross alpha equiv. ^{241}Am).

4.2 If the measurement quality objectives (MQOs) do not require a low detection limit, an aliquant of the sample may be mixed directly with a suitable liquid scintillation cocktail for analysis.

5. Significance and Use

5.1 This test method is intended for the measurement of gross alpha- and beta-activity concentrations in the analyses of

[6] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[7] Available from American Water Works Association (AWWA), 6666 W. Quincy Ave., Denver, CO 80235, http://www.awwa.org.

[8] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

environmental and drinking waters. For samples submitted to satisfy regulatory or permit requirements, the submitter should assure that this or any other method used is acceptable to the regulator or permit issuer.

5.2 This test method is also applicable to the direct analysis of gross alpha- and beta-activity concentrations in water when low detection limits are not required. Direct analysis provides a rapid method for determination of gross alpha- and beta-activity concentrations when low detection limits are not required.

5.3 This test method is not capable of discriminating among alpha emitting radionuclides or among beta emitting radionuclides. Those intending to identify and quantify specific radionuclides should use test methods specific to the radionuclides of interest.

5.4 This test method may not be cited as a method for the determination of gross alpha- or beta-activity concentrations in a solid/soil matrix or the acid digestate of the same. The use of this test method for such applications brings the potential for serious bias and incomparability of results dependent on the matrix constituents, manner of sample preparation or treatment, or both.

6. Interferences

6.1 The counting efficiencies and spillover for both the alpha and beta components are dependent on the energy of the alpha- or beta-emitter chosen to determine the calibration coefficient. Biases may occur if the energies of the alpha- or beta-particle emitting nuclides in the test sample differs significantly from those used to determine the respective counting efficiencies. Best results are obtained when the radionuclide composition of the sample is known and the calibration radionuclide is selected to match as closely as possible the energy of the sample radionuclide.

6.2 The use of $^{137}Cs/^{137m}Ba$ as a calibration standard for samples containing radionuclides other than ^{137}Cs may introduce a low bias in the analytical results unless there is a correction for conversion electron emissions. The conversion electrons from the ^{137m}Ba progeny are detected by liquid scintillation yielding greater than 100 % detection efficiency for the $^{137}Cs/^{137m}Ba$ calibration standard.

6.3 When using uranium as a calibration standard the isotopic abundance of each of the isotopes (^{234}U, ^{235}U, and ^{238}U) must be known to accurately determine the standard activity concentration. Many uranium standards used for mass measurements are depleted uranium. Natural isotopic abundance uranium and depleted uranium standards contain short-lived decay progeny (^{234}Th, ^{234m}Pa) which interfere with the spillover calibration unless they are removed immediately prior to calibration.

6.4 Radon is a noble gas, and therefore easily emanates from most matrices. If the radon progeny of the uranium (^{222}Rn), thorium (^{220}Rn), and actinium (^{219}Rn) series emanate from the sample test source prior to counting, radioactive equilibrium is disrupted. EPA 900.0 recognizes this disruption by suggesting a delay of 72 h before the prepared sample is counted for gross alpha. Other published methods such as Standard Methods 7110C provide for a shorter delay of 3 h. Thus the activity of samples containing ^{226}Ra will increase significantly with time during the first several weeks after preparation. This delay will result in overestimation of the activity of samples relative to their true ^{226}Ra concentration. This test method advises that any such delay period used by the laboratory be based on the MQOs inherent in the intended data use (see 11.7).

6.5 Radionuclides may be present in the sample in disequilibrium with their parent radionuclides. Many factors, including differential solubility of radionuclides from the matrix in which the parent radionuclide occurs can cause this disequilibrium. Where these radionuclides have a half-life on the order of a few days or shorter, the time elapsed between sampling and the beginning of sample counting will tend to bias the final result low. In those cases, the MQOs inherent in the intended data may dictate the maximum time between sample collection and the beginning of sample counting. The laboratory should be aware of such requirements and be prepared to comply with them.

6.6 Radionuclides incorporated in volatile compounds are lost during the conduct of this test method. These include tritium in HTO or ^{14}C in the carbon dioxide formed during the addition of acid. The pertechnetate ion ($^{99}TcO_4^{2-}$) is an example of a radionuclide which may be lost through semi-volatility. The MQOs should address the potential loss of such radionuclides and provide direction for their quantification by specific methods.

6.7 When counting gross alpha- and beta-activity by a liquid scintillation counter using alpha/beta discrimination, some pulses resulting from alpha particles are misclassified as beta particles and some pulses resulting from beta particles are misclassified as alpha particles. The “spillover” characteristics are determined during the calibration of the specific instrument being used.

6.8 Quenching of the photon output in the liquid scintillation cocktail reduces detection efficiency and introduces additional uncertainty in spillover corrections. Quenching is caused by molecular species in the sample and cocktail mixture that reduce the intermolecular transfer of energy or absorb emitted visible and UV photons prior to detection. This test method describes the use of an external standard source to compensate for the effects of quenching.

6.9 The presence of solid particles in the scintillation cocktail may lead to erroneous results. This test method requires complete dissolution of the sample prior to addition of the scintillation cocktail.

6.10 The sample aliquant/scintillation cocktail mixture ratio should be within the cocktail manufacturer’s recommendations to insure a homogeneous mixture. If the sample aliquant/scintillation cocktail mixture forms two phases, repeat the analysis with a different sample aliquant/scintillation cocktail mixture/ratio.

6.11 The exterior of the vials must be free of dirt, markings, and fingerprints.

6.12 'Dark adapting' of scintillator solutions is dependent upon the fluor used in the scintillation cocktail, the instrument, and the lighting conditions of the count room. Evaluation of these parameters for the adaptation to the 'dark' conditions is necessary for counting optimization.

6.13 Samples and standards should be counted with the same instrument operating parameters including temperature. For refrigerated instruments, time should be allowed for the samples to cool to the operating temperature of the instrument. Be aware of the potential for phase separation when cooling prepared samples.

7. Apparatus

7.1 *Liquid scintillation vials, approximately 20 mL,* of low-potassium glass are recommended.

7.2 *Hot plate,* heating block, drying oven or other appropriate device to evaporate the samples.

7.3 *Liquid scintillation spectrometry system (Liquid Scintillation Counter, LSC),* coincidence-type with alpha/beta discrimination. A guard detector or other background reduction electronics or software may be incorporated to reduce the instrument background.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[9] Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without increasing the background of the measurement. Some reagents, even those of high purity, may contain naturally-occurring radionuclides, such as isotopes of uranium, radium, actinium, thorium, rare earths and potassium compounds and/or artificially produced radionuclides. Consequently, when such reagents are used in the analysis of low-radioactivity samples, the activity of the reagents shall be determined under analytical conditions that are identical to those used for the sample. The activity contributed by the reagents may be considered to be a component of the background and supplied as a correction when calculating the test sample result. This increased background reduces the sensitivity of the measurement.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type III.

8.3 *Alpha-Emitting Radioactive Standard Solution (~2000 Bq/mL in 1M HNO_3)*—traceable to a national standards laboratory (such as the National Institute of Standards and Technology, NIST, in the United States; or the National Physics Laboratory, NPL, in the United Kingdom). For gross alpha calibration the following radionuclides have found general usage: ^{241}Am, ^{239}Pu, ^{230}Th, and natural isotopic abundance uranium (^{234}U, ^{235}U, and ^{238}U).

8.4 *Beta-Emitting Radioactive Standard Solution (~2000 Bq/mL in 1M HNO_3)*—traceable to a national standards laboratory (such as NIST or NPL). For gross beta calibration the following radionuclides have found general usage: ^{90}Sr/^{90}Y and ^{137}Cs/^{137m}Ba.

8.5 *Liquid scintillation cocktail*—Commercially prepared LSC cocktail or equivalent.

8.6 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid.

8.7 *Nitric Acid (2M)*—Mix 128 mL 16*M* HNO_3 (concentrated) with water and dilute to 1 L.

8.8 *Nitric Acid (0.1M)*—Mix 6.4 mL 16*M* HNO_3 (concentrated) with water and dilute to 1 L.

8.9 *Nitromethane (sp gr 1.14)*—Other quenching agents may also be used. Adjust the amount of quenching agent added to the calibration standards to produce a calibration curve covering the typical range of quench found in samples.

9. Sampling

9.1 A representative sample must be collected from the water source and should be large enough so that adequate aliquants can be taken to obtain the required sensitivity. See Practices D3370 and Guides D4448 and D6001 for guidance on sampling.

9.2 Although the container material does not impact the analyte stability, the container choice should generally be plastic instead of glass to minimize losses due to breakage during transportation and handling.

9.3 Unless contrary to the MQOs (for example, radiocarbon or radioiodine analysis is to be performed on the same sample or dissolved gross alpha and beta activity concentrations are sought), it is recommended that the sample be preserved at the time of collection by adding enough 2*M* nitric acid to the sample to bring it to pH 2 or less (5 to 10 mL of 2*M* nitric per litre of sample is usually sufficient). Tightly cap the container and shake well to mix. Confirm the pH with a pH-indicating strip or paper.

9.4 If the dissolved gross alpha and beta activity concentrations are sought, the sample must be passed through a 0.45 micron filter prior to acid preservation of the sample. Drinking water samples are not normally filtered prior to analysis unless the turbidity is >5 Nephlelometric Turbidity Units (NTUs). The use of suction or pressure will speed the filtration process.

9.5 If samples are collected without preservation, they should be delivered to the laboratory as quickly as practicable, but no later than 5 days following collection. Upon receipt at the lab, the unpreserved samples may be filtered, as required, and then acid preserved. Once preserved at the lab, the samples should be held for a minimum of 16 h prior to initiation of sample preparation.

9.6 Sample analysis should be completed within 180 days from the time of sample collection. Samples may be held for up to one year to allow for compositing of quarterly samples.

[9] *Reagent Chemicals, American Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

10. Calibration and Standardization

10.1 For gross alpha and gross beta measurement, the scintillation counter must be calibrated to determine the alpha particle detection efficiency in the alpha region of interest (ROI), the alpha particle detection efficiency in the beta ROI, the beta particle detection efficiency in the beta ROI, and the beta particle detection efficiency in the alpha ROI. For gross alpha calibration the following radionuclides have found general usage: ^{241}Am, ^{239}Pu, ^{230}Th, and natural isotopic abundance uranium (^{234}U, ^{235}U, and ^{238}U). For gross beta calibration the following radionuclides have found general usage: ^{90}Sr/ ^{90}Y and ^{137}Cs/^{137m}Ba. The laboratory must ensure that the client is aware of the radionuclides used for the alpha and beta calibrations because the intercomparability of results from other laboratories will be impacted if they used different calibration nuclides.

NOTE 1—When using uranium as a calibration standard the isotopic abundance of each of the isotopes (^{234}U, ^{235}U, and ^{238}U) must be known to accurately determine the standard activity concentration. Many uranium standards used for mass measurements are depleted uranium. Natural isotopic abundance uranium and depleted uranium standards contain short-lived decay progeny (^{234}Th, ^{234m}Pa) which interfere with the spillover calibration unless they are removed immediately prior to calibration.

10.2 Place the instrument into operation according to the manufacturer's instructions. The instrument should be set to acquire counts in the alpha/beta counting mode with discrimination of alpha and beta events.

10.3 The regions of interest (ROIs) for alpha and beta counting in the alpha and beta MCAs should be set to optimize the figure of merit (E^2/B) while ensuring that all radionuclides of interest are included in each respective region. For an unquenched sample an ROI from 400 keV to 700 keV would include most alpha emitting radionuclides of concern. Based on the quench characteristics of the samples, the ROI should be adjusted to include the radionuclides of concern, while minimizing the background count rate. For the sample to cocktail mixture used in this test method (5 mL sample plus 15 mL of scintillation cocktail) an ROI from 50 keV to 400 keV generally includes the alpha-emitting radionuclides of concern. For beta-emitting radionuclides an ROI from 2 to 2000 keV is generally used. A low energy window setting of 2 keV is generally sufficient to eliminate luminescence and low energy noise.

10.4 The optimum setting for discrimination between alpha- and beta- particles is the setting where there is equal and minimum spill of alpha pulses into the beta MCA and beta pulses into the alpha MCA. This occurs at the crossover point of the alpha-to-beta spillover and beta-to-alpha spillover curves. However, when only the alpha emitter is of interest, a discriminator setting greater than the instrument determined cross-over point may be used, to minimize misclassification of beta events into the alpha MCA at the expense of reduced alpha detection efficiency. Similarly when only the beta emitter is of interest, a discriminator setting below the optimum may be used. This minimizes the misclassification of alpha events into the beta MCA at the expense of reduced beta detection efficiency.

10.4.1 Prepare a scintillation vial containing approximately 200 Bq of an alpha-emitting radionuclide such as ^{241}Am, ^{239}Pu, or ^{230}Th in 5 mL of 0.1*M* HNO_3 plus 15 mL of scintillation cocktail.

10.4.2 Prepare a second scintillation vial containing approximately 200 Bq of a beta- emitting radionuclide, such as ^{90}Sr/^{90}Y or ^{137}Cs/^{137m}Ba in 5 mL of 0.1*M* HNO_3 plus 15 mL of scintillation cocktail.

10.4.3 Count the vials for an amount of time required to obtain a relative standard uncertainty of 1 % or less in the count (generally at least 10 000 net counts) at varying discriminator settings. Plot the alpha-to-beta spillover and beta-to-alpha spillover versus discriminator setting. The point at which the two curves intersect is the crossover point.

10.5 For each instrument the alpha particle detection efficiency in the alpha ROI, the alpha particle detection efficiency in the beta ROI, the beta particle detection efficiency in the beta ROI and the beta particle detection efficiency in the alpha ROI, at varying levels of quench are determined using the optimized ROIs and discriminator setting. The alpha and beta radionuclide standards used should be traceable to a national standards laboratory (such as NIST or NPL).

10.5.1 For the alpha particle detection efficiency in the alpha ROI and the alpha particle detection efficiency in the beta ROI, a minimum of five alpha calibration standards are prepared containing varying amounts of quenching agent. For each calibration standard, aliquot 5.00 mL of 0.1M nitric acid into a scintillation vial. Spike each of the vials with approximately 200 Bq of the alpha calibration standard. Add 15 mL of scintillation cocktail and 0 µL to 50 µL of nitromethane to each of the vials to create a series of quench standards.

10.5.2 For the beta particle detection efficiency in the beta ROI and the beta particle detection efficiency in the alpha ROI, a minimum of five beta calibration standards are prepared containing varying amounts of quenching agent. For each calibration standard, aliquot 5.00 mL of 0.1M nitric acid into a scintillation vial. Spike each of the vials with approximately 200 Bq of the beta calibration standard. Add 15 mL of scintillation cocktail and 0 µL to 50 µL of nitromethane to each of the vials to create a series of quench standards.

10.5.3 Prepare a background subtraction sample by aliquoting 5.00 mL of 0.1 M nitric acid into a scintillation vial and adding 15 mL of scintillation cocktail.

10.5.4 Count both sets of calibration standards and the background subtraction sample using the optimized ROIs and discriminator settings to obtain a relative standard uncertainty of 1 % or less in each count (10 000 counts).

11. Procedure

NOTE 2—To ensure sample integrity, step 11.1, if required, and step 11.2 should be done promptly after sample receipt at the laboratory if these actions were not performed at the time of sample collection. Samples may be kept at room temperature between receipt and analysis.

11.1 If filtration of the sample is required by the MQOs and the sample was not filtered at the time of collection, pass a sample aliquant sufficient for analysis through a 0.45 µm pore membrane filter. Drinking waters normally are not filtered prior to analysis (unless turbidity is >5 NTU).

11.2 If the sample was not preserved at the time of collection, add enough 2*M* nitric acid to bring the sample to pH 2 or less (5 to 10 mL of 2*M* nitric per litre of sample is usually sufficient). Tightly cap the container and shake well to mix. Confirm the pH with pH-indicating strip or paper. Hold the acidified sample for at least 16 h before starting the analysis. Samples should be analyzed within 180 days after sample collection, or within one year when compositing quarterly samples.

11.3 When steps 11.4 and 11.5 are not performed within four days of step 11.2, recheck the pH of the sample just prior to analysis to ensure that the pH is 2 or less. If the pH is not 2 or less, add sufficient 2*M* nitric acid to accomplish this, and then hold the sample for at least 16 h prior to the next step.

11.4 Transfer to a clean beaker a measured aliquant of the water that contains no more than 400 mg of residue mass. The amount of dissolved solids in a given sample can be approximated by evaporating a small amount (for example, 5 mL) of the sample in a tared planchet and weighing to find the net solids. Alternatively the conductance of the unpreserved sample can be measured and the amount of dissolved solids approximated (see Test Methods D1125).

NOTE 3—The collaborative study for this method indicated a much larger variability in the analytical results for spiked deionized water samples. Addition of approximately 60 mg of the Alternative Test Procedure (ATP) matrix (Appendix X2) used in the collaborative study improved the precision of the measurements.[4]

NOTE 4—The goal is to use a sufficient aliquot of the sample to meet the MQOs and to maintain a homogeneous mixture when the concentrated sample is mixed with the scintillation cocktail. An in-homogenous mixture is evidenced by the presence of an emulsion or separate layers. During method development and robustness testing several possible causes for an in-homogeneous mixture were observed including: (*1*) dissolved solids greatly in excess of 400 mg/sample; (*2*) acid concentrations greatly exceeding 0.1 M HNO_3; and (*3*) refrigeration of the sample/scintillation cocktail mixture. The dissolved solids are controlled by the sample aliquot size. The acid concentration is controlled by carefully drying the sample to ensure any excess acid from sample preservation is removed without causing loss of the sample through spattering or creating an insoluble solid by over-heating. This may be effected by carefully controlling the drying temperature (for example, monitoring the hot plate temperature, using a heating block or drying oven). Counting of the samples in a refrigerated liquid scintillation counter may cause the formation of a gel (opaque sample with no phase separation). Formation of a gel does not necessarily compromise the analytical results. The ruggedness of the implementation of this method using typical laboratory samples should be verified under the conditions used.

11.5 Evaporate the sample aliquant to approximately 4 to 5 mL. Quantitatively transfer to a tared glass scintillation vial using 0.1*M* HNO_3. Slowly evaporate to near dryness. Adjust heat carefully to avoid spattering or boiling.

11.6 Add 5 mL of 0.1*M* HNO_3, loosely cap the vial and warm gently to dissolve the solids. Do not allow the sample to evaporate. After the sample has cooled to room temperature, add 15 mL of scintillation cocktail and mix thoroughly. The resultant sample should be a clear homogeneous solution with no evidence of phase separation as evidenced by the presence of an emulsion or separate layers. There should be no solid residue in the vial. If phase separation occurs, or there is solid residue in the vial, a significantly smaller sample aliquant should be taken for analysis which will avoid phase separation in the subsequent sample preparation.

11.7 The MQOs inherent in the intended data use determine if the sample must be counted immediately after preparation to determine the activity concentration of any short-lived radionuclides (for example, ^{224}Ra) or if the sample should be held for a period of time prior to counting to allow for re-establishment of equilibrium in any present radionuclide decay chains.

11.8 Prepare a background subtraction sample by aliquoting 5.00 mL of 0.1M nitric acid into a scintillation vial and adding 15 mL of scintillation cocktail.

11.9 Place the samples and the background subtraction sample in a calibrated liquid scintillation counter and allow for dark-adaptation and temperature equilibrium if required.

11.10 Count the sample in the liquid scintillation counter for a period of time necessary to obtain the required MQOs.

12. Calculation

12.1 Fitting the detection efficiency to the quench relationships.

12.1.1 For each of the alpha calibration vials prepared in 10.5.1 through 10.5.4, calculate the alpha particle detection efficiency in the alpha ROI, $\varepsilon_{\alpha\alpha}$, and the alpha particle detection efficiency in the beta ROI, $\varepsilon_{\alpha\beta}$, using the following equations:

$$\varepsilon_{\alpha\alpha} = \frac{R_{\alpha\alpha} - R_{\alpha b}}{c_\alpha \times V_{s\alpha}} \quad (1)$$

$$\varepsilon_{\alpha\beta} = \frac{R_{\alpha\beta} - R_{\beta b}}{c_\alpha \times V_{s\alpha}}$$

where:

$\varepsilon_{\alpha\alpha}$ = alpha particle detection efficiency in the alpha ROI,
$\varepsilon_{\alpha\beta}$ = alpha particle detection efficiency in the beta ROI,
$R_{\alpha\alpha}$ = count rate of the alpha standard aliquant in counts per second in the alpha ROI,
$R_{\alpha\beta}$ = count rate of the alpha standard aliquant in counts per second in the beta ROI,
$R_{\alpha b}$ = count rate of the background subtraction sample in counts per second in the alpha ROI,
$R_{\beta b}$ = count rate of the background subtraction sample in counts per second in the beta ROI,
c_α = activity concentration of the reference alpha standard in becquerels per millilitre (Bq/mL), and
$V_{s\alpha}$ = volume of the reference alpha standard added to the vial in millilitres (mL).

12.1.2 For each of the beta calibration vials prepared in 10.5.1 through 10.5.4, calculate the beta particle detection efficiency in the beta ROI, $\varepsilon_{\beta\beta}$, and the beta particle detection efficiency in the alpha ROI, $\varepsilon_{\beta\alpha}$, using the following equations:

$$\varepsilon_{\beta\beta} = \frac{R_{\beta\beta} - R_{\beta b}}{c_\beta \times V_{s\beta}} \quad (2)$$

$$\varepsilon_{\beta\alpha} = \frac{R_{\beta\alpha} - R_{\alpha b}}{c_\beta \times V_{s\beta}}$$

where:

$\varepsilon_{\beta\beta}$ = beta particle detection efficiency in the beta ROI,

$\varepsilon_{\beta\alpha}$ = beta particle detection efficiency in the alpha ROI,
$R_{\beta\beta}$ = count rate of the beta standard aliquant in counts per second in the beta ROI,
$R_{\beta\alpha}$ = count rate of the beta standard aliquant in counts per second in the alpha ROI,
$R_{\alpha b}$ = count rate of the background subtraction sample in counts per second in the alpha ROI,
$R_{\beta b}$ = count rate of the background subtraction sample in counts per second in the beta ROI,
c_β = activity concentration of the reference beta standard in becquerels per millilitre (Bq/mL), and
$V_{s\beta}$ = volume of the reference beta standard added to the vial in millilitres (mL).

12.1.3 Use least-squares regression to fit curves to the four series of data points obtained in steps 12.1.1 and 12.1.2, where the abscissa for each point is the quench indicating parameter and the ordinate is the detection efficiency as calculated by Eq 1 or Eq 2. Whatever mathematical model is chosen for each curve, the curve should be continuous and smooth over the working range of quench indicating parameter. A quadratic polynomial may be an adequate model for this purpose.

12.1.4 Regression provides the parameters for each curve in the form of a solution vector. It also provides the solution's variance-covariance matrix, whose elements are the variances and covariances of the parameters.

12.1.5 At any value of the quench indicating parameter, the two detection efficiencies for alpha particles, $\varepsilon_{\alpha\alpha}$ and $\varepsilon_{\alpha\beta}$, are correlated because of the uncertainty of the alpha activity concentration of each calibration source. Similarly the two detection efficiencies for beta particles, $\varepsilon_{\beta\beta}$ and $\varepsilon_{\beta\alpha}$, are correlated because of the uncertainty of the beta activity concentration of each calibration source. However, the effects of these correlations on the overall measurement uncertainty are considered to be negligible.

12.2 Determination of the detection efficiencies from the efficiency-to-quench relationships.

12.2.1 From the sample quench indicating parameter, determine the alpha detection efficiency in the alpha ROI, $\varepsilon_{\alpha\alpha}$, the alpha detection efficiency in the beta ROI, $\varepsilon_{\alpha\beta}$, the beta detection efficiency in the beta ROI, $\varepsilon_{\beta\beta}$, and the beta detection efficiency in the alpha ROI, $\varepsilon_{\beta\alpha}$.

12.3 Determination of the uncertainties of the detection efficiencies.

12.3.1 Equations for the uncertainties of the four detection efficiencies, $\varepsilon_{\alpha\alpha}$, $\varepsilon_{\alpha\beta}$, $\varepsilon_{\beta\beta}$, and $\varepsilon_{\beta\alpha}$, depend on the mathematical model chosen for each detection efficiency curve. In general, the uncertainty for a detection efficiency calculated from a multi-parameter calibration curve includes not only an uncertainty component for each of the parameters but also additional terms that account for correlations between the parameters. The variances (that is, squared uncertainties) and covariances of the curve parameters may be obtained from the variance-covariance matrix described in step 12.1.4.

12.4 Determination of the spillover factors.

12.4.1 The alpha-to-beta spillover factor and the variance of the alpha-to-beta spillover factor can be calculated as follows:

$$X_\alpha = \frac{\varepsilon_{\alpha\beta}}{\varepsilon_{\alpha\alpha}} \tag{3}$$

$$u^2(X_\alpha) = X_\alpha^2\left(\frac{u^2(\varepsilon_{\alpha\beta})}{\varepsilon_{\alpha\beta}^2} + \frac{u^2(\varepsilon_{\alpha\alpha})}{\varepsilon_{\alpha\alpha}^2}\right)$$

where:

X_α = alpha-to-beta spillover factor,
$\varepsilon_{\alpha\alpha}$ = alpha particle detection efficiency in the alpha ROI (a function of the quench parameter),
$\varepsilon_{\alpha\beta}$ = alpha particle detection efficiency in the beta ROI (a function of the quench parameter),
$u(X_\alpha)$ = standard uncertainty of the alpha spillover factor,
$u(\varepsilon_{\alpha\alpha}))$ = standard uncertainty of the alpha particle detection efficiency in the alpha ROI, and
$u(\varepsilon_{\alpha\beta})$ = standard uncertainty of the alpha particle detection efficiency in the beta ROI.

12.4.2 The beta-to-alpha spillover factor and the variance of the beta-to-alpha spillover factor can be calculated as follows:

$$X_\beta = \frac{\varepsilon_{\beta\alpha}}{\varepsilon_{\beta\beta}} \tag{4}$$

$$u^2(X_\beta) = X_\beta^2\left(\frac{u^2(\varepsilon_{\beta\alpha})}{\varepsilon_{\beta\alpha}^2} + \frac{u^2(\varepsilon_{\beta\beta})}{\varepsilon_{\beta\beta}^2}\right)$$

where:

X_β = beta-to-alpha spillover factor,
$\varepsilon_{\beta\beta}$ = beta particle detection efficiency in the beta ROI (a function of the quench parameter),
$\varepsilon_{\beta\alpha}$ = beta particle detection efficiency in the alpha ROI (a function of the quench parameter),
$u(X_\beta)$ = standard uncertainty of the beta spillover factor,
$u(\varepsilon_{\alpha\alpha}))$ = standard uncertainty of the beta particle detection efficiency in the beta ROI, and
$u(\varepsilon_{\alpha\beta})$ = standard uncertainty of the beta particle detection efficiency in the alpha ROI.

12.5 The net count rates and the standard uncertainties of the net count rates in the alpha ROI and beta ROI are calculated as follows:

$$R_\alpha = R_{\alpha\alpha} - R_{\alpha b} \tag{5}$$

$$u(R_\alpha) = \sqrt{\frac{R_{\alpha\alpha}}{t_s} + \frac{R_{\alpha b}}{t_b}}$$

$$R_\beta = R_{\beta\beta} - R_{\beta b}$$

$$u(R_\beta) = \sqrt{\frac{R_{\beta\beta}}{t_s} + \frac{R_{\beta b}}{t_b}}$$

where:

R_α = net count rate of the sample aliquant in counts per second in the alpha ROI,
$R_{\alpha\alpha}$ = count rate of the sample aliquant in counts per second in the alpha ROI,
$R_{\alpha b}$ = count rate of the background subtraction sample in counts per second in the alpha ROI,
R_β = net count rate of the sample aliquant in counts per second in the beta ROI,

$R_{\beta\beta}$ = count rate of the sample aliquant in counts per second in the beta ROI,
$R_{\beta b}$ = count rate of the background subtraction sample in counts per second in the beta ROI,
t_s = count time for the sample in seconds, and
t_b = count time for the background subtraction sample in seconds.

12.6 The corrected alpha and beta count rates (net alpha and beta count rates corrected for spillover) can be calculated as follows:

$$R'_\alpha = \frac{R_\alpha - R_\beta X_\beta}{1 - X_\alpha X_\beta} \quad (6)$$

$$R'_\beta = \frac{R_\beta - R_\alpha X_\alpha}{1 - X_\alpha X_\beta}$$

where:

R'_α = alpha count rate corrected for spillover, and
R'_β = beta count rate corrected for spillover.

12.7 The combined standard uncertainties of the corrected count rates are calculated as follows:

$$u_c(R'_\alpha) = \sqrt{\frac{u^2(R_\alpha) + X_\beta^2 u^2(R_\beta) + R'^2_\alpha X_\beta^2 u^2(X_\alpha) + R'^2_\beta u^2(X_\beta)}{1 - X_\alpha X_\beta}} \quad (7)$$

$$u_c(R'_\beta) = \sqrt{\frac{u^2(R_\beta) + X_\alpha^2 u^2(R_\alpha) + R'^2_\beta X_\alpha^2 u^2(X_\beta) + R'^2_\alpha u^2(X_\alpha)}{1 - X_\alpha X_\beta}}$$

12.8 The sample gross alpha activity concentration and the combined standard uncertainty of the gross alpha activity concentration can be calculated from the following:

$$AC_\alpha = \frac{R'_\alpha}{\varepsilon_{\alpha\alpha} \times V} \quad (8)$$

$$u_c(AC_\alpha) = \sqrt{\frac{u_c^2(R'_\alpha)}{\varepsilon_{\alpha\alpha}^2 \times V^2} + AC_\alpha^2 \times \left(\frac{u^2(V)}{V^2} + \frac{1 + X_\alpha X_\beta}{1 - X_\alpha X_\beta} \times \frac{u^2(\varepsilon_{\alpha\alpha})}{\varepsilon_{\alpha\alpha}^2} \right)}$$

where:

AC_α = sample gross alpha activity concentration in becquerels per litre (Bq/L),
V = sample aliquot volume in litres (L), and
$u_c(AC_\alpha)$ = combined standard uncertainty of the sample gross alpha activity concentration in becquerels per litre (Bq/L).

(other symbols are defined as above)

12.9 The sample gross beta activity concentration and combined standard uncertainty of the gross beta activity concentration can be calculated from the following:

$$AC_\beta = \frac{R'_\beta}{\varepsilon_{\beta\beta} \times V} \quad (9)$$

$$u_c(AC_\beta) = \sqrt{\frac{u_c^2(R'_\beta)}{\varepsilon_{\beta\beta}^2 \times V^2} + AC_\beta^2 \times \left(\frac{u^2(V)}{V^2} + \frac{1 + X_\alpha X_\beta}{1 - X_\alpha X_\beta} \times \frac{u^2(\varepsilon_{\beta\beta})}{\varepsilon_{\beta\beta}^2} \right)}$$

where:

AC_β = sample gross beta activity concentration in becquerels per litre (Bq/L),
V = sample aliquot volume in litres (L), and
$u_c(AC_\beta)$ = combined standard uncertainty of the sample gross beta activity concentration in becquerels per litre (Bq/L).

(other symbols are defined as above)

12.10 The uncertainty due only to counting statistics can be calculated from the following:

$$u_{cC}(AC_\alpha) = \frac{\sqrt{u^2(R_\alpha) + X_\beta^2 u^2(R_\beta)}}{\varepsilon_{\alpha\alpha} \times V \times (1 - X_\alpha X_\beta)} \quad (10)$$

$$u_{cC}(AC_\beta) = \frac{\sqrt{u^2(R_\beta) + X_\alpha^2 u^2(R_\alpha)}}{\varepsilon_{\beta\beta} \times V \times (1 - X_\alpha X_\beta)}$$

where:

$u_{cC}(AC_\alpha)$ = standard uncertainty due only to counting statistics for the sample gross alpha activity concentration in becquerels per litre (Bq/L), and
$u_{cC}(AC_\beta)$ = standard uncertainty due only to counting statistics for the sample gross beta activity concentration in becquerels per litre (Bq/L).

12.11 A detection decision for gross alpha activity concentration may be made when required by comparing the net alpha count, R_α, to the critical value of the net count rate corrected for spillover, $R_{\alpha C}$.

12.11.1 Calculate the critical value for the net alpha count rate corrected for spillover, $R_{\alpha C}$, as follows:

$$R_{\alpha C} = R_\beta X_\beta + 1.645 \sqrt{\frac{R_{\alpha+\beta} X_\beta}{t_s} + \left(R_{\alpha b} + X_\beta^2 R_{\beta b}\right)\left(\frac{1}{t_s} + \frac{1}{t_b}\right)} \quad (11)$$

where:

$$R_{\alpha+\beta} = \begin{cases} R_\alpha + R_\beta \text{ if } R_\alpha + R_\beta \geq 0 \\ 0 \quad\quad\quad \text{if } R_\alpha + R_\beta < 0 \end{cases} \quad (12)$$

12.11.2 If $R_\alpha > R_{\alpha C}$, decide that alpha activity is present in the sample. When the preceding criterion is used for a detection decision, the *a priori* minimum detectable concentration (MDC) for alpha activity concentration can be calculated from the following:

$$MDC_\alpha = \quad (13)$$

$$\frac{2.71 \frac{1 + X_\alpha X_\beta^2}{t_s(1 - X_\alpha X_\beta)} + 3.29 \sqrt{\frac{AC_\beta V \varepsilon_{\beta\alpha}(1 + X_\beta)}{t_s} + \left(R_{\alpha b} + X_\beta^2 R_{\beta b}\right)\left(\frac{1}{t_a} + \frac{1}{t_b}\right)}}{\varepsilon_{\alpha\alpha} V (1 - X_\alpha X_\beta)}$$

where:

AC_β = specified gross beta activity concentration in the sample (nonnegative),
t_s = sample aliquant count time in seconds,
t_b = background subtraction sample count length time in seconds,
$\varepsilon_{\alpha\alpha}$ = alpha detection efficiency in the alpha ROI,
$\varepsilon_{\beta\alpha}$ = beta detection efficiency in the alpha ROI (equal to $\varepsilon_{\beta\beta} \times X_\beta$), and
V = volume of sample aliquant.

12.12 A detection decision for gross beta activity concentration may be made when required by comparing the net beta count, R_β, to the critical value of the net count rate corrected for spillover, $R_{\beta C}$.

12.12.1 Calculate the critical value for the net beta count rate corrected for spillover, $R_{\beta C}$, as follows:

$$R_{\beta C} = R_\alpha X_\alpha + 1.645 \sqrt{\frac{R_{\alpha+\beta} X_\alpha}{t_s} + \left(R_{\beta b} + X_\alpha^2 R_{\alpha b}\right)\left(\frac{1}{t_s} + \frac{1}{t_b}\right)} \quad (14)$$

where:

$$R_{\alpha+\beta} = \begin{cases} R_\alpha + R_\beta \text{ if } R_\alpha + R_\beta \geq 0 \\ 0 \quad\quad\quad \text{if } R_\alpha + R_\beta < 0 \end{cases} \quad (15)$$

12.12.2 If $R_\beta > R_{\beta C}$, decide that beta activity is present in the sample. When the preceding criterion is used for a detection decision, the *a priori* minimum detectable concentration (MDC) for beta activity concentration can be calculated from the following:

$$MDC_\beta = \quad (16)$$

$$\frac{2.71 \frac{1 + X_\beta X_\alpha^2}{t_s(1 - X_\alpha X_\beta)} + 3.29 \sqrt{\frac{AC_\alpha V \varepsilon_{\alpha\beta}(1 + X_\alpha)}{t_s} + \left(R_{\beta b} + X_\alpha^2 R_{\alpha b}\right)\left(\frac{1}{t_a} + \frac{1}{t_b}\right)}}{\varepsilon_{\beta\beta} V (1 - X_\alpha X_\beta)}$$

where:

AC_α = specified gross alpha activity concentration in the sample (nonnegative),
t_s = sample aliquant count time in seconds,
t_b = background subtraction sample count length time in seconds,
$\varepsilon_{\beta\beta}$ = beta detection efficiency in the beta ROI,
$\varepsilon_{\alpha\beta}$ = alpha detection efficiency in the beta ROI (equal to $\varepsilon_{\alpha\alpha} \times X_\alpha$), and
V = volume of sample aliquant.

13. Quality Control

13.1 In order to provide reasonable assurance that analytical results obtained using this test method are valid and accurate within the confidence limits of the test method, Quality Control (QC) samples are analyzed with each batch of samples undergoing analysis. Each batch should include not more than 20 samples excluding those used for QC purposes. At a minimum, the QC procedures in this section must be followed when running the test method. Laboratory or project specific quality assurance plans may contain more restrictive process QC procedures.

13.2 Acceptance criteria for quality control samples should be based on applicable regulatory requirements (for example, U.S. EPA Safe Drinking Water Act) or project specific MQOs. In the absence of regulatory requirements or project specific MQOs the acceptance criteria shall be specified in the laboratory's quality assurance program. Information provided in Section 14 may be used as an initial basis for acceptance criteria. These acceptance criteria may be adjusted based on results for routine analyses of quality control samples.

13.3 *Calibration and Calibration Verification:*

13.3.1 Standards used in the method shall be traceable to a national standards laboratory (such as NIST or NPL).

13.3.2 Calibration and optimization of the counting instrument is performed as described in Section 10.

13.3.3 Prepare separate verification standards for alpha and beta by placing known amounts of the alpha and beta standard (approximately 200 Bq) into separate volumes of water having a dissolved content approximately equivalent to those of the test samples and prepare for counting as directed in Section 11. Throughout the analysis the evaporation, transfer and counting shall be identical to that of the test samples.

13.3.4 Verification standards are analyzed immediately following the calibration and monthly or prior to use, which ever is longer.

13.3.5 Acceptance limits for verification standards are based on project specific MQOs or the laboratory's quality assurance program requirements, or both. If the results for the verification standard are outside the limits, recalibrate and reanalyze samples back to the last acceptable verification standard.

13.4 *Initial Demonstration of Laboratory/Instrument/Analyst Capability:*

13.4.1 If a laboratory or an analyst has not performed the test before or if there has been a major change in the measurement system (for example, significant instrument change, new instrument, etc.) a precision and bias study must be performed to demonstrate laboratory, instrument, or analyst capability. A significant change is defined as any change, repair, or alteration of any component in the system, which, as evidenced by performance check results, affects the response of the measurement system.

13.4.2 Analyze seven replicates of a standard solution prepared from an independent reference material (IRM) containing accurately known activity concentrations of alpha and beta emitters sufficient to minimize the counting uncertainty to 5 % or less at one sigma. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The matrix and chemistry of the solution should be equivalent to that of the samples.

13.4.3 Calculate the mean and standard deviation of the replicate values. Ensure that these values meet the required MQOs. Where no MQOs are provided, compare these results to the % recovery and repeatability values in Section 14. Practice D5847 should be consulted on the manner by which precision and mean bias are determined from the initial demonstration study.

13.4.4 Analyze three replicates of a blank solution matrix. The matrix used for the demonstration should represent a water sample typical for which the method will be used (for example, surface water). The total dissolved solids (TDS) of the matrix should approximate that which may be encountered in normal use.

13.4.5 Calculate the gross alpha and gross beta activity concentration for each of these three blank solutions. If the blank results exhibit detectable quantities of alpha or beta, correct the problem and repeat the study until the final gross alpha and gross beta result of each of the three blank solutions is below half the associated MDC for each of the analytes.

13.4.6 This method shall not be used for official samples until precision, bias, and blank requirements are met.

13.5 *Laboratory Control Sample (LCS):*

13.5.1 To ensure that the test method is within control limits, analyze an LCS with each batch of no more than 20 samples. The activity concentration added to reagent water

should be appropriate for the type of samples analyzed and allow sufficient precision to insure a meaningful assessment of accuracy. The LCS should contain the calibration alpha and beta radionuclides. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The results obtained for the LCS should meet the requirements of the project specific MQOs or the laboratory's quality assurance program, or both.

13.5.2 If the result does not meet the requirement, analyses should be stopped and the reason for the failure should be identified and resolved.

13.6 *Method Blank:*

13.6.1 Analyze a reagent water test blank with each batch of no more than 20 samples. The concentration of the analyte found in the blank should be less than half the MDC of the analytes of interest. If the concentration of analyte is found above this level, provide an explanation in a case narrative.

13.7 *Matrix Spike (MS):*

13.7.1 Analyze at least one matrix spike sample with each batch of no more than 20 samples by spiking an aliquant of the sample within the batch with a known concentration of the alpha and/or beta calibration radionuclide.

13.7.2 The spike should produce a concentration of the alpha or beta calibration radionuclide that is 2 to 5 times the anticipated sample concentration or as specified by the laboratory, whichever is greater.

13.7.3 The Matrix Spike must be taken through all the steps of the method.

13.7.4 Calculate the percent recovery of the matrix spike R using the following formula:

$$R = \frac{|AC_{as} - AC_a|}{AC_s} \times 100\,\% \quad (17)$$

where:

AC_{as} = concentration of gross alpha or gross beta in Becquerels (Bq) per litre measured in the spiked sample,
AC_a = concentration of gross alpha or gross beta in Becquerels (Bq) per litre in the sample, and
AC_s = spiked concentration of gross alpha or gross beta in Becquerels (Bq) per litre.

13.7.5 The percent recovery, R, should meet the requirements of the project specific MQOs or the laboratory's quality assurance program, or both. If the concentration does not meet these requirements, provide an explanation in a case narrative.

13.8 *Laboratory Duplicate:*

13.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of no more than 20 samples. Calculate the statistical agreement [duplicate error ratio (DER)] between the two results. This calculation is performed using the combined standard uncertainty of each result as shown below.

$$DER = \frac{|AC_{original} - AC_{dup}|}{\sqrt{u_c^2\,(AC_{original}) + u_c^2\,(AC_{dup})}} \quad (18)$$

where:

$AC_{original}$ = original sample activity concentration,
AC_{dup} = duplicate sample activity concentration,
$u_c(AC_{original})$ = combined standard uncertainty of the original sample, and
$u_c(AC_{dup})$ = combined standard uncertainty of the duplicate sample.

13.8.2 In those cases where there is insufficient sample volume to allow performance of a duplicate sample analysis, a duplicate LCS (LCS-D) should be performed and analyzed using the same DER criteria.

13.8.3 The value of DER should be ≤3.0. If the sample duplicate or LCS duplicate result is not within these limits all samples in the batch must be reanalyzed, or an explanation must be provided in a case narrative.

13.9 *Independent Reference Material (IRM):*

13.9.1 In order to verify the quantitative value produced by the test method, analyze an IRM sample, submitted on at least single-blind basis (if practical) to the laboratory periodically. The IRM should be traceable to a national standards laboratory (such as NIST or NPL) and should be appropriate to the typical purpose for which the method is used. The value obtained shall demonstrate acceptable performance as defined by the program or the outside source.

13.9.2 In the absence of other acceptance criteria, such as U.S. EPA Safe Drinking Water Act, for the RM sample, compare the IRM sample result to the IRM known value as follows:

$$R = \frac{|IRM_{found} - IRM_{known}|}{\sqrt{u_c^2\,(IRM_{found}) + u_c^2\,(IRM_{known})}} \quad (19)$$

where:

R = relative difference,
IRM_{found} = found concentration of the IRM,
IRM_{known} = known concentration of the IRM,
$u_c(IRM_{found})$ = combined standard uncertainty of the IRM found concentration, and
$u_c(AC_{known})$ = combined standard uncertainty of the IRM known.

13.9.3 The value of R should be ≤3.0. If the value of R is greater than 3.0, the method should be investigated to determine the cause.

14. Precision and Bias

14.1 The precision of this test method is based on an interlaboratory study conducted in 2016. Six laboratories tested five different water samples for both alpha and beta activity. Every "test result" represents an individual determination. Data in Table 1 and Table 2 are presented in units of pCi/L as these units are commonly used for determining compliance with U.S. EPA regulations. Practice E691 was followed for the design and analysis of the data; the details are on file at ASTM Headquarters.[4]

14.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and

TABLE 1 Gross Alpha Activity (pCi per L)

	Expected Value	Average[A] Reported Value $\bar{X}$	Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Blank	0	–0.24	NA	0.25	0.31	0.69	0.88
DI Water	15	15.89	105.9	3.41	3.49	9.54	9.78
ATP Matrix 1	7.5	6.87	91.6	0.39	0.47	1.11	1.32
ATP Matrix 2	15	14.23	94.9	0.71	0.86	1.99	2.42
ATP Matrix 3	30	28.17	93.9	1.06	1.72	2.98	4.82

[A] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1195. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Gross Beta Activity (pCi per L)

	Expected Value	Average[A] Reported Value $\bar{X}$	Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Blank	0	0.85	NA	1.47	1.50	4.11	4.19
DI Water	50	51.74	103.5	10.34	10.91	28.95	30.54
ATP Matrix 1	25	25.39	101.6	1.90	2.39	5.32	6.68
ATP Matrix 2	50	50.51	101.0	2.90	2.96	8.13	8.29
ATP Matrix 3	100	98.24	98.2	3.63	4.56	10.17	12.76

[A] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1195. Contact ASTM Customer Service at service@astm.org.

correct operation of the test method, exceed the following values only in one case in 20.

14.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

14.1.1.2 Repeatability limits are listed in Table 1 and Table 2.

14.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

14.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

14.1.2.2 Reproducibility limits are listed in Table 1 and Table 2.

14.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

14.1.4 Any judgment in accordance with statements 14.1.1 and 14.1.2 would have an approximate 95 % probability of being correct.

14.2 *Bias*—Where there was a known or expected value for any given sample, it has been included in the above precision tables.

14.3 The precision statement was determined through statistical examination of 417 results, from 6 laboratories, on 5 materials. These 5 materials were described as the following:

Blank: Modified ATP Matrix
DI Water: Deionized water spiked with ^{241}Am and ^{90}Sr/^{90}Y
ATP Matrix 1: Modified ATP Matrix spiked with ^{241}Am and ^{90}Sr/^{90}Y
ATP Matrix 2: Modified ATP Matrix spiked with ^{241}Am and ^{90}Sr/^{90}Y
ATP Matrix 3: Modified ATP Matrix spiked with ^{241}Am and ^{90}Sr/^{90}Y

To judge the equivalency of two test results, it is recommended to choose the water sample closest in characteristics your test samples.

15. Keywords

15.1 gross alpha radioactivity; gross beta radioactivity; gross radioactivity measurement; liquid scintillation counter; water

APPENDIXES

(Nonmandatory Information)

X1. RESOURCES

X1.1 The following standards may be of value as background information and training resources to laboratories performing this test method:

X1.1.1 *ASTM Standards:*[5]

D1890 Test Method for Beta Particle Radioactivity of Water

D1943 Test Method for Alpha Particle Radioactivity of Water

D3648 Practices for the Measurement of Radioactivity

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

X1.1.2 *Other Standards and Publications:*

Multi-Agency Radiological Laboratory Analytical Protocols Manual[10]

Standard Methods 8010E Table 8010: Recommended Composition for Reconstituted Fresh Water

EPA Protocol for the Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaiminants in Drinking Water Appendix C: SOP for the Preparation of Radiochemistry ATP Drinking Water Test Matrix[11]

ISO 9696 Water Quality—Measurement of Gross Alpha Activity in Non-saline Water—Thick Source Method

ISO 11704:2010 Water Quality – Measurement of Gross Alpha and Beta Activity Concentration in non-saline water – Liquid Scintillation Counting Method

[10] NUREG 1576, EPA 402-B-04-001A-C, NTIS PB2004-105421, MARLAP, Multi-Agency Radiological Laboratory Protocols Manual, Volumes 1-3, Washington, DC, July 2004. Available at www.epa.gov/radiation/marlap/index.html.

[11] Protocol for the Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water, U.S. Environmental Protection Agency, EPA 815-R-14-002, September 2014.

X2. MODIFIED ATP MATRIX

TABLE X2.1 Modified ATP Matrix

Salt Specified	Grade	MW (g/mol)	Salt in Test Matrix (mg/L)	Analyte	Analyte in Test Matrix (mg/L)
$AlCl_3·6H_2O$	ACS	241.43	4	Al	0.45
				Cl	1.76
$BaCl_2·2H_2O$	ACS	244.26	4	Ba	2.25
				Cl	1.16
$Ca(NO_3)_2·4H_2O$	ACS	236.15	50	Ca	8.49
				NO_3	26.26
$FeCl_3$	ACS	162.20	4	Fe	1.38
				Cl	2.62
Na_2HPO_4	ACS	141.96	14	Na	4.53
				HPO_4	9.37
$NaHCO_3$	ACS	84.01	80	Na	21.89
				HCO_3	57.15
$NaNO_3$	ACS	84.99	50	Na	13.53
				NO_3	36.48
NaCl	ACS	58.44	60	Na	23.60
				Cl	36.40
$Mg(NO_3)_2·6H_2O$	ACS	256.41	100	Mg	9.48
				NO_3	48.37
Total			366		305.17

X2.1 Appendix C of the U.S. Environmental Protection Agency "Protocol for the Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water" includes a test matrix developed for use in method performance studies. This test matrix includes interfering radionuclides (^{40}K) and the possibility of coprecipitation of radionuclides with barium sulfate. The collaborative study performed for this method used the modified text matrix in Table X2.1. The modified test matrix substitutes sodium chloride for potassium chloride, and replaces the sulfate salts magnesium sulfate and sodium sulfate with the nitrate salts magnesium nitrate and sodium nitrate.