Designation: D3454 – 11

Standard Test Method for Radium-226 in Water [1]

This standard is issued under the fixed designation D3454; 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 soluble, suspended, and total radium-226 in water in concentrations above 3.7×10^{-3} Bq/L. This test method is not applicable to the measurement of other radium isotopes.

1.2 This test method may be used for quantitative measurements by calibrating with a radium-226 standard, or for relative measurements by comparing the measurements made with each other.

1.3 This test method does not meet the current requirements of Practice D2777.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.5 Hydrofluoric acid (HF) is very hazardous and should be used in a well-ventilated hood. Wear rubber gloves, safety glasses or goggles, and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills promptly and wash thoroughly after using HF.

1.6 *This standard does not purport to address all of the other 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3648 Practices for the Measurement of Radioactivity
D3649 Practice for High-Resolution Gamma-Ray Spectrometry of Water
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
D7282 Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements

3. Terminology

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

4. Summary of Test Method

4.1 This test method[3] is based on the emanation and scintillation counting of ^{222}Rn, a gaseous daughter product of ^{226}Ra, from a solution.

4.2 ^{226}Ra is collected from water by coprecipitation on a relatively large amount of barium sulfate. The barium-radium sulfate is decomposed by fuming with phosphoric acid, and the resulting glassy melt is dissolved by evaporation with dilute hydrochloric acid to form soluble barium-radium phosphates and chlorides. These salts are dissolved and the solution is stored for ingrowth of ^{222}Rn. After a suitable ingrowth period, the radon gas is removed from the solution by purging with gas and transferred to a scintillation counting chamber. About 4 h after ^{222} Rn collection, the scintillation chamber is counted for alpha activity. The ^{226}Ra concentration is calculated from the alpha count rate of ^{222}Rn and its immediate daughters. The radioactive decay characteristics of ^{226}Ra and its immediate decay progeny are listed in Table 1.

[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] 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.

[3] This test method is based on a previously published method by Rushing, D.E., Garcia, W.J., and Clark, D.A. "The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Radium, Polonium and Uranium," Radiological Health and Safety in Mining and Milling of Nuclear Materials, Vol. II, IAEA, Vienna, Austria, 1964), p. 187.

TABLE 1 Radioactive Decay Characteristics of Radium-226 and Its Daughters

Radionuclide	Half-life	Mode of Decay
^{226}Ra	1600 years	α
^{222}Rn	3.82 days	α
^{218}Po	3.10 min	α
^{214}Pb	26.8 min	β, γ
^{214}Bi	19.9 min	β, γ
^{214}Po	164/3 μ s	α
^{210}Pb	22.2 years	β, γ

5. Significance and Use

5.1 The most prevalent of the five radium isotopes in ground water, having a half life greater than one day, are ^{226}Ra and ^{228}Ra. These two isotopes also present the greatest health risk compared to the other naturally occurring nuclides of equal concentrations if ingested via the water pathway.

5.2 Although primarily utilized on a water medium, this technique may be applicable for the measurement of the ^{226}Ra content of any media once the medium has been completely decomposed and put into an aqueous solution.

5.3 The general methodology and basis of this technique are similar to the methodology "^{226}Ra in Drinking Water (Radon Emanation Technique)" as described in the document *EPA-600//4-80-032*.[4]

6. Interferences

6.1 Only the gaseous alpha-emitting radionuclides interfere, namely, ^{219} Rn and ^{220} Rn. Their half lives are 3.9 s and 54.5 s respectively; their presence indicates the presence of their parents, ^{223}Ra and ^{224}Ra. These short-lived radon isotopes decay before the ^{222}Rn is counted; it is their alpha-emitting decay products that would interfere. These interferences are very rare in water samples but are frequently observed in certain uranium mill effluents.

7. Apparatus

7.1 *Radon Bubbler*[5](Fig. 1).

7.2 *Radon Scintillation Chamber* (also known as Lucas Cell) (Fig. 2).

7.3 *Manometer,* open-end capillary tube or vacuum gage having a volume which is small compared to the volume of the scintillation chamber, 0 – 760 mm Hg (Fig. 3).

7.4 *Gas Purification Tube,* 7 to 8 mm outside diameter standard wall glass tubing, 100 mm long, constricted at lower end to hold a glass wool plug (Fig. 3). The upper half of the tube is filled with magnesium perchlorate and the lower half with a sodium hydrate-asbestos absorbent.

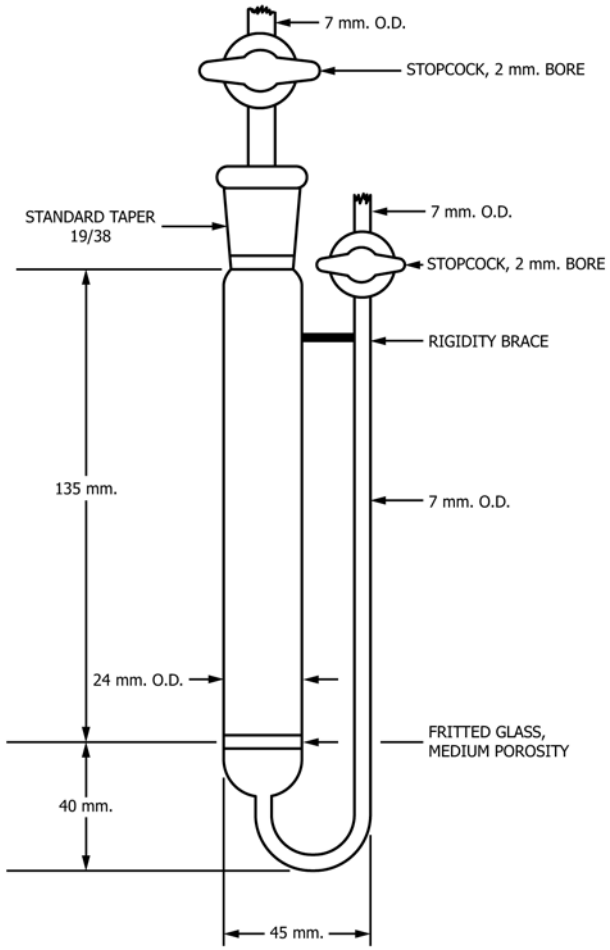

FIG. 1 Radon Bubbler

7.5 *Scintillation Counter Assembly,* consisting of a 50 mm (2 in.) or more in diameter photomultiplier tube mounted in a light-tight housing and coupled to the appropriate preamplifier, high-voltage supply, and scaler. A high-voltage safety switch should open automatically when the light cover is removed to avoid damage to the photomultiplier tube. The preamplifier should incorporate a variable gain adjustment. The counter should be equipped with a flexible ground wire which is attached to the chassis photomultiplier tube by means of an alligator clip or similar device. The operating voltage is ascertained by determining a plateau using ^{222}Rn in the scintillation chamber as the alpha source. The slope of the plateau should not exceed 2 %/100 V. The counter and the scintillation chamber should be calibrated and used as a unit when more than one counter is available. The background counting rate for the counter assembly without the scintillation chamber should range from 0.00 to 0.0005 s^{-1}.

7.6 *Membrane Filters,* 0.45 μm pore size.

7.7 *Silicone Grease,* high-vacuum, for bubbler stopcocks.

7.8 *Platinum Ware,* crucibles, 20 to 30 mL, and one 500 mL capacity dish. Platinum ware is cleaned by immersing and rotating in a molten bath of potassium pyrosulfate, removing, cooling, and rinsing in hot tap water, digesting in hot 6M HCl, rinsing in water, and finally flaming over a burner.

[4] "Radium-226 in Drinking Water (Radon Emanation Technique)," *Prescribed Procedures for Measurement of Radioactivity in Drinking Water,* August 1980.

[5] The sole source of supply of the radon bubbler known to the committee at this time is Corning Glass Works, Special Sales Section, Corning, N.Y. 11830. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee.

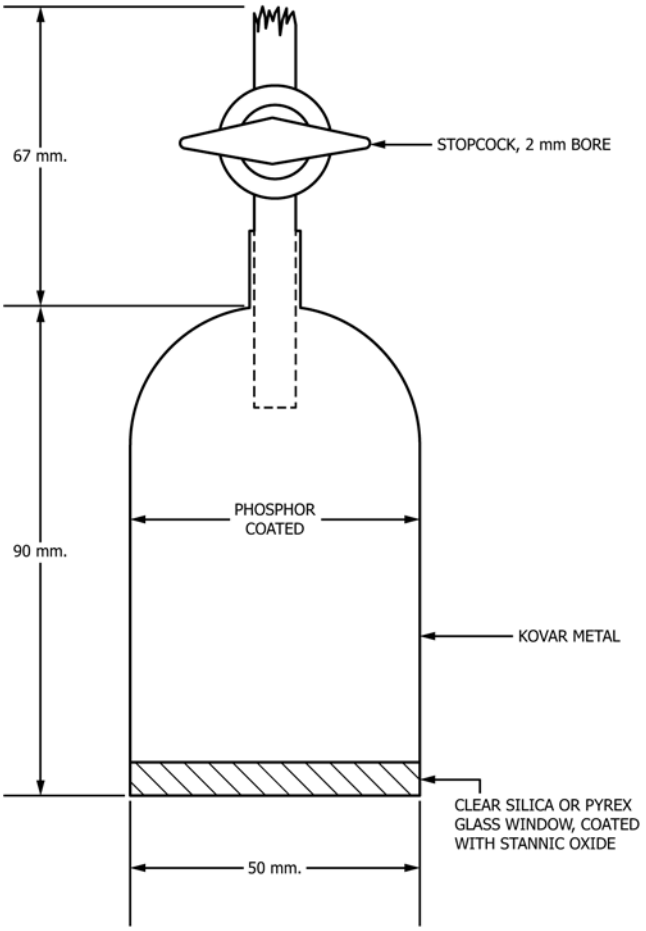

FIG. 2 Radon Scintillation Chamber

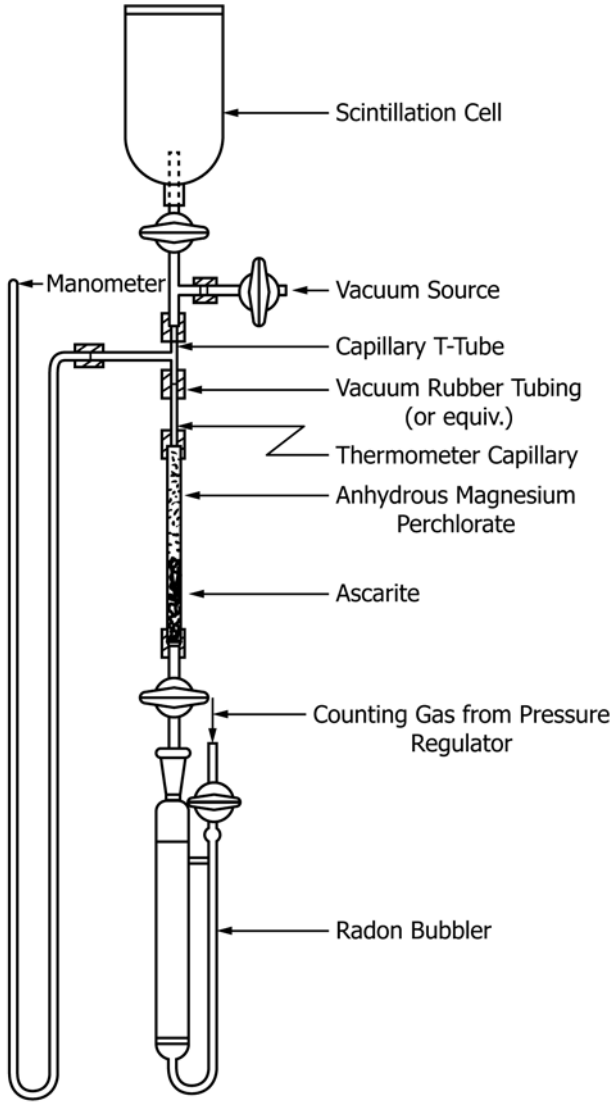

FIG. 3 De-emanation Assembly

7.9 *Laboratory Glassware*—Glassware may be decontaminated before and between uses by heating for 1 h in EDTA-Na_2CO_3 decontaminating solution at 90 to 100°C, then rinsing in water, in 1M HCl and again in water.

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.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

8.3 *Radioactive Purity of Reagents*—Radioactive purity shall be such that the measured results of blank samples do not exceed the calculated probable error of the measurement or are within the desired precision.

8.4 *Ammonium Sulfate Solution (100 g/L)*—Dissolve 10 g of ammonium sulfate ($(NH_4)_2SO_4$) in water and dilute to 100 mL.

8.5 *Barium Chloride Carrier Solution Stock, (17.8 g/L)*—Dissolve 17.8 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L. This solution will contain 10 mg/mL $Ba^{+\ +}$.

8.6 *Barium-133 Tracer Solution* —(approximately 3 kBq/mL).

8.7 *Barium Chloride Carrier Solution, Working*—Add 100 mL of barium chloride carrier stock solution and 10 mL of barium-133 tracer solution to 890 mL of water and mix thoroughly. This solution will contain approximately 1 g/L of $Ba^{+\ +}$. Allow to stand for 24 h and filter through a membrane filter.

8.8 *EDTA-Sodium Carbonate Decontaminating Solution*—Dissolve 10 g of disodium ethylenediaminetetraacetate and 10 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on 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.

8.9 *Flux*—To a large platinum dish (about 500-mL capacity) add 30 mg of $BaSO_4$, 65.8 g of K_2CO_3, 50.5 g of Na_2CO_3, and 33.7 g of $Na_2B_4O_7 \cdot 10\ H_2O$. Mix well and heat cautiously until the water is expelled; fuse and mix thoroughly by swirling. Cool flux, grind it in a porcelain mortar to pass a U. S. Standard No. 10 (2.00-mm) (or finer) sieve. Store in an airtight bottle. (Flux can be prepared in smaller batches.)

8.10 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

8.11 *Hydrochloric Acid Solution 6M (1 + 1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

8.12 *Hydrochloric Acid Solution 1M (1 + 11)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 11 volumes of water.

8.13 *Hydrochloric Acid Solution 0.24M (1 + 49)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 49 volumes of water.

8.14 *Hydrochloric Acid Solution 0.1M (1 + 119)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 119 volumes of water.

8.15 *Hydrofluoric Acid (sp gr 1.15)*—Concentrated hydrofluoric acid (HF). Use extreme caution.

8.16 *Hydrogen Peroxide 3 % (1 + 9)*—Mix 1 volume of H_2O_2 (30 %) with 9 volumes of water.

8.17 *Magnesium Perchlorate*—Anhydrous magnesium perchlorate $Mg(ClO_4)_2$.

8.18 *Phosphoric Acid (sp gr 1.69)*—Concentrated phosphoric acid (H_3PO_4).

8.19 *Radium Standard Solution* (0.37 Bq/mL).[5,7]

8.20 *Sodium Hydroxide-Coated Silicate Absorbent, Proprietary,* [5,8] 8 to 20 mesh.

8.21 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

8.22 *Sulfuric Acid Solution 0.05M (1 + 359)*—Mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) with 359 volumes of water. This solution is 0.1 *N*. Slowly add acid to water.

8.23 *Helium,* in a high-pressure cylinder with a two-stage pressure regulator and needle valve.

9. Sampling

9.1 Collect the sample in accordance with the applicable standards as described in Practices D3370.

10. Calibration and Standardization

10.1 Close the inlet stopcock of a bubbler, (Note 1) add 5 mL of $BaCl_2 \cdot 2H_2O$ carrier solution, 1 mL of concentrated HCl (sp gr 1.19), 3 mL (1.11 Bq) of standard radium solution and fill the bubbler ⅔ to ¾ full with water.

NOTE 1—Before using, test bubblers by placing about 10 mL of water in them and passing air through them at the rate of 3 to 5 mL/min. This should form many fine bubbles rather than a few large ones. Do not use bubblers requiring excessive pressure to initiate bubbling. Reject unsatisfactory bubblers. Corning's "medium-porosity" fritted glass disks are usually satisfactory.

10.2 Insert the outlet stopcock into the bubbler with the stopcock open. Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of bubbler and adjust the inlet pressure to produce a froth a few millimetres thick. Establish a zero ingrowth time by purging the liquid with helium for 15 to 20 min.

10.3 In rapid succession, close the inlet stopcock, remove the gas connection, and the close outlet stopcock. Record the date and time and store the bubbler preferably for 2 to 3 weeks before collecting and counting the ^{222}Rn.

10.4 Attach a scintillation chamber as shown in Fig. 3; *substitute a glass tube with a stopcock for the bubbler* so that the helium gas can be turned on and off conveniently. Open the stopcock on the scintillation chamber; close the stopcock to the gas and gradually open the stopcock to vacuum source to evacuate the cell. Close the stopcock to the vacuum source and check the manometer reading for 2 min to test the system, especially the scintillation chamber for leaks. If leaks are detected they should be identified and sealed.

10.5 Open the stopcock to the helium gas and allow the gas to enter the chamber slowly until atmospheric pressure is reached. Close all the stopcocks.

10.6 Place the scintillation chamber on the photomultiplier tube (in a light-tight housing), wait 10 min, and obtain a background count rate (preferably over a period of at least 100 min). Phototube must not be exposed to external light with the high voltage applied.

10.7 With the scintillation chamber and bubbler in positions indicated in Fig. 3 and all stopcocks closed, open the stopcock to vacuum and then to the scintillation chamber. Evacuate the scintillation cell and the gas purification system. Close the stopcock to vacuum and check for leaks as in 10.4.

10.8 Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of the bubbler.

10.9 Very cautiously open the bubbler outlet stopcock to equalize pressure and transfer all or most of the fluid in the inlet side arm to the bubbler chamber.

10.10 Close the outlet stopcock and very cautiously open the inlet stopcock to flush remaining fluid from the side arm and fritted disk. Close the inlet stopcock.

10.11 Repeat steps 10.9 and 10.10 several times to obtain more nearly equal pressure on the two sides of the bubbler.

10.12 With the outlet stopcock fully open, cautiously open the inlet stopcock so that the flow of gas produces a froth a few millimetres thick at the surface of bubbler solution. Maintain the flow rate by adjusting the pressure with the regulator valve and continue de-emanation until the pressure in the scintillation

[7] The sole source of supply of the standard radium solutions known to the committee at this time is the National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

[8] The sole source of supply of the Ascarite II known to the committee at this time is VWR Scientific, 1310 Goshen Parkway, West Chester, PA 19380.

chamber reaches the atmospheric pressure. The total elapsed time for de-emanation should be 15 to 20 min.

10.13 In rapid succession, close the stopcock to the scintillation chamber, close the bubbler inlet and the outlet stopcocks, shut off and disconnect the gas supply. Record the date and time, which is the end of ingrowth and the beginning of decay.

10.14 Store the bubbler for another ^{222}Rn ingrowth in the event a subsequent de-emanation is desired. The standard bubbler containing the standard may be kept and reused indefinitely.

10.15 Four hours after de-emanation, place the scintillation chamber on the photomultiplier tube, wait 10 min, and count until desired statistical accuracy is achieved. Record the date and time the counting was started and finished.

10.16 Calculate the calibration factor E, for the scintillation chamber as follows:

$$E = \frac{R_n}{A_r \times (1 - e^{-\lambda t_1}) \times e^{-\lambda t_2}}$$

where:

R_n = net count rate, s^{-1} (standard – background),
A_r = activity of ^{226}Ra in the bubbler (Bq),
t_1 = ingrowth time of ^{222}Rn (h),
t_2 = decay time of ^{222}Rn occurring between de-emanation and the midpoint of counting (h), and
λ = decay constant of ^{222}Rn (0.00755 h^{-1}).

10.17 Carry out the background measurements prior to each sample measurement. Perform calibrations with each scintillation chamber used, and repeat at least annually or when calibration verification shows an unacceptable change in efficiency.

10.18 To remove ^{222}Rn and prepare the scintillation chamber for reuse, evacuate and cautiously refill with helium. Repeat this evacuation and refilling twice. For chambers containing high activities of ^{222}Rn repeat the procedure more often.

11. Procedure

11.1 *Soluble ^{226}Ra :*

11.1.1 Filter the sample through a membrane filter. Take a 1-L aliquot, or a smaller volume so as not to exceed 1.11 Bq of ^{226}Ra, and transfer to a 1500-mL beaker. Acidify with 20 mL of concentrated HCl (sp gr 1.19) per litre of filtrate, heat, and add with vigorous stirring 50 mL of $BaCl_2$ working carrier solution. For sample volumes less than a litre, dilute to 1 L with 0.24M HCl prior to the addition of carrier.

11.1.2 Cautiously and with vigorous stirring, add 20 mL of H_2SO_4 (sp gr 1.84). Cover the beaker and allow to stand overnight.

11.1.3 Filter the supernate through a membrane filter, using 0.05M H_2SO_4 to transfer the Ba-Ra precipitate to the filter. Wash the precipitate twice with 0.05M H_2SO_4.

11.1.4 Place the filter in a platinum crucible, add 0.5 mL of concentrated HF (sp gr 1.15) and 3 drops (0.15 mL) of $(NH_4)_2SO_4$ solution, and evaporate to dryness.

11.1.5 Carefully ignite the filter and residue over a small flame until the carbon is burned off (after charring of filter, a Meeker burner may be used).

11.1.6 Cool, add 1 mL of concentrated H_3PO_4 (sp gr 1.69), and heat on a hot plate to about 200°C. Gradually raise temperature to about 300 to 400°C for 30 min.

11.1.7 Swirl the crucible over a low Bunsen flame, adjusted to avoid spattering. Swirl so that the crucible walls are covered with hot concentrated H_3PO_4 (sp gr 1.69). Continue to heat until the $BaSO_4$ dissolves to give a clear melt (just below redness), and then heat for 1 min more to ensure removal of SO_3.

11.1.8 Cool, fill the crucible one-half full with 6M HCl, heat on a steam bath, then gradually add the water to within 2 mm of the top of the crucible.

11.1.9 Evaporate on the steam bath until there are no more vapors of HCl.

11.1.10 Add 6 mL of 1 M HCl, swirl, and warm to dissolve the $BaCl_2$ crystals.

11.1.11 Close the inlet stopcock of a greased and tested radon bubbler. Add a drop of water to the fritted disk and transfer the sample from the platinum crucible to the bubbler using a medicine dropper. Rinse the crucible with at least three 2-mL portions of water. Add water until the bubbler is ⅔ to ¾ full.

11.1.12 De-emanate the solution in accordance with 10.2 and 10.3.

11.1.13 After 3 weeks of ^{222}Rn ingrowth, de-emanate and count as described in 10.7 through 10.15.

11.1.14 Transfer the solution in the bubbler to a gamma-counting container. Wash the bubbler thoroughly with 1M HCl and combine with the sample in a container. Measure the barium-133 activity in a gamma-ray counter. For a discussion of gamma ray counting refer to Practice D3649. Calculate the sample yield, *RY,* by dividing the barium-133 activity of the sample by the barium-133 activity of a 50-mL aliquot of $BaCl_2$ carrier working solution counted under identical conditions of volume and geometry as the sample.

11.1.15 The sample may be stored for a second ingrowth or discarded and the bubbler cleaned for reuse. A thorough rinsing with 0.24M HCl is a satisfactory cleaning procedure. If however, the ^{226}Ra in a bubbler exceeded 0.37 Bq (10 pCi), a more rigorous cleaning may be necessary. Remove the stopcock grease, using a cloth and solvent, and then immerse for 1 h in hot (90 to 100°C) EDTA – Na_2CO_3 solution. Heat the bubblers gradually to avoid thermal shock to the fritted glass disks. Remove, cool at room temperature, and rinse with distilled water. Immerse in 1M HCl and warm for about 30 min. Remove, cool, and rinse with distilled water. Dry and regrease the stopcocks.

11.1.16 Remove ^{222}Rn from the scintillation chamber as described in 10.18.

11.2 *Suspended ^{226} Ra:*

11.2.1 Filter a volume of sample containing up to 1.11 Bq (30 pCi) of ^{226}Ra and 1.0 g of inorganic suspended matter through a membrane filter. If desired the filter and suspended matter from step 11.1.1 may be used.

11.2.2 Place the membrane filter and suspended material into a weighed 30-mL platinum crucible. Carefully ignite over a small flame until the carbon is burned off (after charring of the filter, a Meeker burner may be used).

11.2.3 Cool and weigh the crucible to estimate the residue.

11.2.4 Add 8 g of flux for each gram of residue, but not less than 2 g of flux, and mix with a glass stirring rod.

11.2.5 Heat over a Meeker burner until melting begins, then more carefully to avoid spattering. Continue heating for 20 min after bubbling stops with occasional swirling of the crucible to mix the contents and achieve a uniform melt. A clear melt is usually obtained only when the suspended solids are present in small amounts or have a high silica content.

11.2.6 Remove the crucible from the burner and rotate it as the melt cools to distribute it in a thin layer on the crucible walls.

11.2.7 To a 500 mL beaker containing 120 mL H_2O, slowly add, with stirring, 20 mL of concentrated H_2SO_4 (sp gr 1.84) and 5 mL of 3 % H_2O_2 for each 8 g of flux used.

11.2.8 Place the crucible in the beaker, cover, and swirl the beaker to dissolve the melt.

11.2.9 When the melt is dissolved, lift the crucible with platinum-tipped tongs, and rinse with water, allowing rinse water to go into the beaker.

11.2.10 Save crucible for reuse in step 11.2.13.

11.2.11 Heat the solution and slowly add 50 mL of $BaCl_2$ working solution with vigorous stirring. Cover the beaker and allow to stand overnight for precipitation.

11.2.12 Add 1 mL of 3 % H_2O_2 and if the yellow color (from titanium) deepens, add additional H_2O_2 until there is no further color change.

11.2.13 Continue as described in steps 11.1.3 to 11.1.16.

11.3 *Soluble and Suspended ^{226}Ra:*

11.3.1 Take a 1-L aliquot of the thoroughly mixed sample, or a smaller volume so as not to exceed (1.11 Bq) of ^{226}Ra and transfer to a 1500-mL beaker. Acidify with 20 mL of concentrated HCl (sp gr 1.19) per litre of sample, heat, and add with vigorous stirring 50 mL of $BaCl_2$ working carrier solution. For sample volumes less than a litre, dilute to 1 L with 0.24M HCl prior to the addition of carrier.

11.3.2 Cautiously and with vigorous stirring add 20 mL of concentrated H_2SO_4 (sp gr 1.84). Cover the beaker and allow to stand overnight.

11.3.3 Filter the supernate through a membrane filter, using 0.05M H_2SO_4 to transfer the solids to the filter. Wash the solids twice with 0.05M H_2SO_4.

11.3.4 Continue as described in steps 11.2.2 to 11.2.10.

11.3.5 Digest the sample for 1 h on a steam bath and add 1 mL of 3 % H_2O_2. If the yellow color (from titanium) deepens, add additional H_2O_2 until there is no further color change.

11.3.6 Continue as described in steps 11.1.3 to 11.1.16.

12. Calculation

12.1 Calculate the concentration of ^{226}Ra in becquerels per litre as follows:

$$AC_{226_{Ra}} = \frac{R_a - R_b}{E \times V_a \times RY \times (1 - e^{-\lambda t_1}) \times e^{-\lambda t_2}}$$

where:

$AC_{226}Ra$ = cactivity concentration of ^{226}Ra, (Bq/L),
R_a = sample aliquant count rate (s^{-1}),
R_b = vbackground count rate (s^{-1}),
E = calibration factor for the scintillation chamber (counts per disintegration of ^{222} Rn
V_a = volume of sample used, (L),
RY = recovery factor,
λ = decay constant of 222Rn (0.00755 h^{-1}),
t_1 = elapsed time between the first and second de-emanations (h)
t_2 = time interval between the second de-emanation and the midpoint of counting (h)

NOTE 2—If the user would like to correct for decay during the ingrowth time of the ^{222}Rn daughters in the scintillation chamber and decay time during counting, use the following formula:

$$AC_{226_{Ra}} = \frac{R_a - R_b}{E \times V_a \times RY \times (1 - e^{-\lambda t_1}) \times e^{-\lambda t^*_2}} \times \frac{\lambda t_3}{1 - e^{-\lambda t_3}}$$

WHERE:

t^*_2 = time interval between the second de-emanation and the start of counting (h), and
t_3 = sample aliquant count time (h).

12.2 Estimate the variance (squared standard uncertainty) of the net count rate, $R_n = R_a - R_b$, as follows:

$$u^2(R_n) = \frac{J \times R_n}{t_a} + R_b \times \left(\frac{1}{t_a} + \frac{1}{t_b}\right) \text{ if } R_n > 0, \quad (1)$$

$$u^2(R_n) = \frac{R_a}{t_a} + \frac{R_b}{t_b} \text{ if } R_n \le 0$$

where:

$u^2(R_n)$ = estimated variance of the net count rate (s^{-2}),
R_a = sample aliquant count rate (s^{-1}),
R_b = background count rate (s^{-1}),
J = oindex of dispersion for the net counts produced by ^{222}Rn and its progeny (Eq 2),
t_a = sample aliquant count time (s), and
t_b = background count time (s).

In Eq 1 the value of J is estimated by:

$$J = 1 + E \times M \quad (2)$$

where E is the calibration factor for the scintillation chamber and M is a factor whose value depends on the sample aliquant count time ta. The value of M can be obtained from Table 2 (using interpolation if necessary). Alternatively the value of M may be calculated using Eq 3:

$$M = \frac{c_6 + c_1 e^{-\lambda_1 t_a} + c_2 e^{-\lambda_2 t_a} + c_3 e^{-\lambda_3 t_a} + c_4 e^{-\lambda_4 t_a}}{1 - e^{-\lambda_1 t_a}} \quad (3)$$

where the decay constants λ through λ are given by:

λ_1 = $\lambda(^{222}Rn) = 2.098 \times 10^{-6}$ s^{-1}
λ_2 = $\lambda(^{218}Po) = 0.003\ 727$ s^{-1}
λ_3 = $\lambda(^{214}Pb) = 0.000\ 431$ s^{-1}
λ_4 = $\lambda(^{214}Bi) = 0.000\ 581$ s^{-1}

TABLE 2 Values of *M*

t_a / min	t_a / s	M
5	300	0.0888
10	600	0.1366
15	900	0.1663
20	1200	0.1877
30	1800	0.2208
60	3600	0.3010
90	5400	0.3676
120	7200	0.4200
150	9000	0.4600
180	10 800	0.4905
210	12 600	0.5138
240	14 400	0.5320
300	18 000	0.5582
400	24 000	0.5847
500	30 000	0.6006
600	36 000	0.6113
700	42 000	0.6189
800	48 000	0.6246
900	54 000	0.6290
1000	60 000	0.6325
2000	120 000	0.6485
3000	180 000	0.6538
∞	∞	0.6625

and where the coefficients c through c are given by

c_1 = –0.6665354
c_2 = 0.00012738936
c_3 = 0.0089406007
c_4 = –0.0050473988
c_5 = 0
c_6 = 0.66251481

12.3 Calculate the standard counting uncertainty (one sigma) for the activity concentration using the following equation:

$$u_{cC}(AC_{226_{Ra}}) = \frac{u(R_n)}{E \times Va \times RY \times (1 - e^{-\lambda t_1}) \times e^{-\lambda t_2}} \quad (4)$$

where $u_{cC}(AC_{226_{Ra}})$ denotes the standard counting uncertainty (Bq/L), $u(R_n)$ denotes the square root of the variance calculated by Eq 1, and all other symbols are as defined above.

12.4 Calculate the (total) combined standard uncertainty [kdm3] of the activity concentration as follows:

$$u_c(AC_{226_{Ra}}) = \sqrt{\frac{u^2(R_n)}{(E \times Va \times RY \times (1 - e^{-\lambda t_1}) \times e^{-\lambda t_2})^2} + AC^2_{226_{Ra}} \times (u_r{}^2(E) + u_r{}^2(V_a) + u_r{}^2(RY))} \quad (5)$$

where:

$u_c(AC_{226_{Ra}})$ = combined standard uncertainty (Bq/L),
$u^2(R_n)$ = variance of the net count rate (Eq 1),
$u_r(E)$ = relative standard uncertainty of the calibration factor,
$u_r(V_a)$ = relative standard uncertainty of the sample volume, and
$u_r(RY)$ = relative standard uncertainty of the fractional radium recovery.

12.5 A detection decision can be made if necessary by comparing the measured activity concentration $Ra_{226_{AC}}$ to the critical net activity concentration, which is given by:

$$L_c = \frac{1.645 \sqrt{R_b \times \left(\frac{1}{t_a} + \frac{1}{t_b}\right)}}{E \times RY \times V_a \times (1 - e^{-\lambda t_2})} \quad (6)$$

where L_c denotes the critical net activity concentration (Bq/L) and all other symbols are as defined above.

12.6 The *a priori* minimum detectable concentration (*MDC*) is calculated as follows:

$$MDC = \frac{2.71 \times J + 3.29 \sqrt{R_b \times \left(\frac{1}{t_a} + \frac{1}{t_b}\right)}}{E \times RY \times V_a \times (1 - e^{-\lambda t_2})} \quad (7)$$

where *MDC* denotes the minimum detectable concentration (Bq/L) and all other symbols are as defined above.

13. Precision and Bias[9]

13.1 The available data do not permit a precision and bias statement to be made in accordance with Practice D2777.

13.2 A limited collaborative study of this test method was conducted. Seven labs participated by processing one sample at four levels. These collaborative data were obtained on distilled water with reagent grade chemicals added to vary the hardness. The resultant hardness was 125 mg/L for levels A and B and 610 mg/L for levels C and D.

13.3 *Precision*—The overall precision of this test method within its designated range varies with the quantity being tested according to Fig. 4. The relative precision for this test method is approximately 5 %.

13.4 *Bias*—A limited collaborative study of this test method indicated that a negative bias of approximately 3 % was present, based on the average recovery of the known amount of ^{226}Ra added. Recoveries were as follows:

Level	pCi/L	Added, Bq/L	Found, Bq/L	Bias, %
A	12.12	0.448	0.4351	–2.9
B	8.96	0.331	0.3221	–2.7
C	25.53	0.944	0.9214	–2.4
D	18.84	0.697	0.6831	–2.0 [kdm4]

14. Quality Assurance

14.1 In order to provide reasonable assurance that the analytical results obtained using this method are valid and accurate within the confidence limits of the 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. Laboratory or project quality assurance plans may contain more restrictive process QC requirements. The following minimum QC procedures must be followed when running the test method:

14.2 *Initial Demonstration of Laboratory/Instrument/Analyst Capability*

14.2.1 If a laboratory or analyst has not performed this 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, analyst, or instrument capability. A

[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1120.

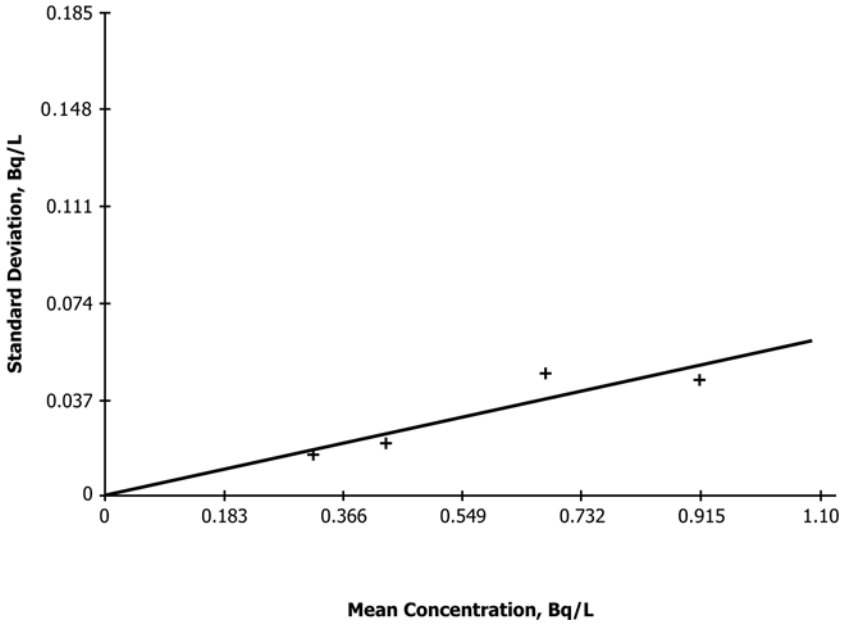

FIG. 4 Overall Standard Deviation versus Mean Concentration

significant change is defined as any change, repair, or alteration of any component in the system, which may be expected to affect the response of the measurement system.

14.2.2 Analyze seven replicates of a standard solution prepared from an independent reference material (IRM) containing accurately known concentrations of ^{226}Ra at concentrations sufficient to minimize counting uncertainty to 2 % or less at one sigma. Each replicate must be taken through the complete analytical test method including any sample pretreatment steps. The matrix used for the demonstration should represent a water sample typical for which the method will be used, e.g. surface water.

14.2.3 Calculate the mean and standard deviation of the seven replicate values and compare to the acceptable ranges of precision and mean bias of 10 % and ± 10 % respectively, based on a review of the collaborative study data. Test Method D5847 should be consulted on the manner by which precision and mean bias are determined from the initial demonstration study. This method shall not be used for official samples until precision and bias are met.

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

14.2.5 Calculate the ^{226}Ra activity for each of these three blank solutions. The result of each of the three blank solutions should be below the critical level.

14.3 *Calibration and Calibration Verification Standards*
Standards used in this method shall be traceable to a national standards laboratory (such as NIST or NPL).

14.3.1 The yield of the ^{133}Ba tracer shall be calculated for each sample and associated QC sample. The standard uncertainty (k = 2) of the yield should be less than 10 % (approximately 400 net counts).

14.3.2 This yield should be reported along with the reported analytical data.

14.4 The detector efficiency shall be verified monthly or prior to use, whichever is longer, using a source traceable to a national standards laboratory.

14.5 *Laboratory Control Sample (LCS)*

14.5.1 To ensure that the test method is in control, analyze an LCS with each batch of no more than 20 samples. The activity 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 must be taken through all steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limit of ±20 % of the expected value.

14.5.2 If the result is not within these limits reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

14.6 *Method Blank (Blank)*
Analyze a reagent water test blank with each batch of no more than 20 samples. This method blank should be taken through all steps of the analytical method. The concentration of analytes found in the blank should be less than half the MDC. If the concentration of the analytes is above the limit, provide an explanation in the case narrative.

14.7 *Matrix Spike (MS)*
The performance of a matrix spike analysis with every batch is not required given the use of a tracer with each sample. The tracer chemical yield would indicate any problems with interferences in a specific sample matrix. Section 14.2 addresses the use of the tracer chemical yield as a measure of result quality.

14.8 *Duplicate*

14.8.1 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 to ensure they agree with a 99 % confidence level. This calculation is performed using the determined standard uncertainty associated with each result as shown below.

$$DER = \frac{\left| AC_{^{226}Ra_{Orig}} - AC_{^{226}Ra_{Dup}} \right|}{\sqrt{\left(CSU_{^{226}Ra_{Orig}}\right)^2 + \left(CSU_{^{226}Ra_{Dup}}\right)^2}} \leq 2.58 \quad (8)$$

where:

AC_S = original sample activity concentration,
AC_D = duplicate sample activity concentration,
$u(AC_S)$ = combined standard uncertainty of the original sample,
$u(AC_D)$ = combined standard uncertainty of the duplicate sample.

14.8.2 In those cases where there is insufficient sample volume to allow performance of a duplicate sample analysis, a duplicate Calibration Verification Standard should be performed and analyzed using the same DER criteria.

14.8.3 The value of DER should be less than or equal to 3.0. If the sample duplicate or Control Standard 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.

14.9 *Independent Reference Material*

In every quarter that the method is performed verify the quantitative value produced by the test method by analyzing an IRM submitted on at least single-blind basis (if practical) to the laboratory. The concentration of analyte in the national standards laboratory traceable reference material 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.

15. Keywords

15.1 coprecipitation; emanation; radioactivity; ^{226}Ra; ^{222}Rn; water

References

(1) Multi-Agency Radiological Laboratory Analytical Protocols Manual – EPA402-B-04-001A, NUREG1576, NTIS PB2004- 105421, July 2004