



Standard Test Method for Alpha-Particle-Emitting Isotopes of Radium in Water¹

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1. Scope

1.1 This test method covers the separation of dissolved radium from water for the purpose of measuring its radioactivity. Although all radium isotopes are separated, the test method is limited to alpha-particle-emitting isotopes by choice of radiation detector. The most important of these radioisotopes are radium-223, radium-224, and radium-226. The lower limit of concentration to which this test method is applicable is 3.7×10^{-2} Bq/L (1 pCi/L).

1.2 This test method may be used for absolute measurements by calibrating with a suitable alpha-emitting radioisotope such as radium-226, or for relative methods by comparing measurements with each other. Mixtures of radium isotopes may be reported as equivalent radium-226. Information is also provided from which the relative contributions of radium isotopes may be calculated.

1.3 *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.* For a specific precautionary statement, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:

- C 859 Terminology Relating to Nuclear Materials²
- D 1129 Terminology Relating to Water³
- D 1193 Specification for Reagent Water³
- D 1943 Test Method for Alpha Particle Radioactivity of Water⁴
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³
- D 3370 Practices for Sampling Water³
- D 3454 Test Method for Radium-226 in Water⁴
- D 3648 Practices for the Measurement of Radioactivity⁴

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

3. Terminology

3.1 Definition:

3.1.1 For definitions of terms used in this standard, see Terminology C 859 and D 1129. For terms not included in these, reference may be made to other published glossaries (1, 2).⁵

4. Summary of Test Method

4.1 Radium is collected from the water by coprecipitation with mixed barium and lead sulfates. The barium and lead carriers are added to a solution containing alkaline citrate ion which prevents precipitation until interchange has taken place. Sulfuric acid is then used to precipitate the sulfates, which are purified by nitric acid washes. The precipitate is dissolved in ammoniacal EDTA. The barium and radium sulfates are reprecipitated by the addition of acetic acid, thereby separating them from lead and other radionuclides. The precipitate is dried on a planchet weighed to determine the chemical yield, and alpha-counted to determine the total disintegration rate of alpha-particle-emitting radium isotopes. This procedure is based upon published ones (3, 4).

5. Significance and Use

5.1 Radium is one of the most radiotoxic elements. Its isotope of mass 226 is the most hazardous because of its long half-life. The isotopes 223 and 224, although not as hazardous, are of some concern in appraising the quality of water.

5.2 The alpha-particle-emitting isotopes of radium other than that of mass 226 may be determined by difference if radium-226 is measured separately, such as by Test Method D 3454. Note that one finds radium-226 and -223 together in variable proportions (5, 6), but radium-224 does not normally occur with them. Thus, radium-223 often may be determined by simply subtracting the radium-226 content from the total: and if radium-226 and -223 are low, radium-224 may be determined directly. The determination of a single isotope in a mixture is less precise than if it occurred alone.

⁵ The boldface numbers in parentheses refer to a list of references at the end of this standard.

6. Interferences

6.1 A barium content in the sample exceeding 0.2 mg will cause a falsely high chemical yield.

7. Apparatus

7.1 For suitable gas-flow proportional or alpha-scintillation counting equipment, refer to Test Method D 1943.

8. Reagents

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.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 precision, or increasing the bias, of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III.

8.3 *Radioactivity Purity Of Reagents*—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 *Acetic Acid, Glacial* (sp gr 1.05).

8.5 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH₄OH).

8.6 *Ammonium Hydroxide* (1+1) Mix 1 volume of concentrated ammonium hydroxide (NH₄OH, sp gr 0.90) with 1 volume of water.

8.7 *Barium Nitrate Carrier Solution* (10 mg Ba/mL)—Dissolve 1.90 g of barium nitrate (Ba(NO₃)₂) in water and dilute to 100 mL.

8.8 *Citric Acid Solution* (350 g/L)—Dissolve 350 g of citric acid (anhydrous) in water and dilute to 1 L.

8.9 *Disodium Ethylenediamine Tetraacetate Solution* (93 g/L)—Dissolve 93 g of disodium ethylenediamine tetraacetate dihydrate in water and dilute to 1 L.

8.10 *Lead Nitrate Carrier Solution* (104 mg Pb/mL)—Dissolve 33.2 g of lead nitrate (Pb(NO₃)₂) in water and dilute to 200 mL.

8.11 *Methyl Orange Indicator Solution*—Dissolve 1.0 g of methyl orange in water and dilute to 1 L.

8.12 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃).

8.13 *Sulfuric Acid* (1 + 1)—Cautiously add with stirring 1 volume of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) to 1 volume of water.

9. Safety Precautions

9.1 When diluting concentrated acids, always use safety glasses and protective clothing, and add the acid to the water.

⁶ *Reagent Chemicals, American Chemical 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*, BDN Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Growth of Alpha Activity into Initially Pure Radium-226

Time, h	Correction, F
0	1.0000
1	1.0160
2	1.0363
3	1.0580
4	1.0798
5	1.1021
6	1.1238
24	1.4892
48	1.9054
72	2.2525

10. Sampling

10.1 Collect the sample in accordance with Practices D 3370 as applicable.

10.2 Sample 1 L, or a smaller volume, provided that it is estimated to contain from 3.7 to 370 Bq (100 to 10 000 pCi) of radium. Add 10 mL of HNO₃/L of sample.

11. Calibration and Standardization

11.1 For absolute counting, the alpha-particle detector must be calibrated to obtain the ratio of count rate to disintegration rate. Use NIST traceable radium-226 standards. Analyze two or more portions of such solution, containing known disintegration rates, in accordance with Section 12. After counting, correct the measured activity for chemical yield, and calculate the efficiency, *E* (see Section 13), as the ratio of the observed counting rate to the known disintegration rate.

12. Procedure

12.1 Add to a measured volume of sample 5 mL of citric acid and make alkaline (pH > 7.0) with NH₄OH. Confirm the alkalinity with pH-indicating paper or strip. Add 2 mL of lead carrier and 1.00 mL of barium carrier, and mix.

12.2 Heat to boiling and add 10 drops of methyl orange pH-indicator solution. With stirring, add H₂SO₄ (1 + 1) until the solution becomes pink, then add 5 drops more.

12.3 Digest the precipitate with continued heating for 10 min. Let cool and collect the precipitate in a centrifuge tube. When large volumes are handled, collection will be facilitated by first letting the precipitate settle, and then decanting most of the clear liquid. Centrifuge then discard the supernatant liquid.

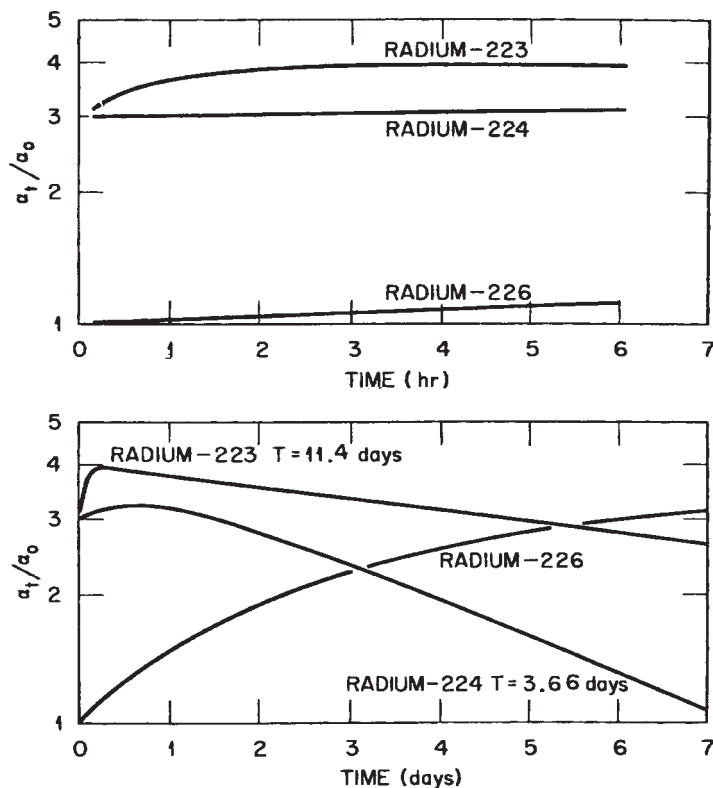
12.4 Wash the precipitate with 10 mL of HNO₃, centrifuge, and discard the washings. Repeat this wash the precipitate.

12.5 Dissolve the precipitate in 10 mL of water, 10 mL of EDTA solution, and 4 mL of NH₄OH (1 + 1). Warm if necessary to effect dissolution.

12.6 Reprecipitate barium sulfate (BaSO₄) by the dropwise addition of acetic acid, then add 3 drops more. Record the time. Centrifuge, then discard the supernatant liquid. Add 10 mL of water, mix well, centrifuge, and discard the supernatant liquid.

12.7 Clean, flame, cool, and weigh a stainless steel planchet that fits the alpha-particle counter being used. Transfer the precipitate to the planchet with a minimum of water. Dry, flame, and weigh the precipitate to determine the chemical yield.

12.8 Promptly count the planchet in an appropriate alpha-particle counter, recording the time. Reserve the planchet for additional measurements, if desired (see 13.4).



NOTE 1—Vertical scale is ratio of radioactivity, a , at later time, t , to radioactivity at initial time of separation. T is half-life.

FIG. 1 Growth and Decay of Alpha Activity into Initially Pure Radium Isotopes

12.9 Measure the background count rate of the detector by counting an empty, cleaned and flamed planchet for at least as long as the precipitate was counted.

13. Calculation

13.1 Calculate the fractional radium recovery (chemical yield of the carrier) as follows:

$$Y = (M_B - M_p) / 0.01699 \quad (1)$$

where:

M_B = mass of planchet with the dried barium sulfate precipitate, g,

M_p = mass of planchet only, g, and
0.01699 = mass of barium sulfate precipitate if all of the added barium carrier were recovered, g.

13.2 Calculate the concentration D of alpha-emitting radium radionuclides as radium-226 in becquerels (Bq) of radium per litre as follows:

$$D = C/EVYF \quad (2)$$

where:

C = alpha counting rate, net counts/s, (sample counts/s minus background counts/s)

E = detection efficiency of the counter for alpha particles, counts/disintegration,

V = sample volume, L

Y = fractional chemical yield for the separation, and

F = correction for the ingrowth of descendents between the time of separation (see 12.6 and Table 1) and the time of counting.

13.3 See section 10 of Practices D 3648 concerning the overall uncertainty in a measurement.

13.4 The total propagated uncertainty (1σ) for the concentration of alpha-emitting radium isotopes is calculated as follows:

$$\sigma_D (Bq)/L = D(Bq/L) * [(\sigma_N/N)^2 + (\sigma_E/E)^2 + (\sigma_V/V)^2 + (\sigma_Y/Y)^2]^{1/2} \quad (3)$$

where:

σ_N = one sigma uncertainty of the net sample counting rate,

σ_E = one sigma uncertainty of the detection efficiency of the alpha counter,

σ_V = one sigma uncertainty of the sample volume, and

σ_Y = one sigma uncertainty in the fractional radium recovery.

13.4.1 The one sigma uncertainty (σ_N) in the net sample counting rate is calculated from:

$$\sigma_N = (G/T_G^2 + B/t_B^2)^{1/2} \quad (4)$$

where:

G = the sample gross counting rate, (s^{-1}) (S^{-1})

B = the background counting rate, (s^{-1}) (S^{-1}),

t_G = the sample counting time, s, and

t_B = the background counting time, s.

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

$$MDC (Bq/L) = \frac{2.71 + 4.65 * (t_G * B)^{1/2}}{t_G * E * Y * V * I} \quad (5)$$

where:

t_G = the counting duration, s, and other terms are as defined earlier.

13.6 The relative contribution of various radium isotopes, if desired, may be obtained by alpha-particle spectroscopy (7). Otherwise, repeated measurements of the activity permit estimation of the isotopic composition. Table 2 lists radioactive properties of radium-226, radium-224, radium-223, and their descendents (8). Fig. 1 shows characteristic growth and decay curves for the three important isotopes, and equations and tables have been published (9).

TABLE 2 Important Alpha-Particle-Emitting Isotopes of Radium and their Descendents^A

Nuclide		Radiation		Half-Life
Parent	Descendents	Type ^B	Energy, MeV ^C	
²²⁶ Ra		α	4.784 (94.5 %) 4.601 (5.5 %)	1.60 × 10 ³ years
	²²² Rn	α	5.490 (99.9 %)	3.83 days
	²¹⁸ Po	α	6.003 (100.0 %)	3.11 min
	²¹⁴ Pb	β (γ)		27 min
	²¹⁴ Bi	β (γ)		19.9 min
	²¹⁴ Po			7.687 (99.9 %) 5.686 (95.1 %) 5.449 (4.9 %)
²²⁴ Ra		α	6.288 (99.9 %) 6.779 (100.0 %)	55.6 s 0.15 s
	²²⁰ Rn	α		10.6 h
	²¹⁶ Po	α		1.01 h
	²¹² Po	β (γ)		
	²¹² Bi	β (64.1 %) (γ) α (35.9 %)		
			6.090 (9.6 %) 6.051 (25.2 %) others	
	²¹² Po	α	8.784	0.30 μs
	²⁰⁸ Tl	β (γ) α (γ)		3.05 min 11.4 days
²²³ Ra			5.716 (52.5 %) 5.607 (24.2 %) 5.747 (9.5 %) 5.540 (9.2 %) others	
	²¹⁹ Rn	α (γ)	6.819 (81 %) 6.553 (12 %) 6.425 (7.5 %)	3.96 s
	²¹⁵ Po	α	7.386 (100.0 %)	1.8 ms
	²¹¹ Pb	β (γ)		36.1 min
	²¹¹ Bi	α (γ)	6.623 (83.8 %) 6.279 (16.0 %)	2.14 min
	²⁰⁷ Tl	β		4.77 min

^ADescendents with half-lives of less than 30 days.

^BGamma ray indicated only when emission probability per decay is more than 5 % and energy is greater than 0.1 MeV.

^CEnergy indicated for alpha radiation only. Emission probability per decay in parentheses.

TABLE 3 Precision Data

Bq/L	s(o)	s(t)
0.455	0.057	0.149
4.588	0.303	0.577
45.51	5.996	7.588

TABLE 4 Determination of Bias

Amount Added Bq/L	Mean	Bias, ±	Bias, %
0.455	0.522	0.067	14.7
4.588	4.67	0.082	1.7
45.51	47.49	1.98	4.3

14. Precision and Bias ⁷

14.1 A limited collaborative test of this test method was conducted. Seven laboratories participated by processing samples at three levels. The results from one laboratory were rejected as outliers according to the statistical tests outlined in Practice D 2777. These collaborative data were obtained on distilled water without chemical interferences. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

⁷ Supporting data for this test method have been filed at ASTM Headquarters. Request RR D19-1003.

14.2 *Precision*—The overall precision of this test method within its designated range varies with the quantity being tested. See Table 3 for the precision data obtained.

14.3 *Bias*—The limited collaborative study of this test method indicated that there was no statistically significant observed bias in the test method for any level. See Table 4 for the bias data obtained.

15. Quality Control

15.1 Whenever possible, the project leader, as part of the external quality control program, should submit quality control samples to the analyst along with routine samples in such a way that the analyst does not know which of the samples are the quality control samples. These external quality control samples which usually include duplicate and blank samples, should test sample collection and preparation as well as sample analysis whenever this is possible. In addition, analysts are expected to run internal quality control samples that will indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples should be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types: blank samples, replicate samples, reference materials, control samples and "spiked" samples.

16. Keywords

16.1 alpha particles; radioactivity; radium isotopes; water

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