

SECTION 6
ALPHA-EMITTING RADIUM ISOTOPES IN DRINKING WATER
METHOD 903.0

1.0 Scope and Application

- 1.1 This method covers the measurement of the total soluble alpha emitting radioisotopes of radium, namely radium-223, radium-224 and radium-226 in drinking water. Part 141 of the Interim Primary Drinking Water Regulations, Federal Register, July 9, 1976, has promulgated the maximum contaminant levels of radium-226 plus radium-228 (see Method 904.0) not to exceed 5 pCi/L.
- 1.2 Although the method does not always give an accurate measurement of the radium-226 content of the sample (when other radium alpha emitters are present), it can be used to screen samples. When the total radium alpha activity of a drinking water sample is greater than 5 pCi/L, then the radium-226 analysis (method 903.1) is required.
- 1.3 Since this method provides for the separation of radium from other water dissolved solids in the sample, the sensitivity of the method is a function of sample size, reagent and instrument background, counting efficiency and counting time. The National Interim Primary Drinking Water Regulations (NIPDWR) require a sensitivity of measurement of 1 pCi/L for radium-226. Using a low background alpha counting system, liter or more size sample aliquots, and sufficient counting times, the detection limit of 1 pCi/L can easily be met.
- 1.4 Absolute measurement can be made by calibrating the alpha detector with standard radium-226 in the geometry obtained with the final precipitate.

2.0 Summary of Method

- 2.1 The radium in the drinking water sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Citric acid is added to the drinking water sample to assure that complete interchange occurs before the first precipitation step. The final BaSO₄ precipitate which includes radium-226, radium-224 and radium-223 is alpha counted to determine the total disintegration rate of the radium isotopes.
- 2.2 The radium activities are counted in an alpha counter where efficiency for determining radium-226 has been calibrated with a standard of known radium-226 activity. By making a correction for the ingrowth of alpha activity in radium-226 for the elapsed time after separation, one can determine radium activity in the sample. Since some daughter ingrowth can occur before the separated radium is counted, it is necessary to make activity corrections for the count rate. A table of ingrowth factors for various times after radium separation is provided. (See Sec. 9.2).

3.0 Sample Handling and Preservation - (See Section 3 - Method 900.0)

4.0 Interferences

- 4.1 Inasmuch as the radiochemical yield of the radium activity is based on the chemical yield of the BaSO_4 precipitate, the presence of significant natural barium in the sample will result in a falsely high chemical yield.
- 4.2 Radium isotopes are separated from other alpha emitting radionuclides by this method.
- 4.3 The alpha count of the separated radium must be corrected for its partially ingrown alpha emitting daughters.

5.0 Apparatus - See Appendix D for details and specifications.

- 5.1 Alpha scintillation or a gas-flow proportional alpha particle counting system with low background (< 1 cpm)
- 5.2 Stainless steel counting planchets
- 5.3 Electric hot plate
- 5.4 Drying oven and/or drying lamp
- 5.5 Glass desiccator
- 5.6 Analytical balance
- 5.7 Centrifuge
- 5.8 Glassware

6.0 Reagents

- 6.1 Distilled or deionized water.
- 6.2 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp.gr. 1.05, 99.8%.
- 6.3 Ammonium Sulfate, 200 mg/mL: Dissolve 20 grams $(\text{NH}_4)_2\text{SO}_4$ in a minimum of water and dilute to 100 mL.
- 6.4 Barium carrier, 16 mg/mL, standardized: Dissolve 2.846g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water, add 0.5 mL 16N HNO_3 , and dilute to 100 mL with water.

Standardization: (in triplicate)

Pipette 2.0 mL carrier solution into a centrifuge tube containing 15 mL water. Add 1 mL 18N H_2SO_4 with stirring and digest precipitate in a water bath for 10 minutes.

Cool, centrifuge and decant the supernatant. Wash precipitate with 15 mL water. Transfer the precipitate to a tared stainless steel planchet with a minimum of water. Dry under infra-red lamp, store in desiccator and weigh as BaSO₄.

- 6.5 Citric acid, 1M: Dissolve 19.2g C₆H₈O₇·H₂O in water and dilute to 100 mL.
- 6.6 EDTA reagent, basic, (0.25M): Dissolve 20g NaOH in 750 mL water, heat and slowly add 93g disodium ethylenedinitrioloacetate dihydrate (Na₂C₁₀H₁₄O₈N₂·2H₂O). Heat and stir-until dissolved, filter through coarse filter paper and dilute to 1 liter.
- 6.7 Lead carrier, 15 mg/ml: Dissolve 2.4g Pb(NO₃)₂ in water, add 0.5 mL 16N HNQ and dilute to 100 mL with water.
- 6.8 Sodium hydroxide, 6N: Dissolve 24g NaOH in 80 mL water and dilute to 100 mL
- 6.9 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H₂SO₄ (conc.) with 1 volume of water.
- 6.10 Sulfuric acid, 0.1N: Mix 1 volume 18N H₂SO₄ with 179 volumes of water.

7.0 Calibrations

The counting efficiency for radium alpha particles with barium sulfate carrier present must be determined using a standard (known) radium alpha activity and 32 mg of barium carrier as BaSO₄ (same carrier amount used with samples). This is done with spiked distilled water samples and the procedure for regular samples is followed. Note the time of the Ra-BaSO₄ precipitation.

- 7.2 The radium-alpha counting efficiency, E, is calculated as follows:

$$E \text{ (cpm/dpm)} = \frac{C}{A \times I}$$

where:

C = sample net cpm (gross counts minus background divided by the counting time in minutes).

A = dpm of radium-226 added to the sample.

I = ingrowth factor for the elapsed time from Ra-BaSO₄ precipitation to mid-point of counting time.

8.0 Procedure

- 8.1 To a 1000-mL drinking water sample, add 5 mL 1M C₆H₈O₇·H₂O, 1 mL lead carrier, and 2.0 mL barium carrier, and heat to boiling.

- 8.2 Cautiously, with vigorous stirring, add 20 mL 18N H₂SO₄. Digest 5 to 10 minutes and let the mixed BaSO₄-PbSO₄ precipitate settle overnight. Decant and discard supernate.
- 8.3 Transfer the precipitate to a centrifuge tube with a minimum amount of 0.1N H₂SO₄. Centrifuge and discard supernate.
- 8.4 Wash the precipitate twice with 0.1N H₂SO₄. Centrifuge and discard washes.
- 8.5 Dissolve the precipitate by adding 15 mL basic EDTA reagent; heat in a hot water bath and add a few drops 6N NaOH until solution is complete.
- 8.6 Add 1 mL (NH₄)₂SO₄ (200 mg/mL) and stir thoroughly. Add 17.4N CH₃COOH dropwise until precipitation begins, then add 2 mL extra. Digest 5 to 10 minutes.
- 8.7 Centrifuge, discard the supernate, and record time.

Note: At this point, the separation of the BaSO₄ is complete and the radon (and daughters) ingrowth commences.

- 8.8 Wash the BaSO₄ precipitate with 15 mL water, centrifuge, and discard wash.
- 8.9 Transfer the precipitate to a tared stainless-steel planchet with a minimum of water, and dry under infra-red lamps.

Note: Drying should be rapid but not too vigorous to minimize any loss of radon-222 that has already grown into the precipitate.

- 8.10 Cool, weigh, and store in desiccator.
- 8.11 Count in a gas-flow internal proportional counter or an alpha scintillation counter to determine the alpha activity.

9.0 Calculation

- 9.1 Calculate the radium-226 concentration, D, (which would include any radium-224 and radium-223 that is present) in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times EVR \times I}$$

where:

C = net count rate, cpm

E = counter efficiency for radium-226 in BaSO₄ predetermined for this procedure (see Sec. 7.2).

V = liters of sample used

R = fractional chemical yield

I = ingrowth correction factor (See Sec. 9.2)

2.22 = conversion factor from dpm/pCi.

- 9.2 It is not always possible to count the BaSO₄ precipitate immediately after separation, therefore, corrections must be made for the ingrowth of the radium-226 daughters between the time of separation and counting according to the following table:

Hours from separation to counting	Ingrowth correction factor
0	1.00
1	1.02
2	1.04
3	1.06
4	1.08
5	1.10
6	1.12
24	1.49
48	1.91
72	2.25
96	2.54
120	2.78
144	2.99
192	3.29
240	3.51

10.0 Precision and Accuracy

- 10.1 Precision and accuracy data for this method is taken from a survey of analyses of radium in water samples in the EMSL-Las Vegas intercomparison program for the period September 1977 to January 1979. Some of the laboratories participating in the

EMSL-Las Vegas intercomparison program used this method because it was included in the approved methods and they did not have the capability for analyzing radium-226 by radon-222 emanation, (Method 903.1), which was also an approved method.

10.2 Eleven laboratories participated in from 1 to 7 of 8 intercomparison studies and analyzed 46 test samples for radium-226 by this method. Of the 46 tests, the data for 40 tests (in triplicate, for a total of 120 aliquots) was used for the laboratory performance statistical analysis. Of the 40 tests used, 29 tests (87 aliquots analyzed) gave acceptable results (results within 3 sigma of the known value, with 1 sigma equal to 15% of the known value). The extent of acceptability in the 40 tests (29 acceptable) was 72.5%.

10.3 The 8 intercomparison studies were conducted quarterly from September 1977 to January 1979. Two of the studies were performance studies in which the samples contained other radionuclides. Also, samples in all of the studies contained a known quantity of radium-228 activity (with the thorium-228 and radium-224 daughters partially ingrown).

10.4 Radium-226, radium-228, and radium-224 activities in study samples:

pCi/L (at separation)			
Study	Radium-226	Radium-228	Radium-224
1	3.5	9.3	0.4
2	10.2	14.6	1.1
3	5.5	16.7	1.7
4	6.5	7.9	0.8
(performance)			
5	3.7	5.6	0.7
6	6.8	20.8	3.0
7	9.2	8.9	1.5
8	5.0	5.4	0.8
(performance)			

10.5 It can be seen from the above table that the radium-224 was a significant contributor to the alpha activity of precipitated radium activity and therefore the samples were biased high for a radium-226 analysis by this method. A waiting period of 14 days after radium separation and purification before counting for alpha activity would reduce the radium-224 contribution to less than 0.1 of its activity at purification (radium-224 separation from its thorium-228 parent). The count would then need to be corrected for the ingrown radon-222 and its alpha emitting daughters.

16.6 The 72.5% acceptable results obtained by this method, even with the samples biased high, show the method to be an acceptable one for screening drinking water samples for radium-226.

Bibliography

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2. Kirby, H.W., Decay and Growth Tables for the Naturally Occurring Radioactive Series, Anal. Chem. 26 1063-1071 (1954).
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