

ALPHA-EMITTING RADIUM ISOTOPES

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 surface and ground waters.

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 is required. If the level of radium-226 exceeds 3 pCi/L, the sample must also be measured for radium-228 (Method 9320).

1.3 Because 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.

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 surface water or ground water sample is collected by coprecipitation with barium and lead sulfate and purified by reprecipitation from EDTA solution. Citric acid is added to the water sample to assure that complete interchange occurs before the first precipitation step. The final BaSO_4 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. Because 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 in Paragraph 7.14.

3.0 INTERFERENCES

3.1 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.

3.2 Radium isotopes are separated from other alpha-emitting radionuclides by this method.

3.3 The alpha count of the separated radium must be corrected for its partially ingrown alpha-emitting daughters.

4.0 APPARATUS AND MATERIALS

4.1 Alpha scintillation or a gas-flow proportional alpha particle counting system with low background (<1 cpm).

4.2 Stainless steel counting planchets.

4.3 Electric hot plate.

4.4 Drying oven and/or drying lamp.

4.5 Glass desiccator.

4.6 Analytical balance.

4.7 Centrifuge.

4.8 Glassware.

5.0 REAGENTS

5.1 Distilled or deionized water (Type II).

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

5.3 Ammonium sulfate, 200 mg/mL: Dissolve 20 g $(\text{NH}_4)_2\text{SO}_4$ in a minimum of water and dilute to 100 mL.

5.4 Barium carrier, 16 mg/mL, standardized:

5.4.1 Dissolve 2.846 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water, add 0.5 mL 16 N HNO_3 , and dilute to 100 mL with water.

5.4.2 To perform standardization (in triplicate): Pipette 2.0 mL carrier solution into a centrifuge tube containing 15 mL water. Add 1 mL 18 N H_2SO_4 with stirring and digest precipitate in a water bath for 10 min. 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 infrared lamp, store in desiccator, and weigh as BaSO_4 .

5.5 Citric acid, 1 M: Dissolve 19.2 g $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ in water and dilute to 100 mL.

5.6 EDTA reagent, basic (0.25 M): Dissolve 20 g NaOH in 750 mL water, heat and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$). Heat and stir until dissolved; filter through coarse filter paper and dilute to 1 liter.

5.7 Lead carrier, 15 mg/mL: Dissolve 2.397 g $\text{Pb}(\text{NO}_3)_2$ in water, add 0.5 mL 16 N HNO_3 , and dilute to 100 mL with water.

5.8 Sodium hydroxide, 6 N: Dissolve 24 g NaOH in 80 mL water and dilute to 100 mL.

5.9 Sulfuric acid, 18 N: Cautiously mix 1 volume 36 N H_2SO_4 (concentrated) with 1 volume of water.

5.10 Sulfuric acid, 0.1 N: Mix 1 volume 18 N H_2SO_4 with 179 volumes of water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of 16 hr before analysis or transfer of the sample.

6.3 The container choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 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 BaSO_4 (same carrier amount used in samples). This is done with spiked distilled water samples, and the procedure for regular samples is followed. Note the time of the Ra-BaSO_4 precipitation.

7.1.2 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 sample.

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

7.2 To a 1,000-mL surface water or ground water sample, add 5 mL 1 M C₆H₈O₇·H₂O, 1 mL lead carrier, and 2.0 mL barium carrier, and heat to boiling.

7.3 Cautiously, with vigorous stirring, add 20 mL 18 N H₂SO₄. Digest 5 to 10 min and let the mixed BaSO₄-PbSO₄ precipitate settle overnight. Decant and discard supernate.

7.4 Transfer the precipitate to a centrifuge tube with a minimum amount of 0.1 N H₂SO₄. Centrifuge and discard supernate.

7.5 Wash the precipitate twice with 0.1 N H₂SO₄. Centrifuge and discard washes.

7.6 Dissolve the precipitate by adding 15 mL basic EDTA reagent; heat in a hot-water bath and add a few drops 6 N NaOH until solution is complete.

7.7 Add 1 mL (NH₄)₂SO₄ (200 mg/mL) and stir thoroughly. Add 17.4 N CH₃COOH dropwise until precipitation begins and then add 2 mL extra. Digest 5 to 10 min.

7.8 Centrifuge, discard the supernate, and record time.

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

7.9 Wash the BaSO₄ precipitate with 15 mL water, centrifuge, and discard wash.

7.10 Transfer the precipitate to a tared stainless steel planchet with a minimum of water and dry under infrared lamps.

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

7.11 Cool, weigh, and store in desiccator.

7.12 Count in a gas-flow internal proportional counter or an alpha scintillation counter to determine the alpha activity.

7.13 Calculation:

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

$$D = \frac{C}{2.22 \times E \times V \times R \times I}$$

where:

C = net count rate, cpm.

E = counter efficiency, for radium-226 in BaSO₄ predetermined for this procedure (see Paragraph 7.1.2).

V = liters of sample used.

R = fractional chemical yield.

I = ingrowth correction factor (see Paragraph 7.14).

2.22 = conversion factor from dpm/pCi.

7.14 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:

<u>Hours from separation to counting</u>	<u>Ingrowth correction factor</u>
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

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample-preparation process.

8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 9315
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