METHOD 9315

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.

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

4.2   <u>Stainless steel counting planchets</u>.

4.3   <u>Electric hot plate</u>.

4.4   <u>Drying oven and/or drying lamp</u>.

4.5   <u>Glass desiccator</u>.

4.6   <u>Analytical balance</u>.

4.7   <u>Centrifuge</u>.

4.8   <u>Glassware</u>.

5.0 REAGENTS

5.1   <u>Distilled or deionized water</u> (Type II).

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

5.3   <u>Ammonium sulfate</u>, 200 mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in a minimum of water and dilute to 100 mL.

5.4   <u>Barium carrier</u>, 16 mg/mL, standardized:

    5.4.1   Dissolve 2.846 g $BaCl_2 \cdot 2H_2O$ 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   <u>Citric acid</u>, 1 M: Dissolve 19.2 g $C_6H_8O_7 \cdot H_2O$ 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 ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$). 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 $Pb(NO_3)_2$ 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:

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

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-$BaSO_4$,
         precipitation to midpoint of counting time.

7.2   To a 1,000-mL surface water or ground water sample, add 5 mL 1 M $C_6H_8O_7 \cdot H_2O$, 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 H_2SO_4. Digest 5 to 10 min and let the mixed $BaSO_4$-$PbSO_4$ precipitate settle overnight. Decant and discard supernate.

7.4   Transfer the precipitate to a centrifuge tube with a minimum amount of 0.1 N H_2SO_4. Centrifuge and discard supernate.

7.5   Wash the precipitate twice with 0.1 N H_2SO_4. 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 $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N CH_3COOH 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 $BaSO_4$ is complete, and the ingrowth of radon (and daughters) commences.

7.9   Wash the $BaSO_4$ 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 $BaSO_4$ 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 $BaSO_4$ 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

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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.
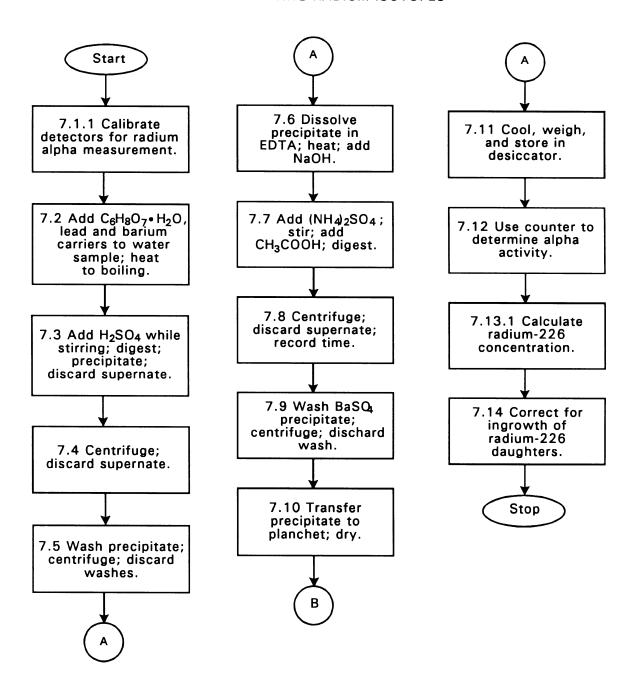

9.0   METHOD PERFORMANCE

     9.1 No data provided.

10.0 REFERENCES

     10.1   None required.

METHOD 9315
ALPHA-EMITTING RADIUM ISOTOPES

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( Start )
   │
   ▼
┌─────────────────────┐
│ 7.1.1 Calibrate     │
│ detectors for radium│
│ alpha measurement.  │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.2 Add C6H8O7•H2O, │
│ lead and barium     │
│ carriers to water   │
│ sample; heat        │
│ to boiling.         │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.3 Add H2SO4 while │
│ stirring; digest;   │
│ precipitate;        │
│ discard supernate.  │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.4 Centrifuge;     │
│ discard supernate.  │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.5 Wash precipitate;│
│ centrifuge; discard │
│ washes.             │
└─────────────────────┘
   │
   ▼
  ( A )
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( A )
   │
   ▼
┌─────────────────────┐
│ 7.6 Dissolve        │
│ precipitate in      │
│ EDTA; heat; add     │
│ NaOH.               │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.7 Add (NH4)2SO4 ; │
│ stir; add           │
│ CH3COOH; digest.    │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.8 Centrifuge;     │
│ discard supernate;  │
│ record time.        │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.9 Wash BaSO4      │
│ precipitate;        │
│ centrifuge; dischard│
│ wash.               │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.10 Transfer       │
│ precipitate to      │
│ planchet; dry.      │
└─────────────────────┘
   │
   ▼
  ( B )
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( A )
   │
   ▼
┌─────────────────────┐
│ 7.11 Cool, weigh,   │
│ and store in        │
│ desiccator.         │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.12 Use counter to │
│ determine alpha     │
│ activity.           │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.13.1 Calculate    │
│ radium-226          │
│ concentration.      │
└─────────────────────┘
   │
   ▼
┌─────────────────────┐
│ 7.14 Correct for    │
│ ingrowth of         │
│ radium-226          │
│ daughters.          │
└─────────────────────┘
   │
   ▼
 ( Stop )
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