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Determination of Radium in Water

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-B



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F. B. BARKER and J. O. JOHNSON

RADIOCHEMICAL ANALYSIS OF WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-B

*Second of a series of reports describing
methods used by the U.S. Geological
Survey for measuring radioactivity
and radionuclides in water*



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RADIOCHEMICAL ANALYSIS OF WATER

DETERMINATION OF RADIUM IN WATER

By F. B. BARKER and J. O. JOHNSON

ABSTRACT

Radium isotopes are common radioactive constituents of natural waters. The concentration of radium-226 in potable water is of particular significance because this isotope is generally considered the most hazardous of all radionuclides with respect to ingestion.

The approximate concentration of radium-226 is determined after coprecipitating radium with barium sulfate. The short-lived daughters of radium are allowed to grow for 10-12 days, then the alpha activity of the precipitate is measured and compared with that of a precipitate containing a known amount of radium-226. Concentrations of the individual alpha-emitting isotopes of radium-223, radium-224, and radium-226, are determined by coprecipitating radium first with lead sulfate, then with barium chloride, and finally with barium sulfate. This final precipitate is initially free of other alpha-emitting nuclides, thus permitting the isotopic composition to be determined by measuring the growth and decay of the alpha activity of the precipitate.

INTRODUCTION

This paper describes the methods in current use at the Denver research laboratory of the Water Resources Division, U.S. Geological Survey, for the determination of the concentrations of radium in natural water. These methods, although not necessarily the most sensitive or precise are usually rapid and inexpensive.

This is the second of a series of reports describing the analytical methods used in the Denver laboratory for determining the concentrations of various radionuclides in natural waters. The first paper of the series (Water-Supply Paper 1696-A) contains a general introduction to the series; discussions of the sources of radioactivity in water, the collection and preservation of samples of water, and the measurement of radioactivity; and a description of a method for determining gross beta activity in water. Additional papers are planned to describe other methods used by the U.S. Geological Survey for radiochemical analysis of water, including those for uranium, radiostrontium, radon, radiocesium, and alpha activity.

Radium is a naturally radioactive element that is widely disseminated in minute quantities throughout the crust of the earth. Four isotopes of radium, members of the natural radioactive series (Barker

and Robinson, 1963, p. 2-5), occur in nature: radium-226, a member of the uranium series; radium-224 and radium-228, members of the thorium series; and radium-223, a member of the actinium series. The relative abundances of these isotopes vary widely in nature, depending on the relative amounts of thorium and uranium in the particular geologic system and on complex geochemical processes that may upset the radioactive equilibrium at several points in the decay chains. Several other isotopes of radium have been produced artificially, but these seldom would be found in natural water and will not be discussed in this paper.

Radium-228 decays by beta emission; the other three natural isotopes decay by alpha emission. The following table shows the half lives and specific activities of the natural radium isotopes:

<i>Isotope</i>	<i>Half life</i>	<i>Specific activity (curies per gram)</i>
Radium-223.....	11.2 days.....	5.3×10^4
Radium-224.....	3.64 days.....	1.6×10^5
Radium-226.....	1,620 years.....	1.0
Radium-228.....	6.7 years.....	2.4×10^2

Water from all types of geologic terranes is apt to contain radium because of the wide distribution of its parent elements, uranium and thorium. Concentrations of radium in fresh ground water (no more than 3,000 ppm dissolved solids) generally are less than a few picocuries per liter (pc per l; 1 pc=2.22 disintegrations per minute). However, water from highly-mineralized zones or from certain geologic formations sometimes contains high concentrations of radium. Concentrations of radium in Cambrian and Ordovician limestone aquifers in the north-central United States commonly exceed 3 pc per l. Wastes from uranium mining and milling operations are usually very high in radium and can be sources of water contamination. Mill-pond wastes may exceed 1,000 pc per l of radium, a large amount of which is usually attributable to the 11-day radium-223 isotope.

The concentrations of radium-226 in potable water supplies are of particular significance because this isotope is generally considered the most hazardous of all radionuclides with respect to ingestion. There is not complete agreement concerning the permissible concentrations of radium-226 in safe drinking water. Commonly used criteria range from 3 pc per l, the drinking-water standard recommended by the U.S. Public Health Service (1962), through 10 pc per l, the maximum permissible concentration (MPC) recommended by the National Committee on Radiation Protection (1959).

METHODS FOR DETERMINING RADIUM

Several methods are available for determining radium-isotopes concentrations of less than 10 pc per l. These methods can be divided

into two general classifications: emanation methods and carrier-precipitation methods. Under ideal conditions, the minimum detection limit of either method is somewhat less than 0.01 pc per l; however, the practical limit for most investigations is about 0.01–0.1 pc per l.

Emanation methods involve the measurement of the radioactivity of the inert gases radon-222 and radon-220 (Evans, 1935; Hursh, 1954; Bate and others, 1953). Concentrations of radium-224 and radium-226 can be determined by measuring the activity of the radon daughter nuclides in equilibrium with the radium parents. Under some conditions radium-223 might be determined from radon-219; however, this generally would be limited to samples of high concentration because of the short half life (3.92 sec) of radon-219.

The U.S. Geological Survey sometimes uses an emanation method for determining radium-226 in water. This use is incidental to the measurement of radon-222, however, and the method will be described in a subsequent report on radon in water.

In the carrier-precipitation methods, radium is removed from solution by physical or chemical attachment to an insoluble salt (carrier) that is precipitated from the solution. Salts that remove radium from solution efficiently include barium sulfate, lead sulfate, and barium chloride. Radium can be separated from other radioactive substances by additional chemical separations using one or more carriers. The final precipitate is collected on a suitable filter or planchet, and radium is determined by measuring the amount of radioactivity. Before measuring the radioactivity, the precipitate can be aged to permit the growth of short-lived daughter nuclides, thus increasing the activity of the precipitate. Individual radium isotopes can be determined from the growth and decay of radioactivity in the sample (Stehney, 1955) or by separating specific daughter nuclides and measuring their radioactivities at predetermined times (Petrov, and others, 1960; Baratta and Herrington, 1960).

This report describes two carrier-precipitation methods for determining radium in water. One of these involves a single precipitation of the barium sulfate carrier, permitting only the determination of the total activity of the alpha-emitting radium isotopes (Barker and Thatcher, 1957). The other method, adapted from one used by Ames and others (1949) and modified by Russell and others (1950), utilizes three carrier precipitations. This method, referred to as the isotope-identification method, permits radium-226 and the short-lived isotopes radium-223 and radium-224 to be determined individually.

SINGLE-CARRIER-PRECIPIATION METHOD

PRINCIPLE OF THE METHOD

Barium and radium form an isomorphous series of crystalline sulfates in which barium and radium ions are interchangeable in the

cationic positions of the crystal lattice. Therefore, when barium sulfate having a slight excess of sulfate ions is precipitated, radium is removed quantitatively from solution by isomorphous replacement even though the solubility product of radium sulfate has not been exceeded. The alpha activity of such a precipitate can be measured and compared with that of another precipitate consisting of the same amount of barium sulfate carrying a known amount of radium-226. Thus, the quantity of alpha-emitting radium isotopes present can be reported in terms of radium-226.

The specific procedure used is based on one coprecipitation of radium by isomorphous replacement in barium sulfate. The single-carrier precipitation method is simple and rapid and requires a nominal investment in equipment. The method is suitable for most purposes where radium need not be determined with high precision and where the activity from radium-224 and radium-226 need not be differentiated. The method is adequate for many geochemical investigations. Also, it is usually satisfactory for monitoring potable water for conformance to health standards, even though the reported result may be somewhat greater than the actual radium-226 content because of the presence of radium-224 and other interfering alpha-emitting nuclides.

This method is sufficiently accurate and specific for most hydrologic investigations of radium in ground water and surface water, at least in the initial phases. A study of the variations of radium and uranium contents in a major aquifer (Barker and Scott, 1958) and an evaluation of the natural levels of radioelements in ground water (Scott and Barker, 1959 and 1962) are examples of such investigations.

APPARATUS

Much of the equipment used in radium determination is of a general nature and is available in a typical analytical laboratory. Special equipment and supplies needed include:

- 2-liter beakers

- 2-liter or larger filter flasks

- Molecular membrane filters, 0.45-micron pore-size, black, 45-mm diameter

- Filtration assemblies for membrane filters, including a clamp, funnel, and base (fig. 1)

- Ring-and-disk sample mounts (fig. 2)

- Alpha-counting equipment, consisting of a windowless alpha-scintillation detector mounted in a suitable sample changer, a regulated high-voltage power supply, and a scaler (the last two items generally are combined in one instrument). Typical assemblies are shown in figure 3.



FIGURE 1.—Filtration assembly for membrane filters.

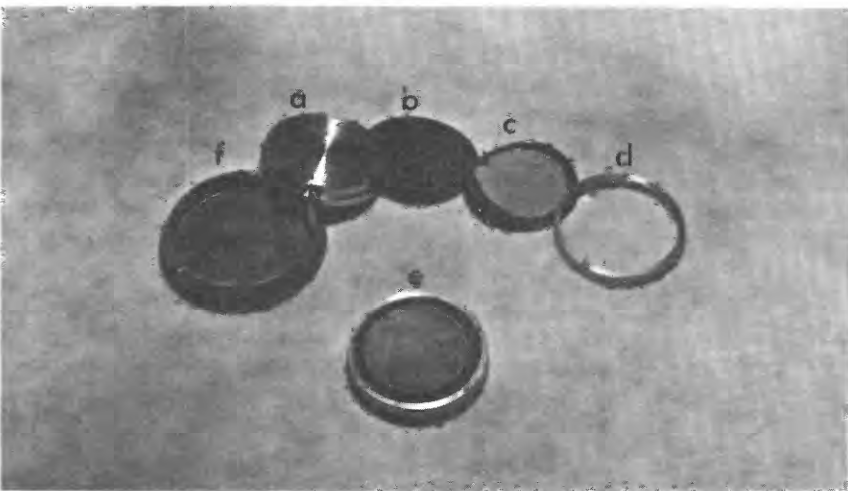


FIGURE 2.—Ring and disk sample mounts, assembled and exploded views.

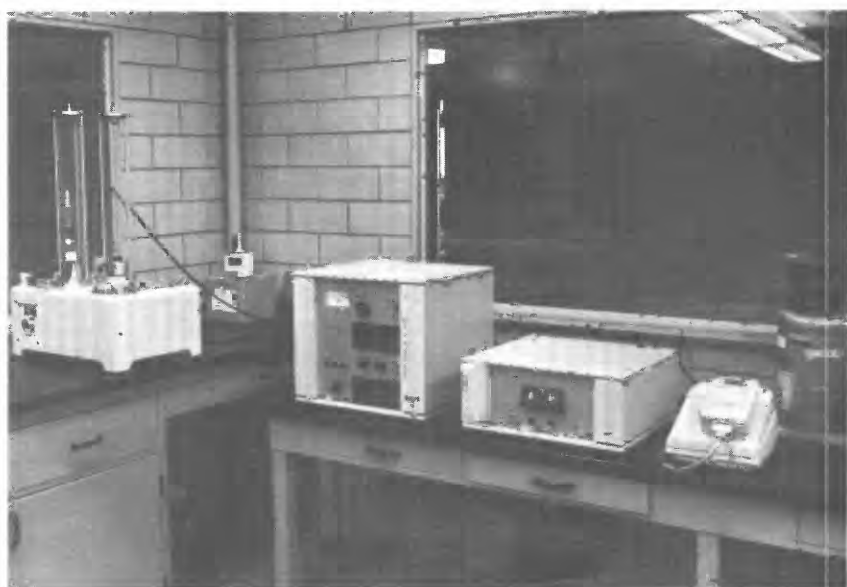


FIGURE 3.—Alpha-counting equipment for automatic (above) and manual (below) operation.

REAGENTS

Ammonium sulfate solution.—Dissolve 400 g of reagent-grade ammonium sulfate in 1 liter of hot distilled water, cool to room temperature, and filter.

Barium carrier solution (1.4 mg Ba^{+2} per ml).—Dissolve 2.5 g of reagent-grade barium chloride dehydrate in distilled water and dilute to 1 liter.

Radium standard solution (1 pc Ra^{226} per ml).—Dilute 10 ml radium standard-stock solution (see p. 21) and 10 ml of concentrated (36–38 percent HCl) reagent-grade hydrochloric acid to 500 ml by adding distilled water.

Sulfuric acid wash solution.—Dilute 5 ml of concentrated sulfuric acid to 1 liter by adding distilled water and then add 10 ml of saturated Aerosol OT solution.

PROCEDURE

1. Measure 1 liter of the sample, previously filtered if necessary, into a 2-liter beaker. If the sample contains more than 350 ppm (parts per million) calcium, take a smaller volume and dilute to 1 liter, so that the solution contains less than 350 ppm of calcium. If a sample is believed to contain sufficient quantities of barium, strontium, or other dissolved or suspended material to add more than 1 or 2 mg to the weight of the precipitate, a "spiking" technique should be used. This technique is described in a later section on procedures for handling difficult samples.

2. Prepare duplicate standard solutions, each consisting of 25 ml of radium standard solution (1 ml=1 pc radium-226) diluted to 1 liter by adding distilled water and a blank solution consisting of 1 liter of distilled water.

3. Heat blank solution, samples, and standard solutions to incipient boiling point and adjust the pH to approximately 3.5 by adding concentrated hydrochloric acid and using several drops of methyl orange as the indicator.

4. Add 3 ml of the barium carrier solution to each beaker and stir vigorously. While stirring, add 15 ml of saturated ammonium sulfate solution; continue stirring intermittently for several minutes.

5. Allow the precipitate to digest at room temperature for 4 hours or longer, then collect the precipitate on molecular membrane filters. Wash with small volumes of the sulfuric acid-aerosol wash solution. The barium sulfate precipitate should be evenly distributed to minimize self-absorption losses for alpha particles. A fine jet of the wash solution can be used to redistribute the precipitate on the filter, the filter permitting the analyst to determine when an even distribution is obtained.

6. When the membrane filter is practically dry, mount it in the ring-and-disc holders. (The nutrient pads, supplied with certain filters or other flat stiff disks of proper diameter, can be used as sample mounts when manual sample changers are used. The membrane filter can be conveniently attached to such disks by using double-surfaced cellophane tape.)

7. Determine the alpha activity of the precipitate after allowing a period of 10–12 days for the growth of the short-lived daughter nuclides. Typical counting times are 15 minutes each for standard solutions, and 1 hour each for blank solutions and samples.

TECHNIQUES FOR HANDLING DIFFICULT SAMPLES

Special techniques are necessary for analyzing many brines or other unusual waters that may contain large concentrations of barium or strontium, and for analyzing samples that contain colloidal or suspended material. Samples containing large amounts of suspended material should be filtered; both the filtrate and residue can be analyzed for radium if desired. If the residue is to be analyzed, it should be leached with dilute nitric acid (approximately 6 *N*), and the analysis should be performed on the clear leachate by the usual procedure. Brines and other samples containing only small amounts of suspended material often can be analyzed by diluting the sample.

A "spiking technique" (use of internal standard solutions) sometimes must be used, particularly if the sample is suspected to contain significant amounts of barium. This technique requires two parts of the sample. A known amount of radium is added to one part and both are analyzed in the usual manner. Comparison of the counting rates of the "spiked" and "unspiked" parts permits evaluation of the increased self-absorption and calculation of the concentration or radium in the sample.

CALCULATION OF RESULTS

Gross radium activity is calculated by means of the formula

$$Ra = \frac{SR_x}{VR_s}$$

where

Ra = total radium, in pc per l expressed as radium-226 activity

V = volume of sample, in liters

S = amount of radium-226, in picocuries, in each standard solution

R_s = average net counting rate of the two standard solutions

R_x = net counting rate of the sample.

When an internal standard solution—or “spike”—is used, gross radium activity is calculated by the following formula:

$$Ra = \frac{SR_x}{V(R_s - R_x)}$$

where

R_x = net counting rate of the “unspiked” sample

R_s = net counting rate of the sample containing the radium-226 “spike”

S = amount of radium-226, in picocuries, used for “spike.”

ERRORS AND PRECISION

The single-carrier precipitation method is not specific for radium because significant amounts of other elements such as thorium, bismuth, lead, and polonium may be carried in the barium sulfate precipitate. Any alpha-emitting isotopes carried in the barium sulfate precipitate are counted as radium, and other alpha-emitting isotopes or descendants of these elements are found in nature. However, study of the uranium and thorium series indicates that the only nuclides producing significant interference probably would be thorium-228, -230, and -232 and polonium-210. Fortunately, the thorium isotopes and polonium-210 do not usually occur in natural waters in detectable amounts. The elements, if present in significant quantities, would be detected as radium. After the prescribed aging period for the barium-sulfate precipitate (11 days), 1 pc each of the aforementioned nuclides would be reported as the following estimated amounts of radium: Thorium-232, 0.15–0.2 pc; thorium-228, about 0.2 pc; thorium-230, 0.15–0.2 pc; and polonium-210, about 0.2 pc.

The practical minimum detection limit for radium in the single-carrier precipitation method is about 0.1 pc per l. The precision of the reported result is somewhat difficult to define, partly because of the lack of specificity for radium-226 and partly because of those factors relating to the measurement of radioactivity that were discussed in chapter A of this series. The two-standard-deviation level is probably about ± 0.1 pc for samples containing 0.1–0.5 pc per l of radium and about 20 percent for samples containing more than 0.5 pc per l of radium.

ISOTOPE-IDENTIFICATION METHOD

PRINCIPLE OF THE METHOD

Ames and others (1949) found radium coprecipitated with barium chloride to be almost entirely free of interfering alpha activities. For solutions containing appreciable sulfate ions, a preliminary separation is necessary to prevent precipitation of barium sulfate. Lead

sulfate coprecipitates radium quantitatively and, unlike barium sulfate, can be dissolved readily. The combination of a lead sulfate precipitation followed by a barium chloride precipitation, therefore, permits quantitative separation of radium from almost all other naturally occurring alpha-emitting nuclides. Slight interference may be found as a result of actinium-227 and bismuth-210 which are carried into the final precipitate (see discussion of errors and precision of this method). This method was used by Ames and others to determine uranium in process waters and was adapted by Russell and others (1950) and used to determine radium in urine and other biological materials. In the absence of interfering alpha emitters, the amounts of the individual radium isotopes in the sample can be determined by measuring the growth and decay of the radioactivity. Stehney (1955) used this technique and a similar method to measure radium-224 and radium-226 in water.

The isotope-identification method used by the U.S. Geological Survey was evolved from these procedures. The water sample is evaporated to dryness, and the carbonates are destroyed by adding nitric acid. The soluble part of the residue is dissolved in dilute nitric acid, and the radium is coprecipitated with lead sulfate. The lead sulfate then is dissolved in a hydrochloric acid-ether solution, and the radium is coprecipitated with barium chloride. Finally, the barium chloride is dissolved in dilute nitric acid, and the radium is coprecipitated with barium sulfate, which is collected on a membrane filter and mounted for counting. The radium isotopes are determined by measuring the growth and decay of alpha activity in the barium sulfate precipitate and fitting the data to the appropriate equations by a suitable method.

If the concentration of radium-223 is small compared to the concentrations of radium-224 and radium-226, it can be ignored, and the data can be put into a form amenable to treatment by the method of least squares for a straight line. A discussion of this treatment and of the derivation of the necessary equations is given on pages B15-B19. Even if the concentration of radium-223 is not negligible, the straight-line equations are reasonably valid. However, the result for radium-226 will be too high by an amount equal to 40 percent of the radium-223, and the result for radium-224 will include all the radium-223. Although it is possible to estimate the concentration of radium-223 and correct the results accordingly, the precision with which the concentrations of radium-223 and radium-224 can be reported is poor, so that it is generally better to report the sum of the two as the concentration of the short-lived isotopes. This topic is discussed in more detail in the section on errors and precision of this method.

The least-squares equation for a multiple linear regression (a plane) could also be used to estimate the concentrations of the three isotopes. However, the small improvements in the precision of the results for radium-223 and radium-224 are somewhat offset by a decrease in the precision of the results for radium-226 and the total short-lived isotopes. Therefore, the more tedious calculation involved in this procedure is not considered justified for any slight advantage that might be gained when working with natural, unpolluted water.

APPARATUS

Much of the apparatus needed is commonly found in a chemical laboratory and will not be listed. Special items are listed below:

Centrifuge, size 1, preferably refrigerated. An unrefrigerated centrifuge can be used if it includes large cups that can be packed with ice so that 50-ml centrifuge tubes can be chilled during the centrifugation.

Molecular membrane filters, 0.45-micron pore size, black, 45-mm diameter

Filtration assemblies for membrane filters (fig. 1)

Ring-and-disk sample mounts (fig. 2)

Alpha-counting equipment as described on page B4 (fig. 3)

REAGENTS

Ammonium hydroxide, concentrated.—reagent-grade, 28–30 percent NH_3 .

Ammonium sulfate solution.—Dissolve 400 g of reagent-grade ammonium sulfate in 1 liter of hot distilled water; cool and filter the solution.

Barium carrier solution (8 mg Ba^{+2} per ml).—Dissolve 1.5 g of reagent-grade barium nitrate in distilled water and dilute to 100 ml.

Hydrochloric acid-ether reagent.—Mix six parts, by volume, of concentrated (36–38 percent HCl), reagent-grade hydrochloric acid with one part of reagent-grade ethyl ether.

Lead carrier solution (100 mg Pb^{+2} per ml).—Dissolve 15.5 g of reagent-grade lead nitrate in distilled water and dilute to 100 ml.

Nitric acid, concentrated.—reagent grade, 69–71 percent HNO_3 .

Nitric acid, 0.1 normal.—Dilute 6.5 ml concentrated nitric acid to 1 liter by adding distilled water.

Radium standard solution (1 pc Ra^{226} per ml).—Dilute 10 ml radium standard-stock solution (p. 21) and 10 ml concentrated (36–38 percent HCl) hydrochloric acid to 500 ml by adding distilled water.

Sodium sulfate solution.—Dissolve 10 g of reagent-grade sodium sulfate in distilled water and dilute to 100 ml.

Sulfuric acid, concentrated.—reagent-grade, 95–98 percent H_2SO_4 .

Sulfuric acid wash solution.—Dilute 5 ml of concentrated sulfuric acid to 1 liter by adding distilled water and add 10 ml of saturated Aerosol OT solution.

PROCEDURE

1. Select a volume of sample containing no more than 350 mg of calcium, and filter if necessary. Add 5 ml of concentrated nitric acid and evaporate to dryness in a 400 ml beaker on a steam table. If the volume of sample exceeds about 300 ml, the evaporation must be performed stepwise; however, the beaker should not be allowed to become dry before adding the next part.

2. Prepare two standard solutions, each consisting of 25 ml of radium standard solution (25 pc) and 1 ml of sodium sulfate solution, and a blank solution consisting of 1 ml of sodium sulfate solution. Dilute by adding distilled water to about 100 ml, add 5 ml of concentrated nitric acid, and evaporate to dryness in the same manner as the samples.

3. Wash each beaker with 0.1 *N* nitric acid, polishing thoroughly, and transfer each residue to a 50 ml centrifuge tube. Centrifuge at about 500 gravities for 5–10 minutes.

4. Transfer the supernatant liquid to a 250 ml centrifuge bottle. Wash the precipitate thoroughly with 30–40 ml of 0.1 *N* nitric acid. Centrifuge, and add the wash solution to the supernatant liquid in the centrifuge bottle. Repeat the washing step, adding the second wash solution to the centrifuge bottle. Discard the residue.

5. Add 2 ml of concentrated sulfuric acid to the combined solutions and mix well. While stirring vigorously, add 1 ml of lead carrier solution (100 mg of lead). Continue stirring for 10 minutes.

6. Place the centrifuge bottle in an ice bath and continue stirring for at least another 15 minutes. Centrifuge and discard the supernatant liquid.

7. Dissolve the precipitate in 20 ml of hydrochloric acid–ether reagent and transfer to a 40–50 ml centrifuge tube. Wash the centrifuge bottle with 5 ml of hydrochloric acid–ether reagent and add to the centrifuge tube.

8. Cool the solution in an ice bath. While stirring, add 0.50 ml of barium carrier solution (4 mg of barium). Continue stirring for at least 5 minutes. Note: steps 8, 9, 10, and 11 should be performed as rapidly as practicable; avoid unnecessary delays.

9. Centrifuge in a refrigerated centrifuge at about 500 gravities for 10 minutes. (An ordinary centrifuge may be used, but the centrifuge tubes must be placed in ice-packed cups.) Discard the supernatant liquid.

10. Dissolve the precipitate in 25 ml of 0.1 *N* nitric acid, warming if necessary, and transfer the solution to a 250 ml beaker. Wash the centrifuge tube several times with 0.1 *N* nitric acid, adding the washings to the beaker.

11. Dilute to about 150 ml by adding distilled water, add a few drops of methyl-orange indicator, and adjust to the yellow end point by adding ammonium hydroxide. Add a few drops of concentrated nitric acid to restore the red color. Heat to incipient boiling point and add 10 ml of ammonium sulfate solution (4 g of ammonium sulfate); stir until the precipitate forms. (Note and record the time of precipitation as the time of separation of radium from its daughter nuclides.)

12. Allow the solution to digest at room temperature for at least 4 hours, then collect and mount the precipitate in the manner described for the single-carrier-precipitation method.

13. Determine the alpha activities of the precipitates at six times by alpha-counting. A near-optimum schedule for the counting, measured from the time of separation of radium from its daughter nuclides, is: 1st day, 2nd day, 3rd day, 5th day, 13th-15th day, and 30th-40th day. One-hour counts are recommended for each precipitate including the standard solutions and the reagent blank solution. If no correction is to be made for radium-223, measurements need not be made after the 15th day. Tabulate the data in a form such as that shown in figure 4.

CALCULATION OF RESULTS

The complete derivation of the equations used in the isotope-identification method are found starting on page B22.

If the results are not to be corrected for any radium-223 present, the concentrations of radium-224 and radium-226 are found as follows:

1. Calculate the average, net counting-rate of the standard solutions for each set of measurements (through the 15th day) by the equation

$$R_s = \frac{N_1 + N_2}{\tau_1 + \tau_2} - B$$

and calculate the net counting-rates of the samples for the same sets by the equation

$$R_x = \frac{N_x}{\tau_x} - B$$

where

R_s = average net counting-rate of standard solutions

R_x = net counting-rate of sample

RADIUM ISOTOPE IDENTIFICATION METHOD

Sample Description										Lab. No. _____					
Final Separation:		Date: _____		Time: _____		Volume _____ ml: Standards _____		pc: Instrument _____							
Date counted	Item	Time	Total count	Δt (min)	Blank (cpm)	Net Rate (cpm)	t (hrs)	$G(t, \Delta t)$	Relative activity (Y)	$\phi(t)$	Weighting factor (W)	$W\phi(t)$	WY	$WY\phi(t)$	$W[\phi(t)]^2$
	Std. A														
	Std. B														
	Samp.														
	Std. A														
	Std. B														
	Samp.														
	Std. A														
	Std. B														
	Samp.														
	Std. A														
	Std. B														
	Samp.														
	Std. A														
	Std. B														
	Samp.														
	Std. A														
	Std. B														
	Samp.														
Totals															

Ra^{223} Assumed negligible

Ra^{226} _____ \pm _____ pc/1

Ra^{224} _____ \pm _____ pc/1

Ra^{223} Determined

Ra^{226} _____ \pm _____ pc/1

Ra^{224} _____ \pm _____ pc/1

Ra^{223} _____ \pm _____ pc/1

FIGURE 4.—Form used to tabulate data and calculate results of isotope-identification method.

N_1 , N_2 , and N_x =total counts observed for the two standard solutions and the sample, respectively

τ_1 , τ_2 , and τ_x =counting times for the two standard solutions and the sample, respectively

B =average counting-rate of the blank solution.

2. Determine the value of the function $G(t, \Delta t)$ from the graph in figure 5, where t is the time elapsed between the separation of radium from its daughter nuclides and the measurement of the alpha activity, and Δt is the difference between the time when the sample was counted and the time when the standard solutions were counted. $G(t, \Delta t)$ is a function to relate standard-solution and sample counts to the same time base.
3. Calculate the value of the function Y for each set of measurements, using the equation

$$Y_i = \frac{SR_x}{R_s G(t_i, \Delta t)}$$

where

S =the amount of radium in each standard solution, generally 25 pc

Y_i =the activity of the sample compared to the standard solution at any time t_i .

4. Determine the values of the function $\varphi(t)$ from the graph in figure 6 and estimate the weighting factors, W_i , from the graph in figure 7. $\varphi(t_i)$ is the ratio of the alpha activity of radium-224 compared to radium-226 at any time t_i . Values of $\varphi(t_i)$ are the x values of the least-square equations. The function $\varphi(t_i)$ is described more fully on pages 23-25.
5. Calculate the concentrations of the radium isotopes from the least-square equations

$$\text{Ra}^{226} = \frac{1000[\sum W_i [\varphi(t_i)]^2 \sum W_i Y_i - \sum W_i \varphi(t_i) \sum W_i Y_i \varphi(t_i)]}{DV}$$

and

$$\text{Ra}^{224} = \frac{1000[\sum W_i \sum W_i Y_i \varphi(t_i) - \sum W_i Y_i \sum W_i \varphi(t_i)]}{DV}$$

where

$$D = \sum W_i \sum W_i [\varphi(t_i)]^2 - [\sum W_i \varphi(t_i)]^2$$

V =volume of sample, in millimeters.

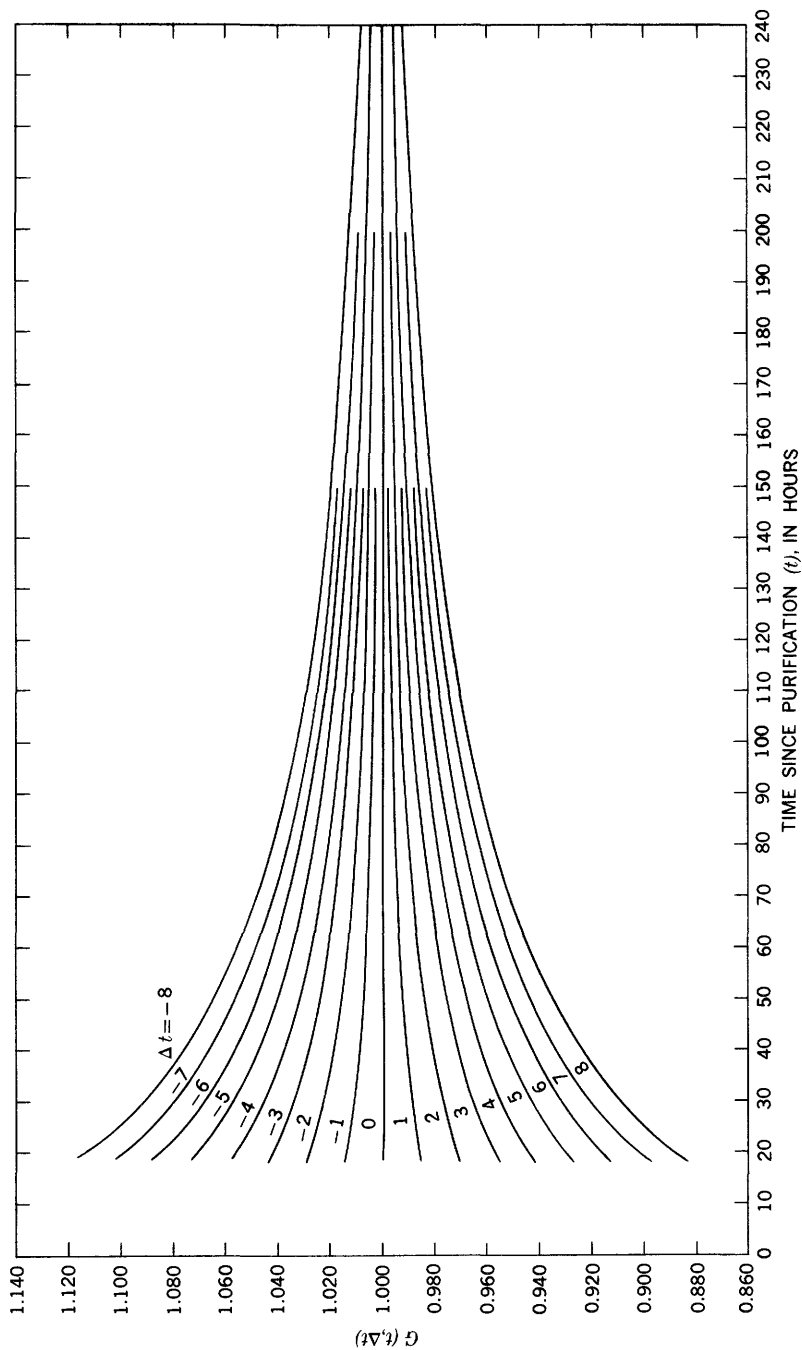
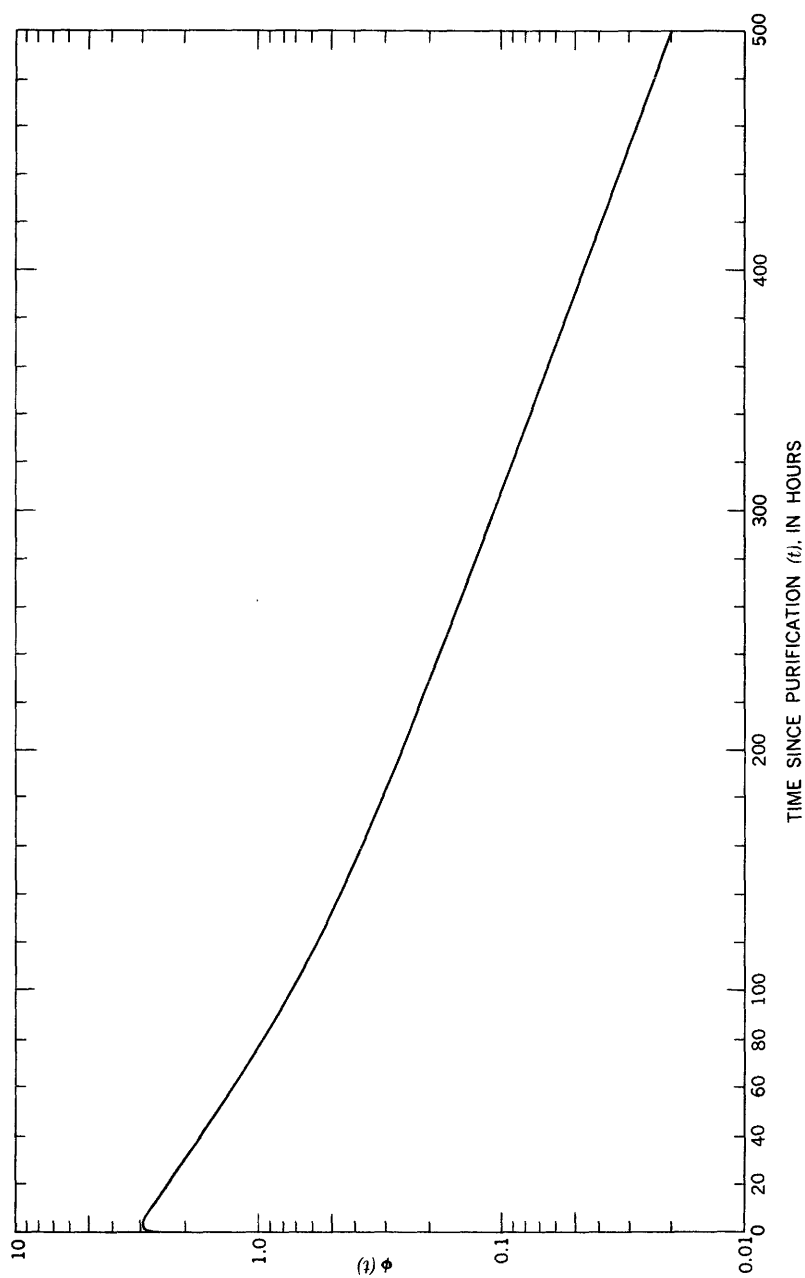


FIGURE 5.—Plot of the function $G(t, \Delta t)$ for different values of t and Δt .

FIGURE 6.—Plot of function $\phi(t)$ as a function of time since purification.

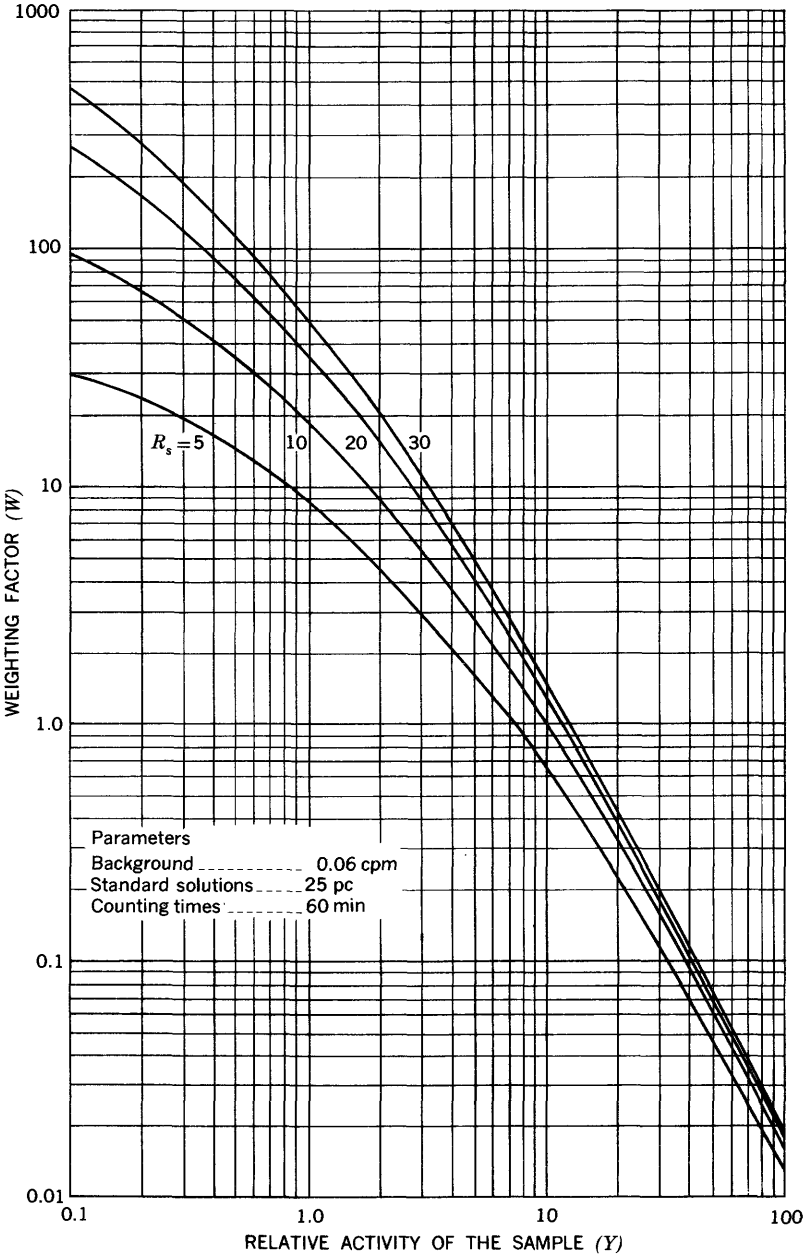


FIGURE 7.—Weighting factors for the individual measurements.

The relative counting rates of various mixtures of radium-226 and radium-224 are plotted against time in figure 8. This graph is useful in estimating the relative amounts of the isotopes and checking the accuracy of the calculated results.

6. Calculate the variances of the concentrations from the equations

$$\sigma^2 \text{Ra}^{226} = \frac{1000 \sum W_t [\varphi(t_t)]^2}{DV}$$

$$\sigma^2 \text{Ra}^{224} = \frac{1000 \sum W_t}{DV}$$

The precisions of the concentrations are best expressed as standard deviations (σ), probable errors (0.675σ), or 95-percent-confidence limits (2σ). The U.S. Geological Survey uses the 2σ index to indicate the precision of radiochemical analyses.

If the results are to be corrected for radium-223, proceed as follows:

1. Determine the least-squares constants from the first five sets of data as described above. These constants are denoted as A (instead of Ra^{226}) and B (instead of Ra^{224}).
2. Calculate the value of the quantity Z from the sixth set of data using the equation

$$Z = \frac{1000SR_z}{VR_s}$$

and determine the value of the function $\psi(t)$ for the time the sample was counted. $\psi(t)$ is the ratio of the growth-decay equation for radium-223 to that of radium-226 and is equal to

$$\frac{4e^{-0.00258t} - e^{1.1520t}}{4.001 - 3.010e^{-0.00755t} + 0.021e^{-1.552t} - 0.012e^{-2.111t}}$$

A graph similar to figure 6 (φt versus t) can easily be prepared for (ψt versus t) to facilitate computation.

3. Calculate the concentrations of the isotopes by the equations

$$\text{Ra}^{226} = \frac{0.40Z - A\psi(t)}{0.40 - \psi(t)}$$

$$\text{Ra}^{224} = B - \frac{A - Z}{0.40 - \psi(t)}$$

$$\text{Ra}^{223} = \frac{A - Z}{0.40 - \psi(t)}$$

$$\text{Ra}^{224} + \text{Ra}^{223} = B$$

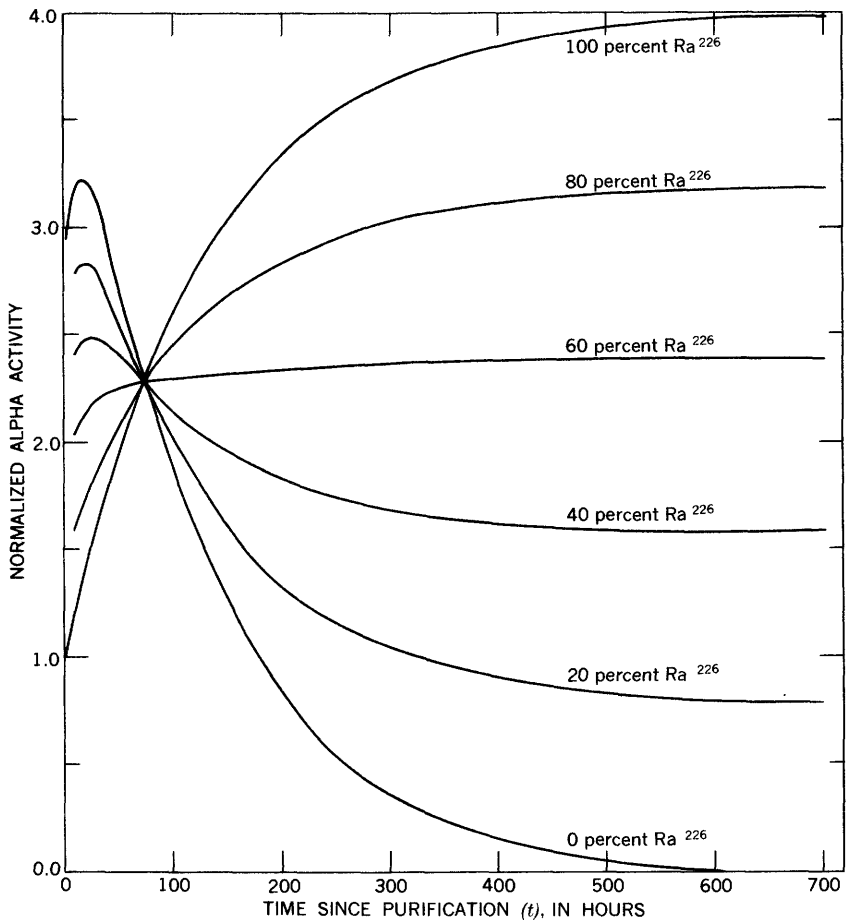


FIGURE 8.—Growth and decay of alpha activity in mixtures of radium-224 and radium-226.

4. Calculate the variances of the concentrations by the equations

$$\sigma^2 \text{Ra}^{226} = \frac{0.16\sigma_z^2 + \psi^2\sigma_a^2}{[0.40 - \psi]^2}$$

$$\sigma^2 \text{Ra}^{224} + \text{Ra}^{223} = \sigma^2 B$$

$$\sigma^2 \text{Ra}^{224} = \sigma^2 B + \frac{\sigma_a^2 + \sigma_z^2}{[0.40 - \psi]^2}$$

$$\sigma^2 \text{Ra}^{223} = \frac{\sigma_a^2 + \sigma_z^2}{[0.40 - \psi(t)]^2}$$

The precision of the results may be expressed in any convenient form as discussed previously.

The calculations described above may be carried out most easily by using a suitable form for tabulating the various quantities and results of the intermediate calculations. A worksheet that is convenient for this purpose is shown in figure 4.

ERRORS AND PRECISION

Although the isotope-identification method is much more specific for the radium isotopes than is the single-carrier-precipitation method, some other radioactive substances may interfere. Small fractions (not exceeding 10 percent) of any actinium and bismuth present are carried in the precipitate. The only natural isotopes of these elements that can have a significant effect on the results, when the prescribed schedule for counting is followed, are actinium-227 and bismuth-210. Actinium-227 interferes owing to the growth of thorium-227 and other alpha-emitting daughter nuclides. The overall effect is that about 9 percent of any actinium-227 is reported as radium-226 and about 0.2 percent of any bismuth-210 is reported as radium-226 and radium-224. These radionuclides generally may be neglected because of the low efficiency and their small natural abundances in most waters; however, some waters polluted by uranium-mill wastes might contain sufficient actinium-227 to cause a significant error in the analysis.

Error also occurs when the isotope radium-223 is not or cannot be measured separately. Under these conditions the value reported for radium-226 will be too large by an amount equal to 40 percent of the radium-223 actually present.

The random errors that determine the precision of the method result mainly from the randomness of the radioactive-decay process and the nonuniformity of the deposit of barium sulfate on the filter. The precision is a function of the ratios of the amounts of the isotopes present, each isotope being determined most precisely when the amounts of the others are small. The precision with which the isotopes radium-223 and radium-224 can be reported individually is always rather poor; however, the precision of the sum of the two is comparable to the precision of the radium-226 value.

PREPARATION OF RADIUM STANDARD-STOCK SOLUTION

A radium standard-stock solution containing 50 pc of radium per milliliter is prepared from a National Bureau of Standards radium-226 gamma-ray standard solution containing 0.1 μg (microgram) of radium-226. The standard solution, as received, consists of about 3 ml of solution in a glass vial. Although the activity is low, care should be

taken to prevent ingestion of the solution or contact of the solution with an open wound; therefore, it is advisable to wear rubber gloves when handling the standard solution and making the initial dilution.

Drop the vial into a clean 1-gallon pyrex bottle fitted with a saran-covered rubber stopper. Break the vial by shaking vigorously, then add approximately 1 liter of distilled water. Shake thoroughly, then let the solution remain in contact with the broken vial for 1–2 hours. Transfer the solution to a 2-liter volumetric flask, leaving the vial in the bottle. Add 50 ml of concentrated hydrochloric acid (36–38 percent HCl) to the bottle, and let the acid remain in contact with the broken vial for at least 12 hours. Transfer the acid to the volumetric flask containing the radium solution, rinsing the bottle several times with small amounts of distilled water which are also added to the volumetric flask. Dilute the solution to 2 liters by adding distilled water and mix thoroughly.

DERIVATION OF EQUATION FOR CALCULATING RESULTS OF ISOTOPE-IDENTIFICATION METHOD

When natural radium is freshly purified, the only alpha activity is that due to the isotopes radium-223, radium-224, and radium-226. However, other radionuclides, called radioactive daughters begin to form immediately as a result of the radioactive disintegration of the radium atoms. The radium isotopes decay, and their radioactive daughters grow and decay at rates characteristic of their several half lives. Some of these daughter nuclides are alpha emitters; thus, the alpha activity of an initially pure radium isotope varies with time in a manner determined by the half life of that isotope and the half lives of its various daughters. The relation between growth and decay of radioactivity and the half lives of the parent and daughter nuclides is discussed in any standard text on radiochemistry—for example, Friedlander and Kennedy (1955, p. 127–137).

The alpha-emitting daughter nuclides that grow into a mixture of radium isotopes to a significant extent within a few weeks are listed in table 1. The half lives of the various radionuclides, the factors that control the rates of growth and decay of radioactivity, differ for each of the decay chains. Therefore, the growth and decay of alpha activity in a mixture of radium isotopes will be a complex function of the amount of each isotope present. Figure 8 shows the variation of

TABLE 1.—*Short-lived alpha-emitting daughters of the radium isotopes*

Parent.....	Ra ²²³	Ra ²²⁴	Ra ²²⁶
Daughter.....	Rn ²¹⁹	Rn ²²⁰	Rn ²²²
	Po ²¹⁵	Po ²¹⁶	Po ²¹⁸
	Po ²¹¹	Po ²¹²	Po ²¹⁴
	Bi ²¹¹	Bi ²¹²	

alpha activity with time for certain binary mixtures of radium-224 and radium-226. Ternary mixtures, containing radium-223 in addition to the other two isotopes, would produce more complex growth-and-decay curves.

Radium-223 is generally not a major constituent of natural water because it is sparsely abundant in nature—less than 5 percent that of radium-226, in terms of radioactivity. Natural waters polluted with uranium-mill wastes often contain considerable amounts of radium-223. Usually, only radium-224 and radium-226 need be considered when measuring the alpha activity of purified radium samples derived from natural water. The equation which describes the alpha activity of such a binary mixture as a function of time is:

$$A = A_1^0(4.001 - 3.010e^{-0.00755t} + 0.021e^{-1.552t} - 0.012e^{-2.111t}) \\ + A_2^0(4.152e^{-0.00793t} - 1.259e^{-0.0654t} + 0.108e^{-0.687t}) \quad (1)$$

where

A = total activity of radium-226 and radium-224 at any time, t

A_1^0 = activity of radium-226 at $t=0$

A_2^0 = activity of radium-224 at $t=0$

t = time elapsed, in hours, since separation of the radium isotopes from their parent and daughters

e = base of natural logarithms.

This equation is only approximate, but it is valid within 0.1 percent over the range from 1 hour to 100 days, assuming the decay constants are accurate to three significant figures. More complete equations for this and other systems involving members of the three natural radioactive series were given by Kirby (1953).

Assuming that the alpha counter used is equally sensitive to alpha particles from all radium isotopes and their daughters, the following equation applies:

$$R_x(t) = E_x A = E_x [A_1^0 f(t) + A_2^0 F(t)] \quad (2)$$

where

$R_x(t)$ = net counting rate of the sample at time, t

E_x = overall efficiency with which the sample is measured.

This includes chemical yield as well as counting efficiency.

$$f(t) = 4.001 - 3.01e^{-0.00755t} + 0.021e^{-1.552t} - 0.012e^{-2.111t}$$

$$F(t) = 4.152e^{-0.00793t} - 1.259e^{-0.0654t} + 0.108e^{-0.687t}$$

Stehney (1955) determined radium-226 and radium-224 in water using a similar equation. Values of $R_x(t)$ and t from two measurements were substituted in the equation, and the resulting simul-

taneous equations were solved for A_1^0 and A_2^0 . A third determination usually was made as a check.

More precise results can be obtained by counting the sample and standard solutions five times during a period of about 15 days from the time of purification and fitting the data to the equation by statistical methods. The basic equation can be transformed into one amenable to treatment by the method of least squares using the procedure described below.

The net counting rate of the radium-226 standard solution at any time, t , is:

$$R_s(t) = E_s S f(t) \quad (3)$$

where

$R_s(t)$ = average net counting rate of radium-226 standard solution at time, t

E_s = overall efficiency with which the standard is measured

S = amount of radium-226 in the standard solution, in picocuries.

Then, assuming the efficiencies are equal for both sample and standard solution,

$$\frac{SR_s(t)}{R_s(t)} = A_1^0 + A_2^0 \frac{F(t)}{f(t)} \quad (4)$$

The standard solution and the sample cannot be counted at the same time in the same instrument; thus a correction factor must be applied to adjust the measurement of the standard solution to the time when the sample was counted. The value of this factor depends on the time elapsed since purification of the radium and on the difference between the time when the sample was counted and that when the standard solution was counted. The equation describing the counting rate of the standard solution as a function of time (t) can be written in the form

$$R_s = E S f(t + \Delta t) \quad (5)$$

Taking the arbitrary time to be that time at which the sample is counted, and combining equations (3) and (5), the net counting rate averaged for the two standard solutions is

$$R_s(t) = \frac{f(t)}{2} \sum \frac{R_s}{f(t + \Delta t)} = \frac{1}{2} \sum R_s G(t, \Delta t) \quad (6)$$

where

$$G(t, \Delta t) = \frac{f(t)}{f(t + \Delta t)}$$

The function $G(t, \Delta t)$ has been evaluated over the range of interest and is shown graphically in figure 5.

By combining equations (4) and (6), the equation for the variation of counting rate as a function of both time and the amounts of radium isotopes present can be written

$$\frac{2SR_x(t)}{\sum R_i G(t, \Delta t)} = A_1^0 + A_2^0 \varphi(t) \quad (7)$$

where

$$\varphi(t) = \frac{F(t)}{f(t)}$$

The values of $\varphi(t)$ for times from 20 to 500 hours are shown graphically in figure 6.

Equation 7 is of the form $Y = a + bX$ and can be evaluated by a method of least squares for linear regression. The values of $\varphi(t)$ for times from 20 to 500 hours are known very accurately compared with values of the quantity on the left-hand side of the equation; therefore, the least-squares equations for the case where only Y is subject to error can be applied. This method is described in most texts on statistics or data-handling techniques—for example, see Worthing and Geffner (1943, p. 238-266). Letting

$$Y = \frac{2SR_x}{\sum R_i G(t, \Delta t)} \quad (8)$$

the appropriate equations are

$$A_1^0 = \frac{\sum w_i [\varphi(t_i)]^2 \sum w_i Y_i - \sum w_i \varphi(t_i) \sum w_i Y_i \varphi(t_i)}{D} \quad (9)$$

$$A_2^0 = \frac{\sum w_i \sum w_i Y_i \varphi(t_i) - \sum w_i Y_i \sum w_i \varphi(t_i)}{D} \quad (10)$$

$$D = \sum w_i \sum w_i [\varphi(t_i)]^2 - \sum w_i [\varphi(t_i)]^2 \quad (11)$$

where the subscript i refers to any individual set of measurements and w_i is a weighting factor which adjusts the contribution of each measurement of Y according to its reliability.

In the absence of conflicting information, weighting factors usually are considered to be proportional to the inverse of the variance. Thus,

$$w_i = \frac{K}{\sigma_i^2}$$

where

K =any arbitrary proportionality constant applied to a set of data

σ_i^2 =variance of the i th measurement of Y .

The overall efficiency does not appear in the final equation because the efficiencies for the samples and standard solutions were considered equal and, therefore, were cancelled. However, there is an uncertainty in this equality owing to variations in the instrument, barium sulfate deposits, sample position, and so forth. This uncertainty must be considered in calculating the variances and the weighting factors for the measurements. The statistics of counting also must be considered.

Placing the individual values of the efficiencies into equation 8,

$$Y = \frac{2SE_s R_x}{E_x \sum R_s G(t, \Delta t)} \quad (13)$$

The net counting rates are obtained by subtracting the counting-rate of the blank solution from the observed counting-rates. Thus,

$$R_x = C_x - B, \quad (14a)$$

and

$$R_s = C_s - B \quad (14b)$$

where

C =an observed counting-rate

B =background counting-rate.

The variance of an observed counting-rate, including background, depends only on the total number of counts observed and the counting time (provided instrument variations are negligible) according to the equation

$$\sigma_c^2 = N/\tau^2$$

where

N =observed number of counts

τ =time interval during which N counts were collected.

Applying the general equation for calculating the variance of an indirectly measured quantity to equation 13, and using equations 14a, 14b, and 15 for substitutions, the variance of Y is found to be

$$\sigma_y^2 = Y^2 \left\{ \frac{\sigma_c^2}{E_s^2} + \frac{\sigma_c^2}{E_x^2} + \frac{N_x}{\tau_x^2 R_x^2} + \frac{N_b}{\tau_b^2} \left[\frac{\sum G(t, \Delta t)}{\sum R_s G(t, \Delta t)} - \frac{1}{R_x} \right]^2 + \frac{\sum N_s [G(t, \Delta t)]^2 / \tau_s^2}{[\sum R_s G(t, \Delta t)]^2} \right\} \quad (16)$$

where

σ_e^2 = variance of counting efficiency of samples and standards

N_x = number of sample counts in time, τ_x

N_b = number of background counts in time, τ_b

N_s = number of sample counts in time, τ_s .

When Y is equivalent to several picocuries, both standard solutions are counted for the same length of time, and Δt is only a few hours, the following approximations and equalities may be used:

$$E_s = E_x = E$$

$$N_x = R_x \tau_x$$

$$N_b = B \tau_b$$

$$\sum R_s [G(t, \Delta t)]^2 \approx \sum R_s G(t, \Delta t)$$

$$\sum G(t, \Delta t) \approx 2$$

The variance of Y then is approximately

$$\sigma_y^2 \approx Y^2 \left\{ \frac{2\sigma_e^2}{E^2} + \frac{1}{\tau_x R_x} + \frac{1}{\tau_s \sum R_s G(t, \Delta t)} + \frac{B [2R_x - \sum R_s G(t, \Delta t)]^2}{\tau_b R_x^2 [\sum R_s G(t, \Delta t)]^2} \right\} \quad (17)$$

Under conditions generally met in the Denver laboratory and for samples containing more than about 2 pc of radium, the following figures may be used:

$$\sigma_e^2/E^2 \approx 0.0025$$

$$\tau_x = \tau_s = 60$$

$$\sum R_s G(t, \Delta t) \approx 15-50 \text{ (depending mainly on time after separation)}$$

$$B \approx 0.09$$

$$\tau_b = 300$$

The approximate equation for the variance then can be put in the form

$$\sigma_y^2 = \left[0.0050 + \frac{0.017}{\sum R_s G(t, \Delta t)} + \frac{0.0012}{[\sum R_s G(t, \Delta t)]^2} \right] Y^2 + \left[\frac{0.058}{\sum R_s G(t, \Delta t)} + \frac{0.030}{[\sum R_s G(t, \Delta t)]^2} \right] Y + \frac{0.75}{[\sum R_s G(t, \Delta t)]^2} \quad (18)$$

The weighting factors, calculated as the reciprocals of the variances given by this equation, are shown as functions of Y and $\sum R_s G(t, \Delta t)$ in figure 7.

Because only the ratios of the weighting factors, not their absolute values, are significant, and even these need be only approximate, this

graph can be used in many situations where the numerical values of certain parameters are not equal to those used in making the graph.

If some radium-223 is present in the sample, the above derivation is not valid. However, it can be shown that a straight line fit to the data will provide consistent results over a wide range of concentrations of the radium isotopes. The ternary-mixture equivalent of equation 7 can be written

$$Y = A_1^0 + A_2^0 \varphi(t) + A_3^0 \psi(t) \quad (19)$$

where $\psi(t)$ is the ratio of the growth-and-decay equation for radium-223 to that for radium-226. The least-squares equations for a straight line through the values of Y then take the forms

$$A = \frac{\left[nA_1^0 \sum \varphi^2 + A_2^0 \sum \varphi \sum \varphi^2 + A_3^0 \sum \varphi^2 \sum \psi \right]}{\left[-A_1^0 [\sum \varphi]^2 - A_2^0 \sum \varphi \sum \varphi^2 - A_3^0 \sum \varphi \sum \varphi \psi \right]} \\ = A_1^0 + \frac{\sum \varphi^2 \sum \psi - \sum \varphi \sum \psi}{n \sum \varphi^2 - [\sum \varphi]^2} A_3^0 \quad (20)$$

$$B = \frac{A_1^0 n \sum \varphi + nA_2^0 \sum \varphi^2 + nA_3^0 \sum \varphi \sum \psi - A_1^0 n \sum \varphi - A_2^0 [\sum \varphi]^2 - A_3^0 \sum \varphi \sum \psi}{n \sum \varphi^2 - [\sum \varphi]^2} \\ = A_2^0 + \frac{n \sum \varphi \psi - \sum \varphi \sum \psi}{n \sum \varphi^2 - [\sum \varphi]^2} A_3^0 \quad (21)$$

Evaluation of the coefficients of A_3 in the above equations, for the counting times recommended in this report (1, 2, 3, 5, and 15 days), gives values of A and B of

$$A = A_1^0 + 0.4A_3^0 = \text{Ra}^{226} + 0.4\text{Ra}^{223} \quad (22)$$

$$B = A_2^0 + A_3^0 = \text{Ra}^{224} + \text{Ra}^{223} \quad (23)$$

The individual isotopes can be evaluated if another measurement is available after the radium-224 has decayed to a negligible value, say 30 days after purification. The quantity is calculated from this measurement by the equation

$$Z = \frac{2SR_x}{\sum R_s} \quad (24)$$

The value of Z is a function of the amounts of radium-223 and radium-224 in the sample:

$$Z = \text{Ra}^{226} + (t) \text{Ra}^{223} \quad (25)$$

where (t) is the alpha activity of an originally pure radium-223 sample t days after purification. Equations 22, 23, and 25 can be solved simultaneously to give values for the three isotopes. However, the precisions of the individual values are generally rather poor.

REFERENCES CITED

- Ames, D. P., Sedlet, J., Anderson, H. H., and Kohman, T. P., 1949, Rapid radio-metric assay for radium and application to uranium ore process solutions, Paper 22.70, in Seaborg, G. T., Katz, J. J., and Manning, W. M., The trans-uranium elements: New York, McGraw-Hill Book Co., Nat. Nuclear Energy Series, Div. 4, v. 14B, p. 1700-1716.
- Baratta, E. J., and Herrington, A. C., 1960, The determination of isotopic radium: U.S. Atomic Energy Comm. WIN-118, 27 p.
- Barker, F. B., and Robinson, B. P., 1963, Determination of beta activity in water: U.S. Geol. Survey Water-Supply Paper 1696-A, 32 p.
- Barker, F. B., and Scott, R. C., 1958, Uranium and radium in the ground water of the Llano Estacado, Texas and New Mexico: Am. Geophys. Union Trans., v. 39, p. 459-466.
- Barker, F. B., and Thatcher, L. L., 1957, Modified determination of radium in water: Anal. Chemistry, v. 29, p. 1573-1575.
- Bate, G. L., Volchock, J. L., and Kulp, J. L., 1953, A low level radon counting system: U.S. Atomic Energy Comm. NYO-6202, 21 p.
- Evans, R. D., 1935, Apparatus for the determination of minute quantities of radium, radon, and thoron in solids, liquids, and gases: Rev. Sci. Instruments, v. 6, p. 99-112.
- Friedlander, Gerhart, and Kennedy, J. W., 1955, Nuclear and radiochemistry: New York, John Wiley and Sons, 468 p.
- Hursh, J. B., 1954, Radium content of public water supplies: Am. Water Works Assoc. Jour., v. 46, p. 43-54.
- Kirby, H. W., 1953, Decay and growth tables for the naturally occurring radio-active series: U.S. Atomic Energy Comm. MLM-859, 30 p.
- National Committee on Radiation Protection, 1959, Maximum permissible body burdens and maximum permissible concentrations of radionuclides in air and in water for occupational exposure: U.S. Nat. Bur. Standards Handb. 69, 95 p.
- Petrow, H. G., Nietzel, O. A., and DeSesa, M. A., 1960, Radiochemical deter-mination of radium in uranium process samples: Anal. Chem., v. 32, p. 926.
- Russell, E. R., Lesko, R. C., and Shurbert, J., 1950, Determining radium in exposed humans: Nucleonics, v. 7, p. 60-64.
- Scott, R. C., and Barker, F. B., 1959, Radium and uranium in ground water of the United States: United Nations Conf. on the Peaceful Uses of Atomic Energy 2nd, Geneva 1958, Proceedings, v. 2, p. 154-157.
- 1962, Data on uranium and radium in ground water in the United States 1954 to 1957: U.S. Geol. Survey Prof. Paper 426, 115 p.
- Stehney, A. F., 1955, Radium and thorium in some potable waters: Acta Radio-logica, v. 43, p. 43-51.
- U.S. Public Health Service, 1962, Drinking water standards, 1962: U.S. Public Health Service Pub. 956, 61 p.
- Worthing, A. G., and Geffner, Joseph, 1943, Treatment of experimental data: New York, John Wiley & Sons, 342 p. (sixth printing, 1950).

