Determination of Radium-228 in Natural Waters

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-G

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By JESSE O. JOHNSON

RADIOCHEMICAL ANALYSIS OF WATER

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RADIOCHEMICAL ANALYSIS OF WATER

DETERMINATION OF RADIUM-228 IN NATURAL WATERS

By JESSE O. JOHNSON

ABSTRACT

Radium isotopes are important radioactive constituents of most natural waters, although they are present in extremely minute quantities. This paper describes a method for determining the beta-active isotope radium-228; extensions of the method for determining the alpha-emitting radium isotopes are discussed.

Radium-228 is determined by coprecipitating the radium isotopes with barium and lead sulfates. The sulfate precipitates are then dissolved in alkaline ethylenedinitrilotetraacetic (EDTA) acid after washing with concentrated nitric acid. Barium and radium sufates are precipitated by pH adjustment, redissolved, then reprecipitated using strontium and yttrium as "holdback" carriers.

The barium sulfate precipitate is again dissolved in alkaline EDTA. Lead and yttrium carriers are added to the solution, which is aged for 36 hours or longer. Ammonium sulfide is then added to the solution to precipitate lead sulfide, and after the lead sulfide is removed, excess sodium hydroxide is added to precipitate yttrium hydroxide.

Radium-228 is determined by beta counting the yttrium hydroxide precipitate, which contains the actinium-228, daughter of radium-228.

INTRODUCTION

Radium isotopes from mass No. 219 and 230 are known, but only the naturally occurring radium isotopes are usually of concern in natural waters. The naturally occurring radium isotopes include radium-226 of the uranium series, radium-224 and radium-228 of the thorium series, and radium-223 of the actinium series. All are alpha emitters with the exception of radium-228, which is a very weak beta emitter— β max = 0.055 Mev (million electron volts). The only reactor produced radium isotopes that have half lives long enough to be detected in natural waters are radium-225 (14.8 day β^-) and radium-227 (41 minute β^-). These isotopes could enter a water supply by accidental discharge of process waste from a nuclear installation.

The following table gives the half lives and decay information of these radium isotopes:

Radium isotope	*Mode of decay*	*Half life*	*Source*
223; (AcX)	α	11.4 days	Natural (U^{235}).
224; (ThX)	α	3.64 days	Natural (Th^{232}).
225	β-	14.8 days	Daughter (Th^{229}).
226; (Ra)	α	1,620 years	Natural (U^{238}).
227	β-	41 minutes	Ra^{226} (n, γ).
228; $MsTh_1$	β-	6.7 years[1]	Natural (Th^{232}).

[1] Holden, N. E., and Walker, F. W., 1968, in the Chart of the Nuclides Rev. list the half life of radium-228 as 5.75 years.

Figure 1 shows the main members of the natural radioactive series and the location of the radium isotopes in the decay schemes. A more complete chart showing minor branch decays will be found in radiochemistry texts such as Friendlander, Kennedy, and Miller (1964).

The determination of the alpha-emitting radium isotopes, particularly radium-226, in various materials has been the object of many studies; and a large number of procedures are available for special studies. Kirby and Salutsky (1964) gave an excellent review on the radiochemistry of radium, and 43 procedures were described in detail for determining radium in a variety of materials. Most are concerned with the determination of radium-226 in miscellaneous substances. A few of the procedures describe the determination of radium-228 in natural waters.

Radium-226 has the lowest maximum permissible concentration (MPC) of any radioactive nuclide in food and domestic water. The U.S. Public Health Service (1962) listed this MPC for radium-226 at 3 pCi/l (picocuries per liter). The U.S. Public Health Service does not cover the other radium isotopes specifically; but the National Committee on Radiation Protection and the International Commission on Radiological Protection (1959) gave the MPC for radium-228 at 9 pCi/l, radium-223 at 210 pCi/l, and radium-224 at 600 pCi/l. Radium-228 has the lowest MPC of any beta-emitting nuclide and is known to be present in food and water and biological materials in small but significant amounts; therefore, some knowledge of its concentration in those materials is desirable. The data on radium-228 concentrations in various materials are limited compared to the data on concentrations of radium-226, mainly because of the difficulty of measuring the weak beta radiation from

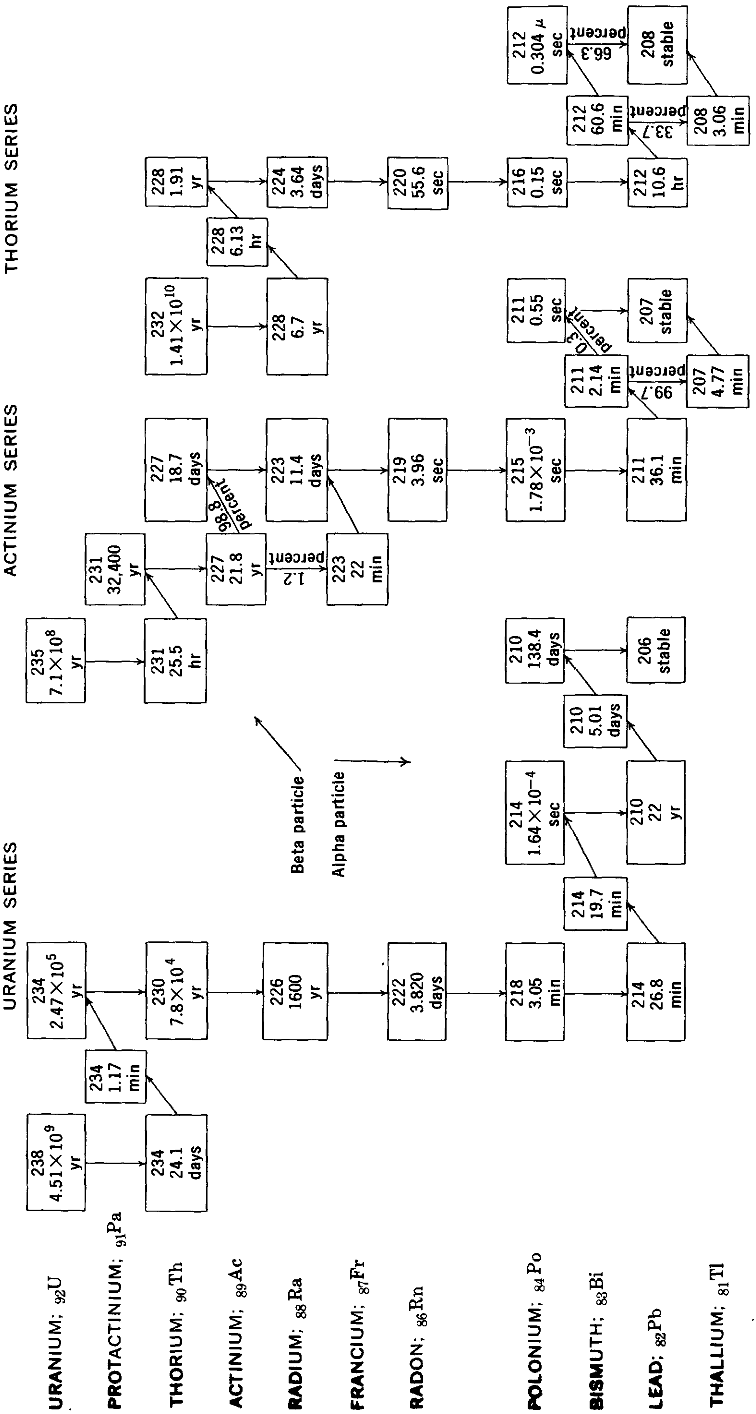


FIGURE 1.—The natural radioactive decay series. Minor decay schemes not shown. Nuclide's half life from Holden and Walker, (1968). Half lives are rounded to 3 significant figures when known to greater accuracy.

radium-228 at very low concentration levels. However, Eisenbud, Petrow, Drew, Roser, Kegel, and Cullen (1964) analyzed a variety of materials including food, water, and biological materials for radium-228.

The U.S. Geological Survey is interested in radium-228 concentration at this level as part of its general studies regarding the occurrence and distribution of radioelements in natural waters.

Barker and Scott (1958), and Scott and Barker (1959, 1962) measured the radium and uranium concentrations of various natural waters in the United States. They established correlations between uranium and radium concentrations and the major geologic provinces. No radium-228 determinations were made in these studies as it did not seem that equipment and methods at that time were sufficiently sensitive for finding the expected concentrations. The presence of radium-228 was indicated, as some samples showed detectable concentrations (unpublished) of radium-224. The concentration of radium-228 in the hydrosphere is of interest both because of its geochemical reactions and because radium-228 is an undesirable contaminant of certain domestic water supplies. It is probable that when the hydrosphere as a whole is considered, the total dissolved radium-228 and radium-226 (in terms of radioactive disintegrations per unit time) would be approximately equal. This is inferred from the parent abundance ratio Th^{232}/U^{238} of about 3 in the earth's mantle and the inverse specific radioactivity ratio of about one-third.

Studies are in progress by the U.S. Geological Survey to determine radium-228 and thorium in some of the streams and waters from various aquifers that were previously analyzed for radium-226 and uranium.

The radium-226 content in many phases of man's environment has been studied intensively for many years. Radium-226 has been measured in water, food, minerals, plants, and soils. The various organs of the human body have also been assayed for radium. From these studies and others, an increased cancer incidence of individuals having unusually high radium content was established (Looney and others, 1955). Maximum permissible concentrations for radium-226 in water, food, and the body itself have been assigned.

Radium-228 studies are few compared with radium-226 studies, although the content and distribution of radium-228 in nature should be similar to that of radium-226. The MPC of radium-228 is one of the lowest of all radionuclides, and radium-228 content in food and drinking water is of concern from a public health aspect. The main reason that more studies have not been made regarding the content and distribution of radium-228 in environmental samples is that most of the published radium-228 methods are for a particular type of sample and are not applicable to general use. The U.S. Geological Survey has developed a method suitable for the determination of radium-228 in natural waters. Before describing this method, a brief review of methods and studies of others is presented.

REVIEW OF RADIUM-228 METHODS AND STUDIES

An environmental study of importance was made by Krause (1959), who measured the radium-228 content of water samples from public water supply wells in the States of Iowa, Illinois, Wisconsin, and Missouri. The waters had been previously analyzed for radium-226 by Lucas and Ilcewitz (1958), and many of the wells had radium-226 concentrations in excess of 4 pCi/l. The total population consuming water having a radium-226 content in excess of 4 pCi/l was estimated at 480,000. The waters having the highest radium-226 concentrations were from deep sandstone formations of Ordovician to Precambrian age.

The radium-228 content of many of the shallow wells was also high, most had concentrations above 1 pCi/l. The waters from the deeper formations, such as the Galesville Sandstone of Cambrian age and older Precambrian rocks, had a radium-228 content as high as 9.1 pCi/l. The average radium-228 to radium-226 ratio was approximately unity for waters from the deep sandstone formations.

Petrow, Cover, Schiessle, and Parsons (1964) developed a procedure for the determination of radium-228 and thorium-228 in biological materials. The method is sensitive to 1 pCi of radium-228 and 0.02 pCi of thorium-228. Analyses were made on a variety of biological materials, including fruits and vegetables from both the United States and Brazil. The materials from Brazil were from a thorium-rich area, and the amount of radium-228, as expected, was considerably greater in the Brazilian samples than in the United States samples. The average concentration of radium-228 in the Brazilian foods was about 10 times that of radium-228 in the American foods. The Ra^{228}/Th^{228} in biological materials was always greater than unity, showing that the uptake of radium by plants is greater than the uptake of thorium.

Petrow and Allen (1961) published a method for determining the radium isotopes in uranium mill effluents. They used lead-carrier precipitations to obtain radium free of other radioactive contaminants. Radium-223, radium-224, and radium-228 are determined from radioassay of their respective daughters, lead-211, lead-212, and actinium-228. Actinium-228 is separated from radium isotopes by extraction into Di (2-ethylhexyl) phosphoric acid (EHPA). Actinium-228 is then extracted from the EHPA with dilute hydrobromic acid. Lead and bismuth interferences are removed by extraction into Aliquat-336 (a high-molecular-weight quaternary amine). Radium-228 is determined from the beta activity of actinium-228.

Henry, Loveridge, and Weaver (1963) cited a method for the assay of radium-228 in reactor effluents. They used a lead-barium sulfate precipitation to isolate radium from solution; an ethylenedinitrilotetracetic acid (EDTA) separation was used to remove lead carrier; ion-exchange resins were used to separate actinium from radium and the rare-earth activities. The method was stated to have decontamination factors of greater than 10^4 for barium-lanthanum-140 and greater than 10^5 for rare-earth activities. High decontamination factors from those isotopes is of especial importance in analyzing reactor effluents for radium-228.

A method suitable for the determination of actinium-227 and radium-228 in uranium mill effluents and natural waters was discussed by Barrata and Feldman (1961). Actinium is coprecipitated with lanthanum carrier. Decontamination is achieved by the use of ion-exchange resins and (or) solvent extraction separations. After purification, lanthanum and actinium are precipitated as the oxalate and then transferred to a counting planchet. Actinium-227 and actinium-228 (radium-228) are determined by beta assay of the precipitate. When both actinium isotopes are present, actinium-228 is first determined by masking the beta radiation of actinium-227 with a thin absorber. After actinium-228 has decayed, actinium-227 may be determined by beta counting of the precipitate or by storing for several days for buildup of alpha-emitting daughters, and then using alpha-counting techniques.

The process history of thorium becomes important when the metal or its alloys are to be fabricated, as about 100 microcuries of radium-228 will be present in a kilogram of old thorium which has been chemically undisturbed for 60 years or longer. This amount of radium-228 only weighs about 0.4 μg (microgram), and its concentration in small volumes of chemical and metallurgical process solutions is to be expected. It is therefore important that thorium process wastes be analyzed for radium-228 to assure that any release to the hydrologic environment is within safe limits.

Radium-228 might also be concentrated in an inhomogeneous manner in thorium or its compounds. In this case the possibility of airborne contamination of radium-228 would be increased during fabrication processes.

In any event the amount of gamma radiation from thorium is dependent to a large extent on the radium-228 concentration and, if not already at its maximum concentration, will increase with time. Fresco, Jetter, and Harley (1952) presented a graphical solution to the Bateman equations describing the alpha and beta activities of the members of the thorium series under various conditions of radioactive disequilibrium. The graphs in conjunction with an alpha and (or) beta analysis enables one to estimate the concentration of radium-228 and other members of the series.

Allison, Moore, Richardson, Peterson, and Voight (1954) published a procedure for measuring radium-228 in thorium and thorium nitrate. Lead and lanthanum carriers are added to the thorium solution, and thorium is extracted into theonyltrifluoroacetone (TTA) at pH 2. The pH is then raised to 6 and lead, actinium, and lanthanum are extracted. Lead interference is removed by precipitation as the sulfide, and lanthanum and actinium-228 are precipitated as the oxalate. Radium-228 is measured by the activity of actinium-228.

Volkova and Ziv (1961) presented a different method that may be used to determine the radium-228 content of thorium. In this procedure, thorium hydroxide is precipitated by the addition of carbon dioxide free ammonia. The supernatant liquid, which contains barium "holdback" carrier and the radium, is evaporated to dryness and calcined to remove ammonium salts. The barium-radium residue is leached with 0.1 *N* HBr. After aging the solution for 1½ months, barium and radium bromides are precipitated by the addition of 5 volumes of ether. After allowing for ingrowth of actinium-228, that isotope is extracted by washing the precipitate with a very small volume of a 2:1 ether-ethanol mixture.

The U.S. Geological Survey is studying radium-228 concentrations in various surface and ground waters. Some of the preliminary results of radium-228 from surface waters are given in table 1. The samples analyzed are from major streams draining the Front Range of Colorado. The radium-228 activity for most of the streams is several times that of radium-226. The higher radium-228 concentration could be caused, in part, by the fact that the average thorium concentration of rocks in the Front Range is over twice that of the average continental rocks (Phair and Gottfried, 1964). More study would be necessary to confirm this. Table 2 gives the radium-228 concentrations of several ground waters,

TABLE 1.—*Radioactive element content of Front Range streams*

Stream and location	Date sampled	Gross β activity (pCi/l)	Gross α[1] activity (µg/l)	Ra^{226} (pCi/l)	Ra^{228} (pCi/l)	U (µg/l)
South Platte River at Waterton, Colo. (gaging station)	11–08–67	5.6	18.	<0.1	1.0	2.3
Bear Creek at Morrison, Colo. (gaging station)	11–09–67	3.0	3.9	<.1	.3	1.1
Clear Creek at roadside park 9 miles above canyon mouth	11–08–67	9.1	3.4	.2	1.1	2.3
South Boulder Creek at Eldorado Springs, Colo	11–09–67	2.7	2.2	<.1	1.4	1.0
Boulder Creek at highway bridge, downtown Boulder, Colo	11–09–67	2.2	1.5	<.1	---------	1.4
Left Hand Creek at gaging station near canyon mouth	11–09–67	9.0	23.	.2	1.3	14.
South St. Vrain River at Lyons, Colo. (gaging station)	11–13–67	3.6	3.3	<.1	.8	1.3
Cache La Poudre River at U.S. 287 bridge, Ft. Collins, Colo	11–13–67	5.9	27.	.1	1.1	7.9
Plum Creek at Colorado state highway "spur" 75 bridge	11–08–67	6.6	24.	.3	.8	3.9
Turkey Creek at junction of U.S. 285 and road to Tiny Town, Colo	11–09–67	4.6	5.6	<.1	1.2	1.0
Coal Creek, 3 miles above canyon mouth	11–09–67	2.5	1.1	<.1	1.7	1.0
Thompson River at Estes Park, Colo., U.S. 287 bridge	11–13–67	2.8	4.3	.1	1.2	.8

[1] Gross alpha activity is in units of equivalent natural uranium.

mostly from the Dawson Arkose, which is a major aquifer in the Denver area. These radium-226 ratios are closer to unity than the radium-228 ratios of the Front Range streams.

TABLE 2.—*Chemical analyses and radioactive*

[Well data and analytical information mostly from Scott and

Water-bearing unit	Location	Silica, SiO_2 (mg/l)	Calcium, Ca (mg/l)	Magnesium, Mg (mg/l)
Curie Spring, Precambrian granite	NE¼ sec.29, T.2 N., R.71 W, Boulder County.	--	384	54.
Well, 801 ft Dawson Arkose	NE¼ sec.3, T.7 S., R.67 W, Douglas County.	34	39	2.9
Well, 1,795 ft Dawson Arkose	do	7	36	1.0
Well, 165 ft Dawson Arkose	NW¼ sec.20, T.10 S., R.66 W, Douglas County.	34	19	.5
Well, 715 ft Dawson Arkose and Arapahoe Formation	SE¼ sec.33, T.6 S., R.68 W, Douglas County	14	42	2.9
Well, 110 ft Dawson Arkose	SW¼ sec.31, T.10 S, R.66 W, Douglas County.	33	24	2.9
Well, Dawson Arkose	NW¼ sec.30, T.10S., R.66W, Douglas County.	--	---	---
Spring, Dawson Arkose	SE¼NE¼ sec.22, T.10 S., R.66 W, Douglas County.	--	---	---

COLLECTION OF WATER SAMPLES FOR RADIUM-228 ANALYSIS

The collection and preservation of water samples for radium-228 analysis generally involves the same problems that are encountered in other radionuclide or trace-element studies. The sample should be as representative as possible of the water unit being sampled, within the reasonable limits of economics.

The problems associated with water sampling are discussed in detail by Barker and Robinson (1963), Rainwater and Thatcher (1960), and Hem (1959) and will be reviewed very briefly here. The preferred method of sampling lakes and large sluggish streams is to obtain a depth integrated sample across a section of the water body. If the radioelement discharge of a stream is being studied, a time-integrated and discharge-integrated sample is most desirable. Sometimes continuous samplers are used to obtain a composite sample. Wells should be pumped before sampling to remove stagnant water. Springs should be sampled by inserting a tube into the orifice and drawing the water into an evacuated flash.

Pyrex, polyethylene, and teflon bottles have been found generally satisfactory for sample collection. New bottles should be washed thoroughly, filled with dilute nitric acid, and allowed to stand for several days to dissolve any leachable trace elements that might be present. The sample bottle should be rinsed with the water to be sampled before being used for collection.

element content of selected ground waters

Vogeli (1961). Constituents given in milligrams per liter]

Sodium, Na (mg/l)	Potassium, K (mg/l)	Bicarbonate, HCO_3 (mg/l)	Chloride, Cl (mg/l)	Nitrate, NO_3 (mg/l)	Dissolved solids (mg/l)	Beta-gamma, activity (pCi/l)	Gross radium, Ra (pCi/l)	Radium-228, Ra^{228} (pCi/l)	Uranium, U (μg/l)	Remarks
500	32.	921.	75.	0.0	2,940	230	17.	6.5	7.0	Radium-224 17 pCi/l.
15	4.2	156.	2.0	2.4	220	21	19.	.9	1.1	Radium-228 sample from tank supplied by wells.
24	4.0	154.	2.0	.0	168	14	1.3	.9	.2	Do.
Na+K=12.		76	2.0	3.2	114	6	.8	1.4	.3	
32	5.	160.	1.0	1.7	248	<13	1.7	1.3	2.3	
Na+K= 10.		44	8.5	44.	161	10	1.2	2.2	<.1	
---	---	---	--	---	----	---	.9	2.0	---	No chemical analysis.
---	---	---	--	---	----	---	1.3	2.5	---	Do.

If the water sample is clear and free from suspended material, the sample is acidified and sealed with an airtight stopper. The U.S. Geological Survey has used acetic acid-chloroform mixture, nitric acid, or hydrochloric acid as fixing agents for trace elements and radioelements. At present, hydrochloric acid is used more than nitric acid because nitric acid interferes with the uranium analysis. Two milliliters of concentrated nitric or hydrochloric acid added to 1 liter of distilled water produces a pH of 1.5. This amount of acid will prevent the precipitation of ferric hydroxide, calcium sulfate, and calcium carbonate in almost any natural water. Precipitation of these compounds will remove several trace elements, including radium, from solution.

A complicated analytical decision arises when the water sample contains suspended material such as, clay, sand, silt, organic debris, oils, or greasy materials. The problem is to accurately separate the solute and suspended phases so that the radium content of each may be independently determined. This separation is impractical (if not impossible) to do on an absolute basis because of the difficulty of separating colloidal and fine suspended matter from true solute in a practical field procedure. It is necessary to treat each sample in exactly the same way so that relative comparison of values is possible. This is achieved by allowing a filter medium to define solute and suspended phases. Porosity of the filter medium is specified, and the designated filter is used each time in exactly the same way in the same filter apparatus.

A field apparatus for filtering large volumes of samples, designated for use in the Water Resources Division, is described by Skougstad and Scarbro (1968). It has a reservoir of 1.5–2.5 liters, and the water is filtered under pressure of an ordinary tire pump through a 0.45 micron cellulose ester filter. The use of this filter is a reasonable compromise between complete removal of colloidal material and filtration speed. The filter removes most of the clay particles, and only the finest clay particles and colloidal particles remain.

The filtered water sample is acidified with nitric acid for fixation of the radium.

DEVELOPMENT OF THE RADIUM-228 METHOD

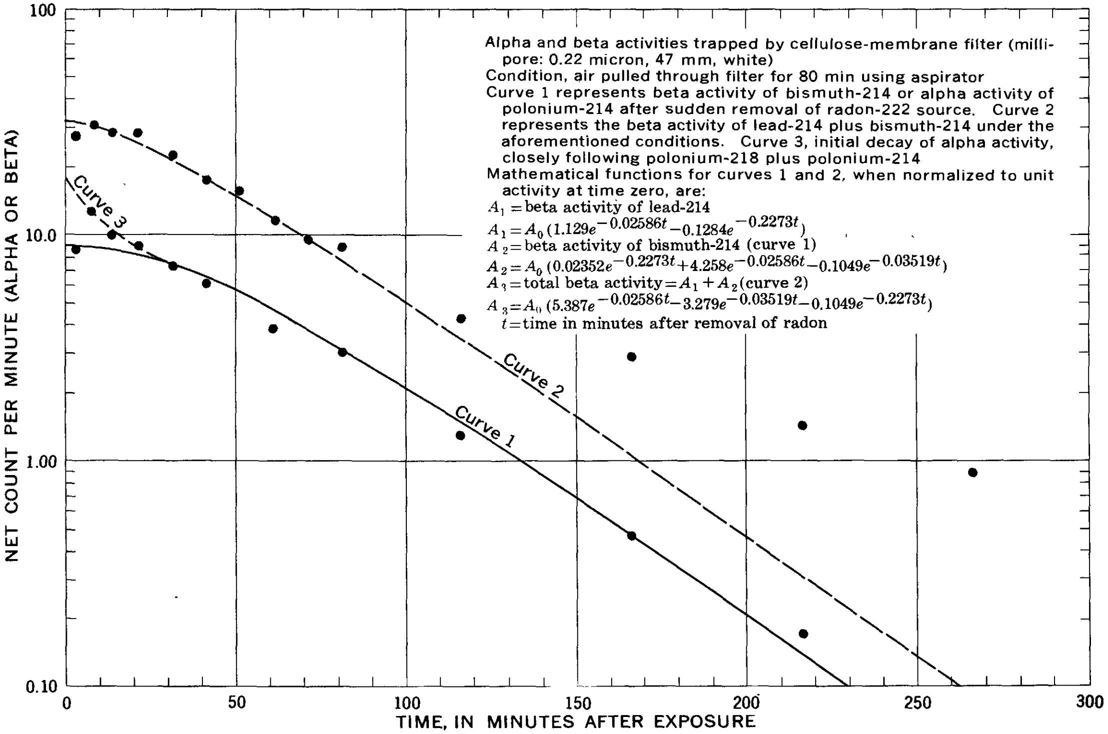
NATURAL RADIOACTIVE NUCLIDE INTERFERENCE

Two radioactive nuclide contamination problems were encountered in the development of the radium-228 method. Yttrium and lanthanum compounds were found to contain considerable amounts of radioactive impurities. An unexpected source of contamination was found from radioactive atmospheric aerosols which were attracted to the filters.

A small amount of reagent contamination in some of the reagents was anticipated, but the amount of contamination of lanthanum and yttrium carriers by nuclides of the uranium-235 series, mostly actinium-227 and daughters, exceeded expectations. A source of yttrium oxide was obtained which was free of detectable radioactive impurities (American Potash and Chemical Co., West Chicago, Ill.), and a yttrium-carrier solution was prepared from this compound. However, after collecting yttrium and actinium hydroxides on a cellulose ester-membrane filter, radioactivities other than the 6.13-hour half life of actinium-228 were observed. The radioactive impurities consisted of a long-lived activity(several days or longer) and a short-lived activity (approximately 30 minutes). A study was made to determine if the short-lived activity could be a combination of lead-214 (26.8 minutes) and bismuth-214 (19.6 minutes). It was thought that these activities were trapped during the filtration process.

Figure 2 shows the decay of radioactive aerosols collected on a membrane filter. The aerosols were collected by passing air through the filter for a period of 80 minutes using a water-aspirator suction. The decay data for the first 2 hours approximates the expected decay of short-lived daughters of radon-222. The presence of longer-lived activities is indicated after about 120 minutes, as the points no longer follow the theoretical decay (Curve 2). Later studies showed that the longer-lived activities consisted of radioactive aerosols from the thorium series (Pb^{212}–Bi^{212}) and probably, (Pb^{210}–Bi^{210}–Po^{210}). If the filtration process were the only method by which radioactive aerosols could be trapped on the filter, filtrations could be done in an inert atmosphere. However, later experiments showed that the electrostatic attraction between the filters and the atmospheric aerosols is sufficient to contaminate the filters. The filters are stated by the manufacturer to have a high-negative electrostatic charge; it is well known that radon-daughter ions are predominantly positively charged and attach themselves to atmospheric aerosols (Wilkering, 1964).

The attractive force between membrane filters (0.22μ) and radioactive aerosols was tested by simply exposing the filter to the atmosphere for a period of 10 minutes. The net beta and alpha activities immediately after exposure were found to be 20 and 5 cpm (counts per minute) respectively. These activities indicate that cellulose ester membrane filters, when exposed to the atmos-



Alpha and beta activities trapped by cellulose-membrane filter (millipore: 0.22 micron, 47 mm, white)

Condition, air pulled through filter for 80 min using aspirator

Curve 1 represents beta activity of bismuth-214 or alpha activity of polonium-214 after sudden removal of radon-222 source. Curve 2 represents the beta activity of lead-214 plus bismuth-214 under the aforementioned conditions. Curve 3, initial decay of alpha activity, closely following polonium-218 plus polonium-214

Mathematical functions for curves 1 and 2, when normalized to unit activity at time zero, are:

A_1 = beta activity of lead-214

$A_1 = A_0(1.129e^{-0.02586t} - 0.1284e^{-0.2273t})$

A_2 = beta activity of bismuth-214 (curve 1)

$A_2 = A_0(0.02352e^{-0.2273t} + 4.258e^{-0.02586t} - 0.1049e^{-0.03519t})$

A_3 = total beta activity = $A_1 + A_2$ (curve 2)

$A_3 = A_0(5.387e^{-0.02586t} - 3.279e^{-0.03519t} - 0.1049e^{-0.2273t})$

t = time in minutes after removal of radon

FIGURE 2.—Decay of airborne radioactivity trapped by membrane filters. Mathematical functions (Bateman equations) assumes decay products to be in secular equilibrium with radon at end of exposure.

phere, attract the radioactive lead, bismuth, and polonium aerosols from the atmosphere to a degree that seriously limits their usefulness for low-level radioactivity determinations. Membrane filters of different composition from other manufacturers were tested for aerosol attraction and all showed detectable radioactivity when exposed to the atmosphere for several minutes or longer. Treatment with antistatic compounds reduced the attraction effect but did not eliminate it. Very fine porosity filter paper (Whatman 42) was found to have a detectable radioactive ($\approx$0.5 cpm beta and $\approx$ 0.1 cpm alpha) initial activity after a short exposure to the atmosphere. The attraction exhibited by various membrane filters for radioactive atmospheric aerosols is unfortunate because the filters offer a very convenient method of preparing precipitates for assay of radioactivity.

Stainless steel planchets were tested for attraction of atmospheric aerosols. After a 200-minute exposure to the atmosphere, no detectable radioactivity was observed. This test indicated that the yttrium-actinium hydroxide precipitate would have to be transferred directly to a planchet, at least until aerosol contamination of membrane filters could be eliminated.

Direct transfer of precipitates to planchets is tedious, and it is difficult to obtain uniform distribution of the precipitate. A glove box was constructed to determine the improvement obtained by carrying out filtration and sample mounting in an inert atmosphere. These studies have not yet been completed, and therefore, the analytical results are from the direct-transfer technique.

RADIUM-228 STANDARD PREPARATION

A problem was encountered in obtaining an accurately standardized radium-228 solution. Radium-228 standard solutions obtained commercially were found to vary considerably from the stated activity. Yttrium-91 made a useful substitute standard for this procedure until a suitable radium-228 standard solution was obtained. The isotope is available in accurately standardized solutions and the isotope's chemical behavior is similar to actinium-228, the isotope actually counted in this procedure. The detection efficiencies are quite comparable; for our equipment they are: 0.71 cpm per pCi for yttrium-91 and 0.61 cpm per pCi for actinium-228.

The best sources for obtaining radium-228 of accurately known concentrations are "old" thorium or thorium compounds. ("Old" throughout this discussion means the preparation was processed at least 40 years ago.) Thorium preparations that old contain an amount of radium-228 with a disintegration rate of at least 99 percent of that of thorium-232. Radium-228 standards of less precise calibration can be directly prepared from thorium preparations that are only 20 years old. These standards may be satisfactory for some purposes. A 20-year-old preparation would contain 87–100 percent of the equilibrium radium-228 concentration. The lower value assumes complete removal of radium-228 on the date at which the thorium was processed.

If "old" thorium reagents are not available for the preparation of radium-228 standards, satisfactory standards can be prepared by removing radium-228 from a thorium reagent and allowing the thorium to age for a specified period. Usually the thorium must be aged for a period of several months so that a reasonable amount of radium-228 will be formed. Methods for obtaining suitable radium-228 standard solutions from both "recent" and old thorium compounds will be discussed.

The laboratory was fortunate in having a moderate quantity of thorium nitrate (45 years old) on hand; some thorium oxide which was at least 60 years old was obtained later. Both reagents were used to obtain satisfactory radium-228 and thorium-232 standards. Practically any "old" thorium compound, with the probable exception of the sulfate, can be used as a source for the direct preparation of radium-228 standard solution. In this method of radium-228 standard preparation, the radium-228 remains in solution with its parent, thorium-232. This state is preferable for this procedure, but not for other procedures; for them, the radium-228 would have to be removed by a series of multiple barium sulfate precipitations or by other techniques.

The following procedures describe the preparation of combined thorium-232 : radium-228 standard solution from old thorium and its compounds, the nitrate and the oxide. Thorium chloride may also be used, but should first be converted to the nitrate by using several evaporations with concentrated nitric acid. Thorium metal and the oxide require special dissolution techniques.

STANDARDS FROM "OLD" THORIUM NITRATE

Make up the thorium nitrate to the desired concentration in 1 *N* nitric acid. A little barium nitrate solution containing 5–15 μg of Ba^{++} should be added before the solution is made up to volume. A thorium concentration of about 10 mg/ml is convenient for a stock solution.

Transfer several aliquots of the thorium solution containing 50 mg or more thorium to tared platinum crucibles. Reduce the volume of solution by evaporating under an infrared lamp. After the solutions have become viscous, place the crucibles in a muffle furnace with the door open. Carefully raise the temperature until nitrogen oxide fumes are no longer evolved. Close the door and very slowly increase the temperature to 950°C. Maintain this temperature for at least 1 hour, then cool gradually to about 100°C. Transfer to a dessicator and cool to room temperature. The exact thorium concentration is determined by weighing as ThO_2. The radium-228 activity calculated from the equation

$$Ra^{228}\ (\text{dpm/ml}) = 246\,W(1 - e^{-0.1034t}),$$

where

t = years since thorium reagent was processed and
W = thorium concentration in milligrams per milliliter.

STANDARDS FROM "OLD" THORIUM OR THORIUM OXIDE

Thorium metal and thorium dioxide are not readily soluble in the common laboratory acids. Dilute hydrofluoric, nitric, sulfuric, and concentrated perchloric acids attack thorium metal slowly. The metal is attacked vigorously by hydrochloric acid, but a black residue of uncertain composition remains. Thorium oxide is even more difficult to dissolve than the metal. Hot concentrated sulfuric acid converts the oxide to the moderately soluble sulfate.

Schuler, Steahly, and Stoughton (1952) described methods for dissolving thorium and thorium oxide using mixtures of nitric acid and hydrofluoric acid.

The following describes a method for preparing accurately standardized thorium-232 and radium-228 from "old" reagent ThO_2:

1. Weigh out a 1.0000 g sample of thorium dioxide to the nearest 0.1 mg.
2. Transfer the sample to a 250 ml erlenmeyer flask containing 20 ml of acid mixture ($15.7\ N\ HNO_3 - 0.05\ N\ HF$). Carefully heat and stir the mixture until the ThO_2 dissolves. Transfer the solution to a 200 ml volumetric flask and add a little barium nitrate solution containing 5–15 μg of barium. Make up to volume with 1 N nitric acid. The solution should contain 4.3928 mg/ml (W) thorium. The Ra^{228} (dpm/ml) = $246\ W\ (1 - e^{-0.1034t}) = 1{,}080$ (within 1 percent if $t \geq 40$ years).

STANDARDS FROM RECENTLY PROCESSED THORIUM REAGENTS

Henry, Loveridge, and Weaver (1963) described a method for preparing standardized radium-228 from thorium nitrate of recent or unknown age. Their method is as follows:

Dissolve 12 g of thorium nitrate tetrahydrate in 500 ml of water and add 60 ml of 9 M sulfuric acid. Add 2 ml of barium carrier solution (5 mg Ba^{++}/ml) to the mechanically stirred solution at room temperature. The solution is stirred for 15 minutes and then filtered. This process is repeated four times with separate additions of barium solution; the solution is chilled to 5°C before addition of barium. This step insures that the thorium solution will not become supersaturated with respect to barium sulfate at room temperature. A longer aging period before filtration is advisable to be certain that the last traces of barium sulfate crystals have formed. The thorium concentration of the solution is then determined as follows:

Pipet a 10 ml sample of the thorium solution into a 250 ml beaker; add 10 ml of concentrated HCl. Evaporate cautiously until moist solids remain, then add 100 ml of 0.15 *M* hydrochloric acid and heat to incipient boiling. Add 21 ml of 10 percent oxalic acid and digest the precipitate at 90–95°C for about 1 hour. Filter the solution through an ashless filter paper and wash the filter with 50 ml of a 2.5 percent oxalic acid solution containing 3.5 ml of concentrated HCl. Transfer the precipitate and filter to a tared platinum crucible and dry under an infrared lamp. Ignite to 1,100°C to constant weight. Weigh as ThO_2. Two more analyses of the solution plus two blanks should be made. The radium-228 content of the thorium solution is determined on the basis of the number of days (T) since the final barium sulfate precipitation and the weight of thorium in mg/ml (W). Ra^{228} (dpm/ml) $= 246\ W\ (1 - e^{-0.693T/2,447})$.

DISCUSSION OF THE METHOD

The U.S. Geological Survey requires a radium-228 method for water that is capable of measuring concentrations as low as 0.3 pCi/l for a 1 liter sample and 0.1–0.2 pCi/l for larger samples. These concentrations and lower ones are easily obtained for radium-226 when using the radon method (Rushing, 1967). This method has been modified by the U.S. Geological Survey and is used for the determination of radium-226 in water and solid materials with excellent results. Most natural surface-water samples contain only small amounts of radium-226, often 0.1 pCi/l or less, and presumably these samples contain about the same amount of radium-228.

A method for determining the alpha-emitting isotopes of radium was described by Goldin (1961). This method was found suitable for obtaining a radium solution sufficiently free from interferences that, with several extensions, radium-228 could also be determined.

The modified method for determining radium-228 is outlined as follows. Lead and barium carriers together with yttrium "hold-back" carriers are added to the sample; and lead, barium, and radium sulfate are coprecipitated, while yttrium and other rare-earth contaminants remain in solution. The precipitates are washed with concentrated nitric acid, then dissolved in alkaline EDTA. Barium and radium sulfates are precipitated by lowering the pH.

The barium-radium sulfates are further purified by additional reprecipitation steps using small amounts of strontium and yttrium "holdback" carriers. After the reprecipitations, the barium-radium sulfate is dissolved in alkaline EDTA solution for the last time, and yttrium and lead carriers are added to the solution. The solution is aged for a period of 36 hours or longer in order for actinium-228 to approach its equilibrium concentration with radium-228.

After the aging period, ammonium sulfide is added to the solution, and lead sulfide is precipitated. The lead sulfide precipitate is separated from the solution, and a large excess of sodium hydroxide is added to precipitate yttrium and actinium hydroxides.

Several steps of the procedure serve to give high decontamination factors from most radiochemical impurities, especially the naturally occurring radioactive elements.

Goldin (1961) showed that the initial nitric acid wash greatly improved the decontamination factors for polonium. Presumably this step would also be effective in minimizing interferences from thorium and nuclides such as cesium-137 and sodium-24.

The EDTA separations serve to separate the radium from thorium, uranium, and radioactive descendents such as lead-210 of the natural activities, including thorium and lead. Strontium and yttrium carriers were added to improve the decontamination factors for such nuclides as strontium-90, yttrium-90, and rare-earth activities.

The aging process (36 hours or more) for actinium-228 buildup in the purified radium solution results in a buildup of radioactive lead and bismuth nuclides from the alpha-emitting radium isotopes. The bismuth isotopes would be carried on the final yttrium hydroxide precipitate, and a lead sulfide precipitation is made immediately before to remove bismuth interference. The lead sulfide precipitation was shown to be effective in removing bismuth from solution. Equilibrium thorium solution containing 1,455 pCi of each descendent was analyzed repetitively for radium-228, and only actinium-228 was detected in the final yttrium hydroxide precipitate. This fact indicates high decontamination factors for lead and bismuth daughters of alpha-active radium isotopes.

Minimum decontamination factors found for other beta emitters are

Uranium (beta descendents, Th^{234}–Pa^{234})	500
Lead–210; bismuth–210 (equilibrium)	500
Strontium–90; yttrium–90 (equilibrium)	600
Cesium–137	600

A possible interference could occur in analyzing a solution containing the fission product (Ba^{140}–La^{140}). The barium-140 would not interfere, but lanthanum-140 would grow into partial equilibrium with its parent during the aging process. The lanthanum-140 would be carried on the yttrium precipitate. This interference would not normally be encountered in natural waters not contaminated by nuclear wastes. The amount of interference from lanthanum-140 can be determined by resolving the decay curve of actinium-228 and lanthanum-140.

APPARATUS

Most of the equipment used in the analysis of radium-228 is of the type available in most radiochemical laboratories. Special equipment may include some of the following:

Heavy-walled graduated centrifuge tubes.

2-inch stainless steel planchets (preferably concentric ring type).

6-inch teflon stirring rods. This item is very desirable in preventing damage to centrifuge tubes.

Low-background beta counter having a beta background count of less than 2 cpm. Manual low-background counters are generally satisfactory for the method and are much less expensive than the automatic counters. Two or three manual units may be purchased for the price of one automatic unit, and a greater production volume can be achieved.

REAGENTS

All reagents are reagent-grade unless otherwise specified.

1. Barium-carrier solution (16 mg/ml): Dissolve 28.460 g of barium chloride di-hydrate in water, add 2 ml of concentrated nitric acid and dilute to 1 liter.

2a. Lead-carrier solution (15 mg/ml): Dissolve 23.97 g of lead nitrate in water, add 2 ml of concentrated nitric acid and dilute to 1 liter.

2b. Lead-carrier solution (1.5 mg/ml): Dilute 100 ml of lead-carrier solution (15 mg/ml) to 1 liter.

3. Yttrium-carrier solution (18 mg/ml): Add 22.85 g of yttrium oxide (Y_2O_3) to a 250 ml erlynmeyer flask containing 20 ml of water, swirl, then place on a hotplate and heat to boiling. Carefully add small additions of concentrated nitric acid while stirring. Usually about 30 ml of concentrated nitric acid is necessary to dissolve the yttrium oxide. Small additions of water may be required to replace that lost by evaporation. The dissolution is accomplished more easily if a magnetic stirring hotplate is available. After the yttrium oxide has dissolved, add 70 ml of concentrated nitric acid and then dilute to 1 liter.

NOTE.—Yttrium oxide, sufficiently free of radioactive contaminants for use as a carrier, was obtained from American Potash and Chemical Co., West Chicago, Ill. (Code No. 1117, Lot No. LWO 811). All carriers should be tested for radioactivity before using. This is especially true for yttrium.

4. Strontium-yttrium carrier (0.9 mg/ml Sr^{+2} and $\approx$ 0.9 mg/ml Y^{+3}): Dilute 10 ml of yttrium-carrier solution (18 mg/ml) to 100 ml (solution A). Dissolve 434.8 mg of strontium nitrate in water, dilute to 100 ml (solution B). Combine solutions A and B.
5. Citric acid (1*M*): Dissolve 210.1 g of citric acid monohydrate in water and dilute to 1 liter.
6. Sulfuric acid (18 *N*): Add 465 ml of concentrated sulfuric acid (36 *N*) to 535 ml of water while stirring.
7. Ammonium sulfate solution (200 mg/ml): Dissolve 200 g of ammonium sulfate in a minimum of water and dilute to 1 liter.
8. EDTA reagent (0.25 *M* disodium ethylendinitrilotetraacetate dihydrate containing 20 mg/ml NaOH): Dissolve 20 g of sodium hydroxide in about 750 ml of water, heat, then slowly add 93 g of disodium ethylenedinitriloacetate dihydrate while stirring. After the sodium salt of EDTA has dissolved, dilute to 1 liter.
9. Ammonium sulfide solution (2 percent $(NH_4)_2S$): Dilute 10 ml of ammonium sulfide (20–24 percent $(NH_4)_2S$) to 100 ml.
10. Sodium hydroxide (10 *N*): Carefully dissolve 400 g of NaOH pellets in a minimum amount of water; dilute to 1 liter. Store in a polyethylene or teflon bottle.
11. Binder solution: Dissolve 1 ml of "Duco" cement (E.I. DuPont de Nemours and Co., Wilmington, Del.) in 100 ml of acetone.

PROCEDURE FOR ANALYSIS OF RADIUM-228

1. The sample selected for radium-228 analysis is filtered through a 0.45 micron molecular-membrane filter, preferably at the time of collection, and 2 ml of concentrated nitric acid is added for each liter of filtrate. The material on the filter is retained if an analysis is to be performed on the suspended material.
2. In the laboratory add 5 ml of citric acid for each liter of sample and a few drops of methyl-orange indicator. If the solution is yellow, add concentrated nitric acid until the red color is obtained.
3. Add 10 ml of lead-carrier solution (15 mg/ml), 2 ml of barium-carrier solution (16 mg/ml), and 1 ml of yttrium-carrier solution (18 mg/ml). Heat to incipient boiling and maintain at this temperature for about 30 minutes.
4. Add concentrated ammonium hydroxide until the yellow color of methyl orange is obtained, then add a few drops excess. Precipitate lead and barium sulfates by adding 18 *N* sulfuric acid until the red color reappears, then add 0.25 ml excess. Add 5 ml of 200 mg/ml of ammonium sulfate for each liter of solution. Keep the sample at a temperature of about 90°C for 30 minutes and stir the sample frequently. Remove the sample from the hotplate and allow it to settle for at least 2 hours, then siphon or decant most of the supernatant liquid and discard.
5. Transfer the precipitate to a 40 ml centrifuge tube. Centrifuge and discard the supernatant liquid.
6. Wash the precipitate twice with concentrated nitric acid using centrifugation wash techniques. Add 25 ml of EDTA reagent. Heat in a hot water bath and stir intermittently, add a little additional 10 *M* NaOH if the precipitate does not dissolve readily.
7. Add 1 ml of strontium-yttrium carrier solution. Stir thoroughly. Add a few drops of 10 *N* NaOH if any precipitate forms.
8. Add 1 ml of ammonium sulfate solution (220 mg/ml) and stir thoroughly, then add glacial acetic acid dropwise until barium sulfate precipitates and then add 2 ml excess. Allow the precipitate to digest in a hot water bath until the precipitate has largely settled. Centrifuge, then discard the supernatant liquid.

9. Add 20 ml of EDTA reagent, heat, and stir until the barium sulfate precipitate dissolves. Repeat steps 7 and 8. (Note the time of the last barium sulfate precipitation.)
10. Dissolve the barium sulfate precipitate in 20 ml of "EDTA reagent," then add 1 ml of yttrium-carrier solution (18 mg/ml) and 1 ml of lead-carrier solution (1.5 mg/ml Pb^{++}). If any precipitate forms, it can be dissolved by adding a few drops of 10 *N* NaOH. Transfer the solution to a teflon or polyethylene container and age it for 36 hours or longer. The sample should be covered to prevent evaporation.
11. Transfer the aged solution to a centrifuge tube; add 0.3 ml of ammonium sulfide solution. Add 10 *N* NaOH dropwise while stirring vigorously until the lead sulfide precipitates, then add about 10 drops excess. Stir intermittently over a period of about 10 minutes.
12. Centrifuge the solution and transfer the supernatant liquid to a clean centrifuge tube.
13. Place the centrifuge tube in a hot water bath and slowly add 10 *N* sodium hydroxide to the supernatant liquid while stirring until yttrium hydroxide precipitates. Add 1 ml excess and stir intermittently for several minutes. Note the time of the precipitation. Centrifuge as soon as the yttrium hydroxide has largely settled. Transfer the supernatant liquid to a clean centrifuge tube and save if the alpha-emitting radium isotopes are to be determined.

NOTE.—The alpha-emitting isotopes may be conveniently determined at this stage by reprecipitating barium and radium sulfate by the addition of glacial acetic acid. The radium isotopes can then be measured by one of several methods, for example, by Goldin's method (1961).

14. Wash the precipitate thoroughly with 5 ml of water containing about 10 drops of 10 *N* NaOH; centrifuge and discard the wash solution.
15. Transfer the precipitate to a 2-inch counting planchet using small volumes of distilled water while drying under an infrared-light lamp. The last washing should contain 1 ml of binder solution.
16. Count the sample in a low-background beta counter for a sufficient length of time to obtain the best counting statistics. For most natural waters, a counting period of about 300–500 minutes is desirable because of the low concentration of radium-228.

CALCULATION OF RESULTS

The following formula is used to calculate the radium-228 concentration in a water sample:

$$Ra^{228}\ (\text{pCi/1}) = \frac{1{,}000\ (R_s - R_b)\ \lambda t_2}{V_s E e^{-\lambda t_1}\ (1 - e^{-\lambda t_2})} \times \frac{1}{(1 - e^{-\lambda t_3})},$$

where

R_s = gross counting rate of sample,
R_b = count rate of blank, including instrument background,
t_1 = elapsed time from yttrium hydroxide precipitation to the beginning of the counting period in minutes,
t_2 = length of the counting period in minutes,
t_3 = time of ingrowth for Ac^{228} in minutes measured from end of step 9 to yttrium hydroxide precipitation. (See Note 1.)
V_s = volume of sample in milliliters,
λ = decay constant of Ac^{228} (0.001885 min^{-1}),
E = efficiency of detector for Ac^{228} in counts per minute per picocurie (cpm/pCi).

NOTE 1.—The factor $\frac{1}{(1 - e^{-\lambda t_3})}$ may be neglected if t_3 is greater than 2,200 minutes.

NOTE 2.—$e^{-\lambda t_1}$ and $\frac{\lambda t_2}{(1 - e^{-\lambda t_3})}$ may be obtained directly from table 3.

TABLE 3.—*Calculation factors for radium-228 determination*

[λ = 0.001885 min^{-1}]

t (min)	λt	$e^{-\lambda t}$	$(1 - e^{-\lambda t})$	$\frac{\lambda t}{(1 - e^{-\lambda t})}$
1	0.001885	0.998117	0.001883	1.0011
2	.003770	.996237	.003763	1.0018
3	.005655	.994361	.005639	1.0028
4	.007540	.992488	.007512	1.0037
5	.009425	.990619	.009381	1.0047
6	.011310	.988754	.011246	1.0057
7	.013195	.986892	.013108	1.0066
8	.015080	.985033	.014967	1.0075
9	.016965	.983178	.016822	1.0085
10	.018850	.981327	.018673	1.0095
20	.03770	.9630	.0370	1.019
30	.05655	.9450	.0550	1.028
40	.07540	.9274	.0726	1.038
50	.09425	.9101	.0899	1.048
60	.1131	.8931	.1069	1.058
70	.1320	.8763	.1237	1.067
80	.1508	.8600	.1400	1.077
90	.1697	.8440	.1560	1.088
100	.1885	.8282	.1718	1.097
110	.2074	.8127	.1873	1.107

TABLE 3.—*Calculation factors for radium-228 determination*—Continued

t (min)	λt	$e^{-\lambda t}$	$(1 - e^{-\lambda t})$	$\frac{\lambda t}{(1 - e^{-\lambda t})}$
120	0.2262	0.7976	0.2024	1.117
130	.2451	.7827	.2173	1.127
140	.2639	.7681	.2319	1.138
150	.2828	.7537	.2463	1.148
160	.3016	.7396	.2604	1.158
170	.3204	.7258	.2742	1.168
180	.3393	.7123	.2877	1.179
190	.3582	.6990	.3010	1.190
200	.3770	.6859	.3141	1.200
210	.3958	.6731	.3269	1.211
220	.4147	.6605	.3395	1.221
230	.4336	.6482	.3518	1.232
240	.4524	.6361	.3639	1.243
250	.4712	.6242	.3758	1.253
260	.4901	.6126	.3874	1.265
270	.5090	.6011	.3989	1.276
280	.5278	.5899	.4101	1.287
290	.5466	.5789	.4211	1.298
300	.5655	.5680	.4320	1.309
310	.5844	.5574	.4426	1.320
320	.6032	.5471	.4529	1.332
330	.6220	.5369	.4631	1.343
340	.6409	.5268	.4732	1.354
350	.6598	.5170	.4830	1.366
360	.6786	.5073	.4927	1.377
370	.6974	.4979	.5021	1.389
380	.7163	.4886	.5114	1,401
390	.7352	.4794	.5206	1.412
400	.7540	.4705	.5295	1.424
410	.7728	.4617	.5383	1.436
420	.7917	.4531	.5469	1.448
430	.8106	.4446	.5554	1.459
440	.8294	.4363	.5637	1.471
450	.8482	.4281	.5719	1.483
460	.8671	.4202	.5798	1.496
470	.8860	.4123	.5877	1.508
480	.9048	.4046	.5954	1.520
490	.9236	.3971	.6029	1.532
500	.9425	.3897	.6103	1.544
510	.9614	.3824	.6176	1.557
520	.9802	.3752	.6248	1.569
530	.9990	.3682	.6318	1.581
540	1.0179	.3614	.6386	1.594
550	1.0368	.3546	.6454	1.606
560	1.0556	.3480	.6510	1.622
570	1.0774	.3405	.6595	1.634
580	1.0933	.3351	.6649	1.644
590	1.1122	.3288	.6712	1.657
600	1.1310	.3227	.6773	1.670
610	1.1498	.3167	.6833	1.683
620	1.1687	.3108	.6892	1.696
630	1.1876	.3050	.6950	1.709
640	1.2064	.2993	.7007	1.722
650	1.2252	.2937	.7063	1.735
660	1.2441	.2882	.7118	1.748
670	1.2630	.2828	.7172	1.761
680	1.2818	.2775	.7225	1.774
690	1.3006	.2724	.7276	1.788
700	1.3195	.2673	.7327	1.801

Example of a sample calculation

Blank count rate $(R_b) = 1.52$ cpm.
Sample count rate = 900 counts in 500 minutes.
= 1.80 cpm.
Volume of sample V_s = 3,000 ml.
E from efficiency studies using actinium–228:
Ac^{228} = 0.61 cpm/pCi.
t_1 = 120 minutes.
t_2 = 500 minutes.
$e^{-\lambda t_1}$ from table = 0.7976.

$$\frac{\lambda t_2}{(1 - e^{-\lambda t_2})} = 1.544.$$

$$Ra^{228}\ (\text{pCi/l}) = \frac{1{,}000 \times (1.80 - 1.52) \times 1.544}{3{,}000 \times 0.61 \times 0.7976},$$
$$= 0.3\ \text{pCi/l}$$

ERRORS AND PRECISION

The assignment of a precision index to a radium-228 determination involves errors common to both gravimetric-chemical analyses and low-level radiochemical analyses. Barium and radium were assumed to behave identically in the chemical separations, at least to the final barium sulfate precipitation. Barium-carrier recovery was measured by weighing the final barium sulfate precipitate and was found to be nearly quantitative. Recovery of added radium-228 was measured by measuring the activity of actinium-228 in the final yttrium hydroxide precipitate. Recoveries were usually greater than 85 percent above the 5 pCi level.

A radium-228 method suitable for the analyses of most natural water samples should be able to detect concentrations of that isotope of less than 1 pCi/l. The practical minimum detection limit of this method is about 0.3 pCi/l when using a 3-liter sample, although counting statistics alone indicate a lower limit of about 0.15 pCi/l. The calculation of a radium-228 concentration near the minimum detection limit was shown as the example of a sample calculation. The sample was counted for about 8 hours on a low-background beta counter which had a very stable background (1.52±0.10 at the 95 percent confidence limit for the counting period).

Two methods for lowering the detection limit are available: the use of large samples (10 liters or larger) and counting the sample in a counter having a lower background.

Detection systems with beta backgrounds between 0.1 and 0.5

cpm are commercially available. Some problems in sample preparation would be encountered in using the lowest background detectors because of their small detection area.

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