



Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A5

METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

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**Book 5
LABORATORY ANALYSIS**

Carbon-14, dissolved, apparent age Liquid scintillation method, Denver Lab (R-1100-76)

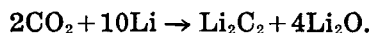
**Parameter and code: Carbon-14, dissolved, apparent age (years):
none assigned**

1. Application

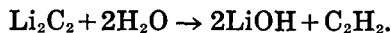
The method determines the apparent age of carbon-14 dissolved in the water sample. It is suitable for the analysis of any natural-water sample from which 5 g of dissolved carbon can be obtained. Only carbon in the form of dissolved CO_2 and its hydrolysis products is determined. The apparent age, determined by comparison with a standard of known age (see sec. 5.10), applies only to the carbon-14 in the sample; use of the determination to date the water itself requires a number of additional measurements and assumptions and a general knowledge of the geohydrologic system from which the sample was obtained. As noted below, a modification of the procedure is used for waters containing sulfate in excess of approximately 200 mg/l.

2. Summary of method

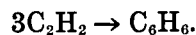
The method is based on that of Noakes and others (1967). Dissolved carbon in the carbonate system is concentrated from a large volume of water by precipitation of barium carbonate. The precipitate is treated with acid to liberate carbon dioxide, which is then allowed to react with metallic lithium to produce lithium carbide:



The carbide is then hydrolyzed to produce acetylene:



Finally, the acetylene is passed over a vanadium-doped aluminum oxide catalyst to form benzene:



The benzene is placed in a tared scintillation counting vial, weighed, and then diluted slightly with a toluene solution containing a mixture of scintillators sensitive to low-energy betas. The activity of the sample is measured in a liquid scintillation counter. From the ratio of carbon-14 activity to the weight of carbon recovered, the apparent age of the carbon in the sample may be determined.

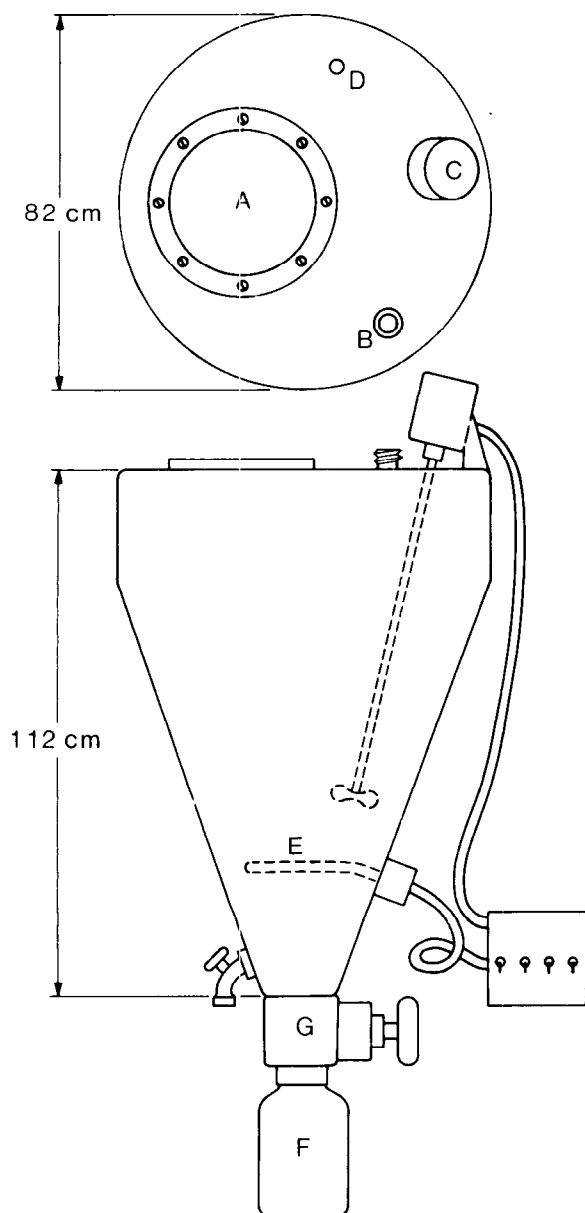
3. Interferences

The conversion from CO_2 to C_6H_6 is apparently free of both chemical and radiometric interferences. During sample collection and precipitation procedures interference may result from contact with the atmosphere or from dissolved sulfate concentrations in excess of approximately 200 mg/l.

The sample collection must minimize atmospheric contact with the water. Sample collection should be in a closed system from the sampling point to the collection containers. Collection containers (normally 15- to 55-gal steel drums) should be filled by inserting tubing to the container bottom, and flow continued until three container volumes have passed through the container. The sampling tube should be removed slowly and the container capped immediately after removal of the delivery tube.

4. Apparatus

- 4.1 *Beakers*, polyethylene, 400 ml.
- 4.2 *Cylinder*, graduated, 50 ml.



- A - PLEXIGLASS VIEWING PORT
 B - CONNECTOR FOR HOSE FROM SAMPLE BARREL
 C - STIRRING MOTOR
 D - PRESSURE RELIEF VALVE
 E - IMMERSION HEATER
 F - MASON JAR
 G - GATE VALVE

Figure 2.—Apparatus for collection of carbonates from a water sample.

4.3 Drums, steel, 15-gal and 55-gal capacity with 1- and 2-inch bungs.

4.4 Liquid scintillation counter.

4.5 pH indicating paper, pH 2.0–5.0 range.

4.6 Precipitator for barium carbonate (fig. 2).

4.7 Vacuum line for storage of acetylene and conversion to benzene (fig. 3).

4.8 Valves for transfer of water sample from drums to precipitator.

5. Reagents

5.1 *Ascarite* (trade name of Arthur H. Thomas Co. for sodium hydroxide-impregnated asbestos).

5.2 *Barium chloride-lanthanum chloride solution*: Dissolve 290 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 g LaCl_3 in distilled water and dilute to 1 liter.

5.3 *Benzene*, spectroscopic grade, free of carbon-14 activity.

5.4 *Catalyst*, vanadium-doped Al_2O_3 , or Mobil Oil Co. Durabead.

5.5 *Dry ice*.

5.6 *Isopropanol*, technical grade.

5.7 *Liquid nitrogen*.

5.8 *Lithium metal*, shot, packed, and stored under argon.

5.9 *Nitrogen gas*. Must be free of CO_2 or scrubbed to remove CO_2 .

5.10 *Oxalic acid*. National Bureau of Standards contemporary standard.

5.11 *Phosphoric acid*, concentrated (85 percent).

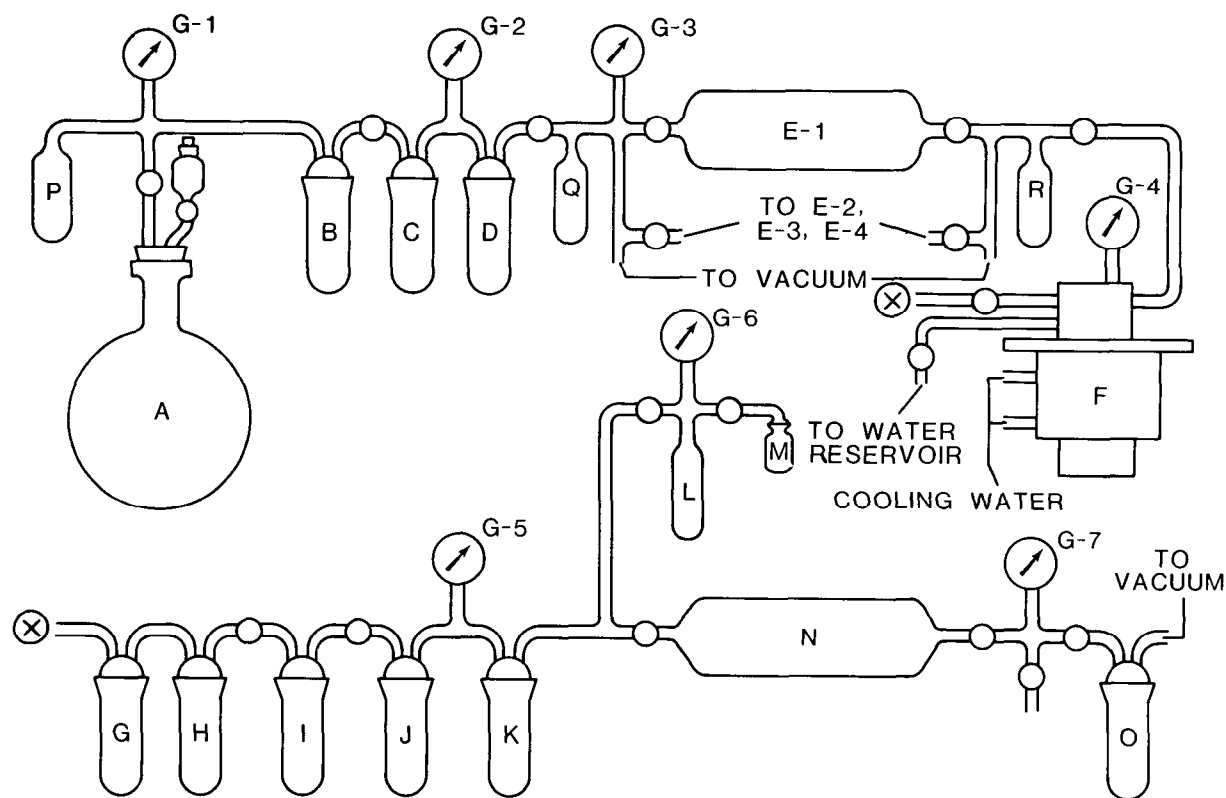
5.12 *Phosphorus pentoxide*, granular.

5.13 *Scintillator solution*: 10 g 2,5-diphenyloxazole (PPO), 0.25 g 1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene (dimethyl POPOP). Dissolve in 250 ml analytical-grade toluene.

5.14 *Sodium hydroxide solution*, 5 M.

5.15 *Sulfuric acid*, 0.0164 N.

5.16 *Strontium chloride-lanthanum chloride solution*: Dissolve 230 g $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 g LaCl_3 in distilled water and dilute to 1 liter.



A - CARBON DIOXIDE EVOLUTION FLASK
 B, C, D, G, H, I, J, K, O - TRAPS
 E-1 - E-4, N - GAS STORAGE CYLINDERS
 F - REACTION CHAMBER

L - CATALYST REACTION TUBE
 M - COLD FINGER FOR BENZENE
 P, Q, R - COLD FINGERS
 G-1 - G-7 - VACUUM GAUGES

Figure 3.—Vacuum line for preparation of acetylene and conversion to benzene.

6. Procedure

6.1 Determine the volume of water sample required to contain 5 g carbon as carbonate or bicarbonate. Alkalinity contributed by silicate, borate, phosphate, and other basic constituents is included in the following estimation of carbonate alkalinity. Therefore, the method underestimates the volume required if noncarbonate alkalinity is also present.

6.1.1 To 50-ml water sample in 400-ml beaker add 30 ml 0.0164 N sulfuric acid. Test the pH, using narrow-range indicating paper or a pH meter. If the pH is above 4.5, sufficient carbon is contained in 15 gal (55 liters) of the water sample.

6.1.2 If the pH is less than 4.5, add a second 50-ml portion of water sample to

the solution in the 400-ml beaker. Again, test the pH. If the pH is now above 4.5, it is satisfactory to use two 15-gal drums of water sample. If the pH is still less than 4.5, repeat the addition of 50-ml sample aliquots to the 400-ml beaker until a pH of 4.5 is obtained. Collect one 15-gal drum for each 50-ml portion of sample required for neutralization of the acid to pH 4.5. Six 15-gal or two 55-gal drums is the maximum volume collected.

6.2 Collection of sample.

6.2.1 Fill each 15-gal drum by inserting a hose to the bottom of the drum and fill until two or more drum volumes have overflowed. Remove hose, insert plugs in bungs and tighten securely, taking care to minimize trapped air. Ship to the laboratory taking care to prevent freezing in cold weather.

6.3 Collect dissolved carbonate species by precipitation as barium carbonate using the precipitation apparatus shown in figure 2.

6.3.1 Attach a 2-liter Mason jar to the bottom of the precipitation cone. Run a hose from the 15-gal drum containing the sample to the precipitator. Seal the top plate and sweep out the unit with nitrogen gas to remove atmospheric carbon dioxide. Apply pressurized nitrogen to the 15-gal drum to force the water sample over into the precipitator.

6.3.2 Precipitate barium sulfate and carbonate by heating the sample with the immersion heater while stirring and adding 2 liters of barium chloride solution. If sulfate in the water sample exceeds approximately 200 mg/l (previously determined in the field or laboratory), strontium chloride is used as precipitant. Add 5 M sodium hydroxide slowly until pH of 10.4 is reached to convert bicarbonate to carbonate. Stir for 1 hr while holding the temperature at approximately 40°C.

6.3.3 Open the bottom valve and permit the barium sulfate-carbonate precipitate to flow into the Mason jar. Rotate stirring rod briefly by flipping control switch after 1 hr. Repeat cycle each one-half hour for next 2 hr. Major portion of precipitate should now be in the Mason jar. Close bottom valve, unscrew Mason jar, cap immediately, and seal exposed cap edges with vinyl or rubber tape.

6.4 Synthesis of benzene. The vacuum line for evolution of carbon dioxide and its conversion to benzene is shown schematically in figure 3.

6.4.1 Evolution of carbon dioxide from barium carbonate.

6.4.1.1 Decant most of the supernate from the barium sulfate-barium carbonate precipitate. Slurry the remaining precipitate and solution and transfer to a 4-liter heavy-walled Pyrex flask (A). Put a magnetic stirrer bar in the flask, cap with a two-hole stopper containing a separatory funnel, and place on the vacuum line. The vacuum line has been previously evacuated. Fill the separatory funnel with 125 ml of 85 percent phosphoric acid.

6.4.1.2 Evacuate the 4-liter flask carefully until bubbles foam in the slurry. Continue evacuation for 2 min.

6.4.1.3 Carefully run the phosphoric acid from the separatory funnel into the 4-liter flask. Carbon dioxide is released from the slurry. Allow the pressure to build up to approximately 120 mm of mercury (gauge G-1) and then open the stopcock to traps C and D so that pressure holds constant. Trap B is cooled with isopropanol-dry ice. Its function is to condense water. Traps C and D are cooled with liquid nitrogen, and their function is to condense carbon dioxide.

6.4.1.4 When the evolution of carbon dioxide is completed as shown by decrease of pressure on gauge G-1 to a constant minimum, carbon dioxide can now be transferred to the storage cylinders E-1, E-2, E-3, and E-4. The quantity of carbon dioxide is calculated from the known volume of each cylinder (slightly more than 6 liters) and the pressure on gauge G-3. Remove the liquid-nitrogen Dewar from trap C. Replace the liquid-nitrogen Dewar at trap D with an isopropanol-dry ice Dewar. Carbon dioxide flows into cylinder E-1 and when atmospheric pressure is reached, cylinder E-2 is opened and filled. The remaining two cylinders are successively filled in the same way.

6.4.1.5 Calculate the number of moles of carbon dioxide collected using volume of each storage cylinder, gauge pressure, and ambient temperature. Determine the grams of lithium metal to be used in the following carbide conversion step by multiplying the number of moles by 60.

6.4.1.6 Weigh out the required lithium shot, and place in the steel reaction chamber F. Evacuate the line and the chamber, start the flow of cooling water through the reaction chamber, and turn on the heater.

6.4.2 Reduction of carbon dioxide to lithium carbide carbide.

6.4.2.1 When lithium is a dull-red heat (as observed through the viewing port) admit carbon dioxide from the storage tanks into the reaction chamber F. Pressure drops sharply as the reaction proceeds (G-4). Con-

tinue heating until pressure drops to minimum. Continue heating for 1 hr. Turn off heat and allow to cool.

6.4.2.2 The lithium carbide containing carbon-14 is treated with water to form acetylene. Unreacted lithium reacts with water to produce hydrogen. Carefully introduce water from the distilled-water reservoir. The pressure rises because of production of acetylene and hydrogen. The acetylene condenses in traps I and K which are cooled with liquid nitrogen. Acetylene is purified before condensation by passage through traps G, H, and I. Traps G and H are cooled with isopropanol-dry ice and trap I contains ascarite and phosphorous pentoxide. One to 1.5 liter of water is required for complete reaction. When the pressure nears atmospheric, open the chamber to the vacuum pump to remove hydrogen as fast as it is produced. Continue pumping after completion of the reaction (bubbling ceases) until pressure falls to full vacuum.

6.4.3 Formation of benzene from acetylene.

6.4.3.1 The reaction tube L contains approximately 150 g of catalyst. Remove the liquid nitrogen Dewars from traps J and K and replace with isopropanol-dry ice coolant around K only. Place a liquid nitrogen Dewar around the cold finger M. Acetylene now sublimates from J and K and condenses in M.

6.4.3.2 Conversion of acetylene into benzene via the aluminum oxide catalyst averages about 97 percent with a good batch of catalyst. Occasionally an inferior batch is encountered, and conversion is much lower. There is no way to predict whether a new shipment of catalyst will give high or low conversion. The percentage of conversion for an individual run is determined by diverting the acetylene into storage cylinder N before it is frozen into cold finger M. The pressure reading shown on gauge G-6 and the known volume of N enables calculation of the moles of acetylene.

6.4.3.3 When acetylene is completely condensed in M transfer it to the catalytic reaction tube by replacing the liquid nitro-

gen Dewar with isopropanol-dry ice. Complete reaction is indicated by constant minimum pressure on gauge G-6. Complete reaction requires 2-3 hr. A second tube of catalyst may be required to achieve complete reaction.

6.5 Preparation for counting.

6.5.1 Transfer the catalyst tube containing benzene to a vacuum-distillation apparatus. Immerse the receiving tube in isopropanol-dry ice, and after the system is evacuated, heat the catalyst tube. When condensation of benzene in the receiving tube is complete, remove and weigh to determine benzene recovery.

6.5.2 Transfer 3.0 ml benzene to a scintillation-counting container, add 1.0 ml scintillator, and count under optimum conditions for carbon-14. Count each sample several times to accumulate at least 400 min of counting time on each sample. Reject early counting run results if instability is displayed.

7. Calculations

Calculate the apparent age of the sample from the following equation:

$$T = 3.32 T_{\frac{1}{2}} (\log A_0 - \log A),$$

where

T = apparent age of sample in years,

$T_{\frac{1}{2}}$ = half-life of carbon-14 in years
(5,568 yr),

A_0 = 0.950 times activity (in net counts per minute per gram of carbon) of NBS oxalic acid contemporary standard. This value is an average of several measurements on contemporary standards, and

A = activity of sample (in net counts per minute per gram of carbon).

8. Report

Report apparent age of dissolved carbon-14 in sample to nearest 50 yr for ages <1,000 and to nearest 100 yr for ages >1,000.

9. Precision

Precision as calculated from the counting variances for the sample, background, and

the standard counts give an optimistic estimation since possible errors involved in the precipitation of the carbon and its conversion to benzene are not included. According to Stuiver (1972), the precision of a carbon-14 date should be ± 100 yr in the 10,000-yr range and ± 800 yr in the 30,000-yr range.

References

- Noakes, J. E., Kim, S., and Akers, L., 1967, Recent improvements in benzene chemistry for radiocarbon dating, *Geochim. Cosmochim. Acta* 31, (6) p. 1094-1096.
- Stuiver, M., 1972, in *Encyclopedia of geochemistry and environmental sciences*, edited by Fairbridge, Van Nostrand Reinhold Co., p. 131.

Cesium-137 and cesium-134, dissolved Inorganic ion-exchange method—gamma counting (R-1110-76)

**Parameters and codes: Cesium-137, dissolved (pCi/l): none assigned
Cesium-134, dissolved (pCi/l): 28410**

1. Application

The combination of a reasonably specific ion-exchange separation of cesium isotopes with the energy discrimination available through gamma spectrometry provides a very specific method with potentially wide applicability. Boni (1966) applied the related KCFC technique to the determination of cesium-137 in milk, urine, seawater and freshwater. Petrow and Levine (1967) applied an ammonium hexacyanocobalt ferrate (NCFC) method to the determination of cesium-137 in precipitation.

2. Summary of method

The method is a development of Janzer, based on the work of Petrow and Levine (1967), who used NCFC for the concentration of cesium isotopes from water. The ammonium compound is superior to the potassium compound (KCFC) used by Prout, Russell, and Groh, (1965) because of elimination of background from potassium-40.

The gamma-counting technique begins with collection of radiocesium from relatively large volumes of water (up to 20 liters) by passing the sample through a column of inorganic ion-exchanger (NCFC). Several standards are prepared by passing a measured amount of standardized cesium-137 solution in water through columns prepared in the same manner as those used for the unknowns. The columns are dried and then counted using a well-type sodium iodide gam-

ma detector and an automatic sample changer and single channel gamma spectrometer. The signal to noise ratio is optimized by adjusting the spectrometer window to the cesium-137 or cesium-134 energy peaks.

Blanks consisting of test tubes with exchanger are counted with the comparator standards and samples for a minimum of three 50-min counts. The cesium concentration is calculated on the basis of the net gamma counts observed in the standards and samples.

3. Interferences

Ruthenium, zirconium-niobium, cobalt, and zinc were reported to be sorbed by KCFC from neutral aqueous solutions. Sorption of interfering radionuclides was reduced to less than 0.1 percent from a 10 N HCl and 0.5 N HF solution (Boni, 1966). Boni also noted that interfering radionuclides could be removed by passing the sample through 50–100 mesh Bio-Rad Celex 100 in the calcium form before collecting the cesium on the KCFC.

Ellenburg and McCown (1968) reported iodine-131 and molybdenum-99 were sorbed in the analysis of reactor-fuel solutions using a slurry technique with 150 ml of sample and 50 mg of KCFC sorber. NCFC probably exhibits similar sorption. The degree to which extraneous radionuclides collected by NCFC may interfere during counting is a function of the energy resolution of the detector. Iodine-131 might interfere using the NaI de-

tector specified, because the cesium-137 photopeak at 662 keV might not be fully resolved from the iodine-131 photopeak at 636 keV. Using a Ge(Li) detector, there would be no interference because resolution would be complete. The combination of decay to eliminate molybdenum-99 ($T_{1/2} = 67$ h) and other short-lived nuclides and high-resolution gamma spectrometry would appear to permit specific determination of cesium isotopes.

4. Apparatus

4.1 *Gamma spectrometer*, single-channel type.

4.2 *Glass and plastic tubing*.

4.3 *Glass wool*.

4.4 *Porous polypropylene disks*: Cut from 1.5 mm thick, 120 micrometer porous hydrophilic polypropylene sheeting (Bel Art F-1256 or equal).

4.5 *Sample changer*, automatic for 16 \times 150-mm test tubes, coupled to a printout system.

4.6 *Slotted 16 \times 150-mm test tubes*: A 2- to 3-mm vertical slot, 1-mm wide, is cut into the bottom of the test tube. Fire-polishing the tubes after cutting reduces breakage.

5. Reagents

5.1 *Ammonium hexacyanocobalt ferrate*, (NCFC) 30–60 mesh prepared after the manner described by Petrow and Levine (1967).

Add 10 ml of 0.5 M sodium ferrocyanide solution dropwise (approximately 35 ml/min) to 240 ml of 0.3 M cobalt nitrate-1.0 M ammonium nitrate solution while stirring on a magnetic mixer. Centrifuge slurry in 250-ml centrifuge tubes, decant, and discard the supernate.

Wash slurry with water several times to remove excess unreacted salts. Dry slurry in tubes by heating overnight in 80°C oven. Crush dried salt and sieve to collect 30–60 mesh fraction. Retain fines for incorporation with next batch of slurry prepared.

The measured cation exchange capacity for 30–60 mesh KCFC was reported by Prout, Russell, and Groh (1965) to range

from 0.3 to 0.5 meq Cs/g KCFC using a cesium nitrate feed solution varying from 0.001 to 0.008 M. They calculated a theoretical exchange capacity of about 6 meq/g for KCFC.

5.2 *Cesium-137 and cesium-134 standard solutions*: Obtain from the National Bureau of Standards or other commercial suppliers. Dilute to approximately 100 pCi/ml for use.

6. Procedure

6.1 Using the slotted 16 \times 150-mm test tubes, prepare exchange columns by placing small plug of glass wool in bottom of tube, add 30–60 mesh NCFC to a depth of 1 cm, and position a porous polypropylene disk on top of the NCFC to keep it in place. Do not compress the NCFC granules, or excessive flow reduction will result from the slight swelling which occurs when the sorber is wetted. Prepare columns as uniformly as possible to obtain reproducible counting geometry in the well-type detector.

6.2 Using 5-mm glass and plastic tubing, prepare a series of siphons which will provide a 1- to 1.5-meter head. Firmly insert the lower end of the siphon into the numbered test tube exchanger using a size 0, one-hole rubber stopper, and place the upper end of the siphon in the water sample. Maximum sample volume normally used is 20 liters.

6.3 Apply suction to the slot of the test tube to start flow. Flow rates of 1–5 ml/min are normal. More rapid flow rates can be obtained by using coarser NCFC or increasing the siphon head, but contact time would be reduced accordingly. Some color may be leached out of the NCFC during the first few milliliters of flow, but this apparently has no effect on the cesium collection.

6.4 When all the solution has passed through the column, disconnect the siphon, wipe the tubes dry, and place in an 80°C oven to dry.

6.5 Prepare several comparator standards by passing a measured amount of cesium-137 standardized solution (20–100 pCi) through additional exchanger tubes.

6.6 Adjust the gamma spectrometer to obtain optimum counting in the cesium-137

energy region (662 keV) or the cesium-134 energy region (605 keV, 796 keV).

6.7 Count reagent blanks, standards, and samples for a minimum of three 50-min counting periods each.

7. Calculations

7.1 Efficiency factors for cesium-137 (E_a) and cesium-134 (E_b) are calculated by the following equations. The efficiency factor includes counting efficiency and chemical recovery. Use of standard equation 2 to correct for cesium-137 decay is not often required.

$$E_a = \frac{\bar{c}_n}{d_n (e^{-\lambda_a t_n})},$$

$$E_b = \frac{\bar{c}_n}{d_n (e^{-\lambda_b t_n})},$$

where

\bar{c}_n = average count rate of standard (cpm) corrected for background and blank,

d_n = disintegration rate of standard (dpm),

λ_a = decay constant of cesium-137 (0.02295 yr^{-1}),

λ_b = decay constant of cesium-134 ($0.0280 \text{ months}^{-1}$), and

t_n = elapsed time between certification of the standard and the count, in same units as the respective λ .

7.2 Calculation of cesium-137 and cesium-134 concentrations: Use equation 1 where Ef

is set equal to E_a or E_b . Decay correction for cesium-137 is usually not required.

$$\text{pCi/l of cesium-137} = \frac{1000\bar{c}}{KVE_a (e^{-\lambda_a t})},$$

$$\text{pCi/l of cesium-134} = \frac{1000\bar{c}}{KVE_b (e^{-\lambda_b t})}.$$

8. Report

Report concentrations to one significant figure for concentrations between 0 and 10 pCi/l and to two significant figures for higher concentrations.

9. Precision

Precision of the method is estimated to be approximately ± 20 percent.

References

- Boni, A. L., 1966, Rapid ion-exchange analysis of radiocesium in milk, urine, sea-water and environmental samples: *Anal. Chemistry*, v. 38, no. 1, p. 89-92.
- Ellenburg, E. J., and McCown, J. J., 1968, Rapid carrier-free method for the radiochemical determination of cesium-137: *Anal. Letters*, v. 1, no. 11, p. 697-706.
- Petrow, H. G., and Levine, H., 1967, Ammonium hexacyanocobalt ferrate as an improved inorganic exchange material for determination of cesium-137: *Anal. Chemistry*, v. 39, no. 3, p. 360-362.
- Prout, W. E., Russell, E. R., and Groh, H. J., 1965, Ion exchange absorption of cesium by potassium hexacyanocobalt (II) ferrate (II): *Jour. of Inorg. Chem.*, v. 27, p. 473-479.

Radiocesium, dissolved, as cesium-137 Inorganic ion-exchange method—beta counting (R-1111-76)

**Parameter and code: Radiocesium, dissolved, as cesium-137 (pCi/l):
none assigned**

1. Application

Application is possible when identification of individual cesium isotopes is not required and when interfering beta-emitting isotopes are in low concentration. Concentration limits for interfering isotopes have not been fully evaluated but would appear to be lower than for the gamma-spectrometry technique for cesium-137 and cesium-134, dissolved (inorganic ion-exchange method—gamma counting, R-1110-76). Until interferences are quantitatively evaluated, examination of each sample for possible interference is advised. Applications to samples where radiocesium is the principal source of radioactivity would appear to be safe.

2. Summary of method

In the beta-counting technique (Janzer, 1973) the same ion-exchanger (NCFC) is used to collect the cesium-137 and cesium-134 isotopes as in the gamma technique, but a simpler batch operation is made possible by the smaller volume of water used. One hundred milligrams of the ion-exchanger are stirred with the buffered water sample and then separated by filtration through a paper or membrane filter. This forms a uniform low-density disk deposit that is optimum for beta counting. Standards are prepared using the same technique. The sample and standard disks are counted in a low-background beta counter with anticoincidence shielding.

The method determines total dissolved radiocesium concentration because individual isotopes are not identified by this beta counting.

3. Interferences

No interferences have been found.

4. Apparatus

4.1 *Low-background counter*, an anti-coincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously. (The Beckman Wide Beta or Low Beta counters or equivalent, with pulse height discriminating circuitry, are satisfactory.)

4.2 *Filter*, nitrocellulose membrane filters, 0.45-micrometer pore size, 47-mm diameter. A suitable filter holder assembly to facilitate vacuum filtration using the 47-mm filters is required. The perforated backup plate under the filter disk must be plastic rather than glass because of the hydrofluoric acid solution used. Millipore Sterifil XX-047-10 or equivalent is satisfactory.

4.3 *Teflon, polyethylene, polypropylene, or other acid resistant beakers*, 600-ml volume.

5. Reagents

5.1 *Ammonium hexacyanocobalt ferrate (NCFC)*: Prepare as described by Petrow and Levine (1967), and sieve to collect the 30-60 mesh fraction.

5.2 *Cesium-137 standard solution.* Obtain from NBS or use commercial standards, approximately 100 pCi/ml.

6. Procedure

6.1 Place a 500-ml water sample in a plastic beaker.

6.2 Acidify with concentrated hydrochloric acid to 1 *N* and with hydrofluoric acid to 0.5 *N*. For a 500-ml sample, this requires 45 ml of concentrated hydrochloric and 10 ml of concentrated hydrofluoric acid.

6.3 Add 100 mg (± 1 mg) of 30–60 mesh NCFC, and stir for 10 min. After allowing the NCFC to settle, decant the supernatant solution and filter it through a 0.45-micrometer membrane filter (47-mm diameter) in a vacuum-filtration assembly. With the last portion of liquid remaining in the beaker, transfer the NCFC to the filter taking care to obtain even distribution. Return the filtrate to the plastic beaker. Filter through the original filter disk a second time, and quantitatively transfer any remaining NCFC to the filter disk with small amounts of distilled water. Rinse down the funnel sides, and carefully wash the filter and retained NCFC several times so that the filter pad is not disturbed and a uniform deposit is maintained.

6.4 Mount the filter disk in a ring holder, and dry under an infrared lamp. Cover the dry material with a small sheet of plastic wrap (kitchen-type).

6.5 Count in the anticoincidence beta counter. Three 50-min counts for each sample are usually adequate.

6.6 Prepare standards in triplicate. Add 5.0 ml of 100 pCi/ml standard cesium-137 solution to 500 ml of distilled water, and carry out the analytical procedure exactly as with a sample. The standards prepared in this way are also covered with plastic film and may be retained for semipermanent use.

If different sample sizes are used, corresponding standards should be prepared.

6.7 Prepare blanks by running the determination on 500 ml of distilled water.

6.8 Count the blanks and standards in the same way as the samples.

7. Calculations

7.1 The cesium-137 efficiency factor (*E*) includes chemical recovery and counting-efficiency corrections and is determined by equation 2 simplified by treating standards and samples the same so that no factor *f* is calculated. The following equation is then used:

$$E = \frac{\bar{c}_n}{d_n (e^{-\lambda t_n})}$$

7.2 Calculation of cesium-137 concentration: Use general equation 1 simplified by eliminating the *f* term. Decay correction is seldom required.

$$\text{pCi/l of cesium-137} = \frac{1000\bar{c}}{KVE (e^{-\lambda t})}$$

8. Report

Report cesium-137 activity to one significant figure below 10 pCi/l and to two significant figures above 10 pCi/l. The minimum concentration reported is that which represents two standard deviations above background. This is approximately 1 pCi/l with a 500-ml sample and a Beckman Low Beta counter or equivalent.

9. Precision

On the basis of limited data the analysis appears to be reproducible to ± 10 percent at concentrations above 10 pCi/l with inferior reproducibility at lower concentrations.

Reference

- Janzer, V. J., 1973, A rapid method for the determination of radioactive cesium isotopes in water: U.S. Geol. Survey Jour. Research, v. 1, p. 113–115.

Gross alpha and beta radioactivity, dissolved and suspended Residue method (R-1120-76)

Parameters and codes: Gross alpha, dissolved as U natural ($\mu\text{g/l}$): 80030
Gross alpha, suspended, as U natural ($\mu\text{g/l}$): 80040
Gross alpha, suspended, specific activity as U natural ($\mu\text{g/g}$): 01518
Gross beta, dissolved, as cesium-137 (pCi/l): 03515
Gross beta, dissolved, as strontium-90/yttrium-90 (pCi/l): 80050
Gross beta, suspended, as cesium-137 (pCi/l): 03516
Gross beta, suspended, as strontium-90/yttrium-90 (pCi/l): 80060
Gross beta, suspended, specific activity as cesium-137 (pCi/g): 03518

1. Application

The method is applicable to any natural-water sample. Because of restrictions on the weight of residue which can be accommodated, the sensitivity falls off with increasing concentrations of dissolved solids.

2. Summary of method

The method is an extension of the procedure published by Barker and Robinson (1963) for gross beta radioactivity.

A representative aliquot, but not more than 1 liter of the sample including suspended solids, is filtered through a tared 0.45-micrometer membrane filter. The filter and retained solids are dried at room temperature and then at 105°C, cooled, and reweighed to determine the weight of nonfilterable residue per liter.

A filtered volume of the sample containing no more than 150 mg of dissolved solids is evaporated to dryness in a Teflon evaporating dish. The residue is transferred to a tared, 2-in. concentric-ring, stainless-steel planchet, dried in a desiccator, weighed, and counted on a low-background alpha-beta counter. The observed radioactivity is compared with the activity of natural uranium

and strontium-90/yttrium-90 and cesium-137 calibration standards, and results are reported relative to these reference isotopes. Thus, the measured sample activity is reported in terms of the amount of natural uranium and equilibrium strontium-90/yttrium-90 and cesium-137 activity which would give the same alpha and beta count rates respectively for the same weight of residue. The gross activities are reported in terms of equivalent quantities of reference standards of the true alpha and beta activities of the sample.

The accuracy of these approximations depends on a number of variables related to the energy distributions of the alpha and beta particles and the similarity of the residues used in preparation of the calibration curves to the actual sample residue. The method must be regarded as a rapid, semiquantitative measure of gross sample activity.

3. Interferences

Within its intended purpose, the method is free of interferences, although the accuracy varies considerably with the nature of the alpha and beta emitters, chemical composi-

tion of the sample, and uniformity of planchet preparation.

4. Apparatus

4.1 *Evaporating dishes*, Teflon, 100 ml.

4.2 *Hotplate* or steam table.

4.3 *Infrared drying lamps*.

4.4 *Low-background counting equipment*.

Proportional counters capable of measuring both alpha and beta activity are desirable (for example, Beckman Instrument Co. Wide-Beta or Low-Beta II, or equivalent).

4.5 *Membrane filters*, 47-mm diameter, 0.45-micrometer pore size, cellulose nitrate or acetate type.

4.6 *Planchets*, stainless steel, 2-in. diameter, concentric-ring type.

4.7 *Specific conductance meter*.

4.8 *Vacuum desiccator*.

4.9 *Vacuum-filtration apparatus*, for 47-mm membrane filters.

5. Reagents

5.1 *Calibration solution A*: Dissolve 0.284 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.070 g NaCl, 0.026 g $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.109 g NaHCO_3 , and 0.245 g CaCO_3 in distilled water, bubbling CO_2 gas through the solution if necessary to obtain clear solution. Dilute to 2.00 liters.

5.2 *Calibration solution B*: Dissolve 1.350 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 3.510 g NaCl, 1.550 g $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.508 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.300 g CaCO_3 in distilled water, using CO_2 bubbling as necessary to dissolve. Dilute to 2.00 liters.

Note: Composition of the calibration solutions should approximate that of the samples to be analyzed. Solutions A and B were selected to approximate the composition average of 12 major rivers in the United States.

5.3 *Cesium-137 standard solution*, approximately 500 pCi/ml and acidified to approximately 1 N with hydrochloric acid.

5.4 *Hydrofluoric acid*, 49 percent.

5.5 *Strontium-90/yttrium-90 standard solution*, approximately 500 pCi/ml combined activity and acidified to approximately 1 N with hydrochloric acid.

5.6 *Uranium standard solution*, 1.00 ml = 100 μg U: Dissolve 0.1773 g of $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ in approximately 500 ml distilled water. Add 15 ml concentrated HNO_3 and dilute to 1,000 ml in a volumetric flask. Store in a Teflon bottle.

6. Procedure

6.1 Preparation of beta calibration curve.

6.1.1 Add the following amounts of calibration solutions A and B to 100-ml Teflon evaporating dishes:

Dish No.	A (ml)	B (ml)	Approx. residue wt. (mg)
1	25		10
2		5	20
3	80		30
4		10	40
5	140		50
6		20	60
7	200		70
8		25	80
9	250		90
10		30	100
11	300		110
12		35	120
13	350		130
14		40	140
15	400		150

To each dish and to four additional 100-ml Teflon evaporating dishes (Nos. 16, 17, 18, and 19) add 1.00 ml of strontium-90/yttrium-90 standard solution. To dishes 18 and 19 also add 5 drops concentrated NH_4OH .

6.1.2 Evaporate all the solutions to dryness on a low-temperature hotplate. When dishes 18 and 19 are dry, raise heat to approximately 350°C to volatilize NH_4Cl .

6.1.3 Perform steps 6.6 through 6.11 of the procedure which follows.

6.1.4 Plot the beta efficiency (net counts per minute per picocurie) against the residue weight to obtain the beta calibration curve.

6.1.5 Prepare a beta calibration curve for cesium-137 following steps 6.1.1 through 6.1.4. Use 1.00 ml of cesium-137 standard.

6.2 Preparation of alpha calibration curve: The alpha calibration curve is obtained in exactly the same manner as the beta curve (step 6.1) except that 100 μg of uranium (1 ml of uranium standard solution) is substituted for the strontium-90/yttrium-90 beta

standard. It is important that the uranium standard be in secular equilibrium with respect to uranium-234. The uranium isotopes ratio may be determined by the method described elsewhere in this manual.

6.3 Sample analysis: Measure the specific conductance of each water sample. Multiply the specific conductance in $\mu\text{mhos/cm}$ at 25°C by 0.65 to obtain an approximate value for the dissolved-solids concentration of the sample in mg/l . Determine the volume of sample which will contain approximately 100 mg of dissolved solids:

$$\text{Sample volume, } V(l) = \frac{100 \text{ mg}}{\text{mg/l}}$$

The actual sample residue should weigh between 50 and 130 mg.

6.4 Gross radioactivity of the suspended solids is determined as follows: Vigorously agitate the sample bottle containing the total amount of sample collected and quickly pour off 1 liter of sample with suspended solids into a graduated cylinder. Allow sediment to settle and then, using suction, filter through a tared membrane filter. When only 100 ml of sample remains to be filtered, swirl to suspend solids and add suspension to filter funnel. Any remaining traces of sediment may be transferred using small amounts of distilled water.

6.5 Carefully rinse solids with a small amount of distilled water, and maintain as uniform a deposit as possible. Remove filter, allow to air-dry, and weigh. If the weight of solids is in excess of 150 mg, refilter a fresh aliquot of appropriate volume to obtain less than 150 mg, weigh, dry at 105°C , and count for alpha and beta radioactivity.

Although not totally comparable, the same absorption or counting efficiency factors for the respective counting instruments are used as for dissolved solids, and the calculations are made in the same way. The weight of suspended solids per liter of sample is also reported (USGS parameter code 00530) and may be used to calculate the radioactivity associated with the total weight of suspended solids per liter of original sample. Specific activity of the solids in pCi/g of suspended

solids for the equivalent strontium-90/yttrium-90 or cesium-137 may also be calculated.

6.6 Gross radioactivity of the dissolved solids is determined as follows: Using a tared Teflon dish, evaporate the required volume of water to dryness on a hotplate or steam bath. Remove Teflon dishes from hotplate as soon as they reach dryness to prevent warping of dishes due to excess heat.

6.7 Determine approximate weight of residue by weighing dish plus residue and subtracting tare weight. If the weight of residue falls outside the 50- to 130-mg range, start a new evaporation using a larger or smaller sample volume as required.

6.8 Quantitatively transfer the residues in the evaporating dishes to tared planchets using rubber policemen and a minimum amount of distilled water to effect the transfers. Confine the solution and residue to the three inner concentric rings of the planchet during the transfer.

6.9 Dry the planchets under infrared heat lamps. Police down the evaporating dishes with small additional amounts of distilled water and transfer to planchets.

6.10 Repeat step 6.6. If a residue remains in the evaporating dish after three washes with distilled water, add a small amount of hydrofluoric acid, and use for a final policing.

6.11 Disperse the final liquid slurry in the planchets as uniformly as possible, using a stirring rod to disrupt large aggregates. Again evaporate to dryness.

6.12 Place the planchets in a vacuum desiccator and evacuate to complete the drying; weigh the planchets and determine the weight of residue.

6.13 Count the planchets in a low-background alpha-beta counter. Obtain three 50-min counts on each sample.

7. Calculations

Determine the equivalent concentration of alpha and beta emitters in each planchet from the net measured activity and the appropriate factor from a table of calibration curves.

$$\text{Gross } \alpha = \frac{Scpm\alpha}{F_a} \times \frac{1000}{V_a} = \mu\text{g/l as U natural,}$$

$$\text{Gross } \beta = Scpm\beta \times \frac{F_\beta \cdot 1000}{V_a}$$

= pCi/l as Sr⁹⁰/Y⁹⁰ or as Cs¹³⁷,

where

$Scpm\alpha$ = alpha count rate of sample in counts per minute,

$Scpm\beta$ = beta count rate of sample in counts per minute,

F_a = alpha factor in cpm/ μ g of natural U,

F_β = beta factor in picocuries per count per minute, and

V_a = aliquot used in milliliters

8. Report

Report values of less than 1 pCi/l to one significant figure. Report higher values to two significant figures.

9. Precision

Results for a particular sample are usually reproducible to about ± 20 percent at the 95-percent confidence level.

Reference

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.

Lead-210, dissolved

Chemical separation and precipitation method (R-1130-76)

Parameter and code: Lead-210, dissolved (pCi/l): none assigned

1. Application

The method may be used with all natural waters where detection of lead-210 with sensitivity to 2 pCi/l is acceptable. Where improved sensitivity is required, a larger sample than the normal 500 ml is concentrated by evaporation before beginning the procedure. Rama and Goldberg (1961) reported they were able to achieve sensitivity to 0.02 pCi/l by use of a 20-liter sample and direct precipitation of lead chromate from this large volume.

Lead recovery may be low in waters containing high concentrations of organic material that can possibly complex lead.

2. Summary of method

The analytical method is designed to isolate lead-210 in a relatively pure lead chromate precipitate. This is allowed to age to produce bismuth-210, a beta emitter with 5-d half-life. Lead-210 is not counted directly because of its very soft beta radiations of 15 and 61 keV, which are greatly attenuated by absorption. The bismuth isotope decays by beta emission with a beta maximum energy of 1.16 MeV, and these beta particles are easily counted.

3. Interferences

Henry and Loveridge (1961) have shown that essentially complete separation from radioisotopes of antimony, cesium, cobalt, iodine, phosphorous, ruthenium, strontium, thallium, zinc, and zirconium is achieved. Radium, thorium, uranium, potassium-40,

and other natural radionuclides do not interfere. Lead-212 does not interfere because of the short half-life (10.6 hr). Stable lead in the water sample should cause no interference by increased beta absorption since lead concentrations seldom exceed a few tenths of a milligram per liter. A problem might be encountered with industrial wastes where lead concentrations could be much higher.

The application of the method to liquid waste should be checked by "spiking" samples with known lead-210 and determining percentage of recovery.

4. Apparatus

4.1 *Centrifuge*, capable of handling 50-ml tubes.

4.2 *Centrifuge tubes*, polypropylene, approximately 50-ml capacity.

4.3 *Copper disks*, 49-mm diameter, minimum thickness 0.1 mm.

4.4 *Ion-exchange columns*, 1-cm inside diameter, 10-cm long with 50-ml reservoir at top;

4.5 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

4.6 *Magnetic stirrer-hotplate*.

4.7 *Membrane filters*, 47-mm diameter, 0.45-micrometer pore size. Must be inert to warm, dilute chromic acid.

4.8 *Planchets*, stainless steel, 5-cm diameter.

4.9 *Tape*, cellulose, 5-cm wide roll, adhesive on both sides.

4.10 *Tape*, "Magic Tape" (Minnesota Mining and Manufacturing Co.), 8 mg/cm² density, 5-cm width.

4.11 *Vacuum-filtration* apparatus, for 47-mm membrane filters.

5. Reagents

5.1 *Acetic acid*, 25 percent by volume: Dilute 1 volume glacial acetic acid with 3 volumes distilled water.

5.2 *Ammonium persulfate*.

5.3 *Hydrochloric acid*, 8 N and 2 N.

5.4 *Ion-exchange resin*, Bio-Rad Ag1-X8, or equivalent, 50–100 mesh.

5.5 *Lead carrier solution*, 1 ml = 4.00 mg Pb⁺²: Dissolve 6.394 g anhydrous Pb(NO₃)₂ in 100 ml of 1 N HNO₃ and dilute to 1,000 ml with distilled water.

5.6 *Lead-210 standard solution*. Suitable standards are available from Amersham/Searle Corp., Arlington Heights, Ill. Solutions must be kept strongly acidic (about 1 N in HNO₃) when dilutions are made.

5.7 *Nitric acid*, 0.01 M: Dilute 0.1 ml of concentrated HNO₃ to 120 ml.

5.8 *Nitric acid*, 0.001 M: Dilute 20 ml of 0.01 M HNO₃ to 200 ml.

5.9 *Potassium dichromate solution*, 4 percent: Dissolve 40 g reagent-grade K₂Cr₂O₇ in distilled water and dilute to 1 liter.

5.10 *Sodium acetate solution*, 10 percent: Dissolve 100 g anhydrous NaC₂H₃O₂ in distilled water and dilute to 1,000 ml.

5.11 *Sodium carbonate solution*, 1.25 M: Dissolve 265 g of anhydrous Na₂CO₃ in distilled water and dilute to 2,000 ml.

5.12 *Sodium sulfate*, anhydrous.

5.13 *Strontium carrier solution*, 1 ml = 60 mg Sr⁺²: Dissolve 145 g Sr(NO₃)₂ in distilled water; add 1 ml concentrated HNO₃ and dilute to 1,000 ml.

5.14 *Surfactant*, Dade Aerosol OT, Scientific Products Co.

6. Procedure

6.1 Preparation of ion-exchange columns.

6.1.1 Slurry 4.0 g of ion-exchange resin with 10 ml of 8 N HCl in a 50 ml beaker. Cover and place in an ultrasonic cleaner for 1 min and allow to stand for at least 20 min.

6.1.2 Plug the end of the column with a small piece of glass wool, and wash with 8 N HCl.

6.1.3 Transfer the resin slurry completely to the column, allow to drain and settle.

6.1.4 Place a small glass-wool plug at the top of the resin column. Avoid packing the resin. Wash with 10 column-volumes each of 8 N HCl, distilled water, and finally 2 N HCl. The column is now ready for use. The resin is discarded after one use.

6.2 Preparation of lead-210 standard planchets: Three or more "permanent" standards are prepared by precipitating a known amount of lead-210 as lead chromate.

6.2.1 Add 5 ml of lead carrier solution and an accurately known amount of lead-210 (approximately 200 pCi is convenient) to 50 ml of 0.001 M nitric acid. Heat to 95°C, slowly add 5 ml of 4 percent potassium dichromate solution, stir for several minutes, and digest on a hotplate for 20 min with occasional agitation.

6.2.2 Cool to room temperature, filter through a tared 0.45-micrometer membrane filter, and wash the precipitate with a small amount of distilled water containing a few drops of aerosol OT solution.

6.2.3 Allow the membrane and precipitate to air-dry, then weigh and calculate the chemical yields. Mount the standards as described in step 6.16.

6.2.4 Allow the standards to age until the count rate becomes constant. This will require 40 d (8 half-lives of bismuth-210) or less, because 75 to 100 percent of the bismuth-210 coprecipitates with the lead chromate.

6.3 Analysis of the water samples: Measure a 500-ml water sample into an 800-ml beaker, add a magnetic stirring bar and a few drops of methyl orange indicator, and place on a magnetic stirrer-hotplate.

6.4. While stirring, add 0.01 M nitric acid dropwise until the indicator turns red. If the sample is initially acid to methyl orange, bring to color change with ammonia, then back to acid side with nitric acid. Add 5 ml of lead carrier solution, 4.5 g of anhydrous

sodium sulfate, and 1 g of ammonium persulfate. Cover with a watch glass, and heat and stir at the incipient boiling point for 1 hr.

6.5 Add 5 ml of strontium carrier solution to the sample and continue heating while stirring at the incipient boiling point for 20 min; retrieve the magnet, remove the beaker from the hotplate, and allow the precipitate to settle and solution to cool slowly to room temperature.

6.6 Decant or syphon off as much of the supernatant liquid as possible without disturbing the precipitate. Wash the residue into a 50-ml round-bottom Teflon or polypropylene centrifuge tube using a small volume of distilled water. Centrifuge, and discard the supernate.

6.7 Place a 1/2-in. Teflon-coated magnet in the centrifuge tube, add 40 ml of hot 1.25 M sodium carbonate solution, and place the tube in a boiling-water bath on a magnetic stirrer-hotplate. Stir vigorously for 20 min.

6.8 Remove the tube from the bath, and wash down any precipitate on the upper part of the tube using a jet of 1.25 M Na_2CO_3 . Centrifuge and decant or syphon off most of the supernate. Syphoning is preferable because of the difficulty of decanting without disturbing the precipitate with the magnetic stirrer.

6.9 Repeat steps 6.7 and 6.8 two more times. Remove the stirring bar before the final centrifugation. Discard the final supernatant liquid.

6.10 Dissolve the lead-strontium carbonate precipitate in the centrifuge tube by cautiously adding 15.0 ml of 2 N HCl followed by 1.0 ml of 8 N HCl. Mix thoroughly and pour the solution onto the ion-exchange column. Be sure the flow rate does not exceed 2 ml/min.

6.11 Rinse the centrifuge tube with two 2-ml portions of 2 N HCl, adding these rinse solutions to the column.

6.12 Wash the column with a volume of 2 N HCl equal to two column-volumes plus the holdup volume in the column below the resin bed. Elute with 30 ml of distilled water, col-

lecting the eluate in a 150-ml beaker. Record the date and time of elution. This fraction contains lead-210 free of daughter activity.

6.13 Add 3 ml of 25 percent (v/v) acetic acid and 5 ml of 10 percent sodium acetate to the eluate, and dilute to approximately 75 ml. Heat to incipient boiling and add slowly 5 ml of 4 percent potassium dichromate solution. Mix thoroughly by swirling the beaker and hold near the boiling point for 20 min with occasional swirling.

6.14 Remove the beaker from the hotplate and filter, while warm, through a tared 0.45-micrometer, 47-mm-diameter membrane filter. Rinse with distilled water, containing a few drops of Aerosol OT solution, to prevent the precipitate from clinging to the filter funnel.

6.15 Remove the filter membrane from the filtration apparatus, place on a clean surface, and allow to air-dry. Weigh the filter to determine chemical recovery.

6.16 Place the filter in the center of a 49-mm copper disk, the surface of which has been covered with a strip of double-faced cellulose tape. Cover the filter disk with a strip of 5-cm "Magic Tape," trim to the size of the copper disk, and place in a 5-cm planchet.

6.17 After an aging period of 7 d (or longer), count the samples in a low-background beta counter with a 5-cm detector for 100 min to attain sensitivity to 2 pCi/l. Extended counting improves the detection. For example, detection to 0.7 pCi/l is possible with a 1,000-min count.

7. Calculations

7.1 Lead-210 efficiency factor (E) and chemical recovery factor (f_n): Although bismuth-210, daughter of lead-210, is actually counted, an in-growth factor is not used in the determination of E . The standard is allowed to reach equilibrium (40-d standing) before counting, and the disintegration rate at this time is controlled by the lead-210 concentration. Determine f_n from the weight of lead chromate. E is determined using equation 2.

$$E = \frac{\bar{c}_n}{d_n f_n (e^{-\lambda_n t_n})} \quad (2)$$

7.2 Calculation of lead-210 concentration: An in-growth factor is used in calculation of concentration in individual samples because the aging time before counting (approximately 7 d) is insufficient to attain equilibrium. The in-growth factor for each sample is obtained from a curve of the growth of activity with time (fig. 4) or, more accurately, by calculation. Chemical recovery factor is determined from the ratio of actual weight of lead chromate recovered to the theoretical weight. For 20-mg lead carrier, the theoretical weight is 31.20 mg of lead chromate. Use

equation 3 with the terms for decay of daughter before counting and decay during counting eliminated. Calculate lead-210 concentrations using the equation below, and correct for decay if excessive time elapsed between the sample collection and analysis.

$$\text{pCi/l of lead-210} = \frac{1000 \bar{c}}{VEf (e^{-\lambda t}) (1 - e^{-\lambda t_i})}$$

where

\bar{c} = net count rate of sample after correction for background and blank

λ = decay constant of lead-210 (0.0315 yr^{-1}),

t = elapsed time between collection of sample and analysis,

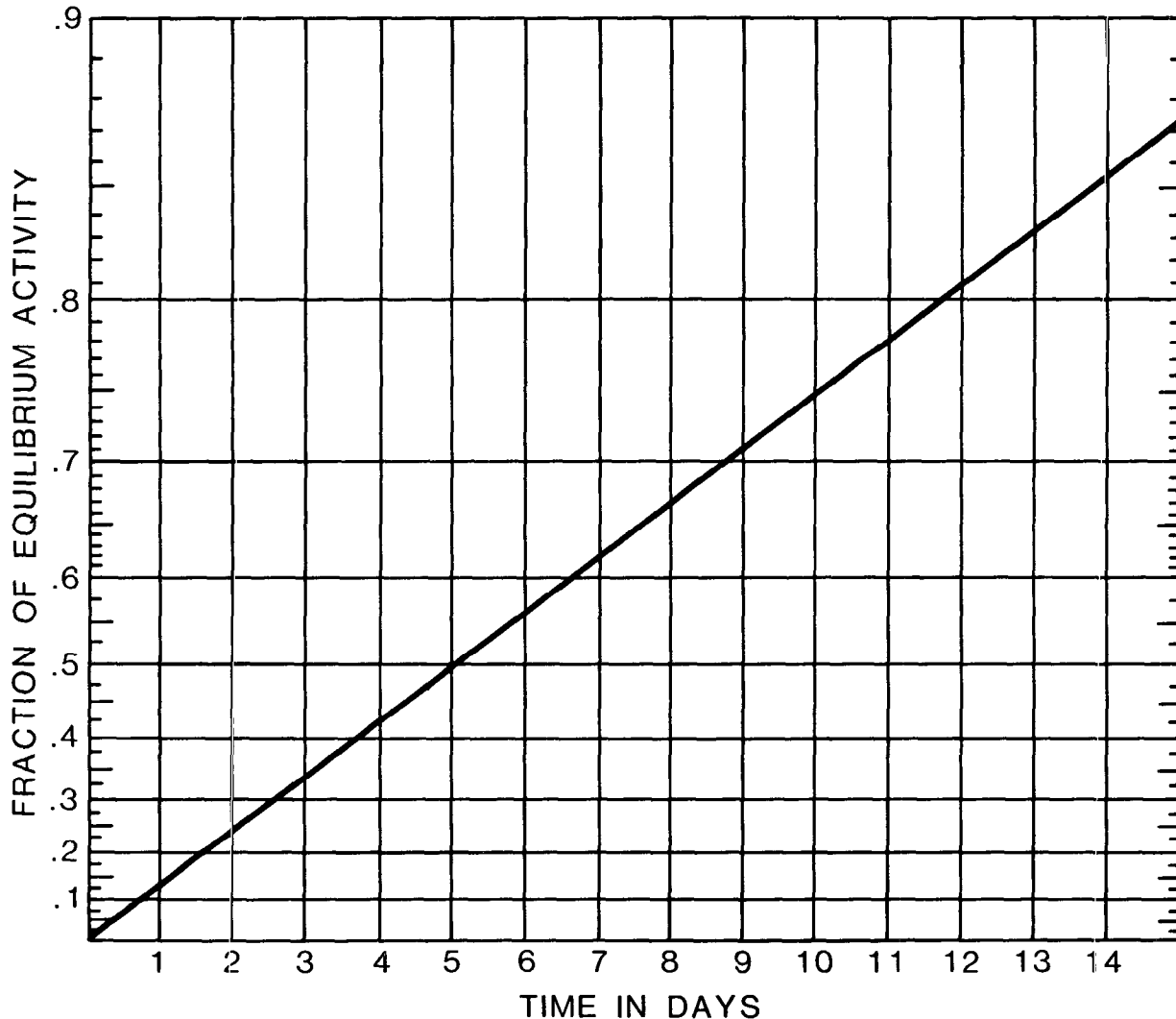


Figure 4.—Growth of bismuth-210 from pure lead-210 source.

λ_1 = decay constant of bismuth-210
(0.1384 d^{-1}),

t_1 = elapsed time between elution of the
ion-exchange column (step 6.12)
and counting, and

V , E , and f are as defined in equation 1.

8. Report

Report concentrations of less than 10 pCi/l to the nearest pCi/l; higher concentrations to two significant figures.

9. Precision

Tests with eight water samples to which known lead-210 was added gave recoveries

averaging 98 percent with a mean deviation of ± 2 percent at concentrations above 15 pCi/l. At lower concentrations the precision is ± 2 pCi/l or ± 10 percent, whichever is larger.

References

- Henry, W. M., and Loveridge, B. A., 1961, Determination of lead-210 in Harwell effluent: Atomic Energy Research Estab. Rept. R-3795, 20 p.
- Rama, M. K., and Goldberg, E. D., 1961, Lead-210 in natural waters: Science, 134 p. 98-99.

Radium, dissolved, as radium-226 Precipitation method (R-1140-76)

Parameter and code: Radium, dissolved, as radium-226 (pCi/l): 09510

1. Application

The method is satisfactory for applications that do not require high precision or radium isotope identification such as routine monitoring for compliance with PCRE standards. The application is straightforward with waters of average composition, but the possibility of increased alpha self-absorption must be considered with waters of high dissolved-solids or alkaline-earth content. The internal standard technique is used when necessary.

2. Summary of method

Radium isotopes are concentrated from a water sample by coprecipitation as the sulfate with barium sulfate. The collection of radium is quantitative even though the solubility product of radium sulfate is not exceeded. Although the coprecipitation collects all radium isotopes, radium-226 is usually the predominant isotope. Results are consequently reported as concentration of radium-226. Isotopes of thorium, lead, and polonium carried down partially or completely by the barium sulfate may also contribute to the alpha count. The analytical procedure is taken from Barker and Johnson (1964).

The precipitate is collected by filtration through a plastic-membrane filter, and is counted in a low-background thin window alpha counter after a suitable delay to allow in-growth of alpha-emitting daughters. This increases the sensitivity by a factor of 4 (at equilibrium). The count rate of the sample is compared against that of a radium-226 standard carried through the procedure.

Radioactive impurities in the reagents may be significant. Reagents are selected, and blanks are run with each set of samples.

Since alpha radiation is strongly absorbed by the precipitate, it is essential to keep the weight of precipitate constant in the samples, standards, and blanks. High salinity (brines), colloidal matter, and high concentrations of strontium or barium may cause problems by adding to the mass per unit area of the precipitate. Correction for increased absorption is made by use of internal standard techniques.

3. Interferences

Alpha-emitting nuclides of thorium and polonium may be carried down with the precipitate, but their concentrations are not sufficiently high in most natural water to constitute a problem.

4. Apparatus

4.1 *Beaker*, 1,500 ml.

4.2 *Filter flask*, 2,000 ml.

4.3 *Membrane filter*, 47-mm diameter, 0.45-micrometer porosity.

4.4 *Filtration assembly*, for membrane filter including funnel, sintered glass-filter support and clamp.

4.5 *Ring-and-disc sample mounts*, 47-mm diameter.

4.6 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

5. Reagents

5.1 *Ammonium sulfate solution* (40 percent, by weight): Dissolve 1,600 g of ammonium sulfate in a minimum volume of hot distilled water. Cool to room temperature and filter. Dilute the solution to approximately 4 liters in a 4-liter bottle.

5.2 *Barium carrier solution* (1.40 mg Ba⁺² per ml): Dissolve 1.246 g of barium chloride dihydrate in distilled water, add 5 ml of concentrated HCl, and dilute to 500 ml.

5.3 *Hydrochloric acid*, concentrated.

5.4 *Methyl orange indicator solution*.

5.5 *Radium standard solution I*, 50.0 pCi/ml. This solution is prepared from National Bureau of Standards' encapsulated radium standard No. 4955 which contains 0.100×10^{-6} curie of radium-226 in 5 ml of 5 percent HNO₃. Rubber gloves should be worn in preparing a standard solution by the following recommended procedure.

5.5.1 Place the vial containing the radium standard in a clean, heavy-wall, small-neck bottle or flask of 250- to 500-ml capacity. Add 50 ml of 3 N HCl, and stopper securely with a polyethylene stopper.

5.5.2 Place the bottle (or flask) in a strong plastic sack and, holding the stopper firmly in place, shake vigorously to break the vial.

5.5.3 Decant the solution into a 2-liter volumetric flask.

5.5.4 Rinse the bottle with 50 ml of 3 N HCl, and decant into the 2-liter flask.

5.5.5 Add another 50 ml of 3 N HCl, and wash thoroughly using the ultrasonic cleaner. Decant into the 2-liter flask.

5.5.6 Rinse with 50 ml of 3 N HCl. Decant into the 2-liter flask.

5.5.7 Repeat steps 5.5.4 and 5.5.5 alternately, three more times each.

5.5.8 Dilute the solution in the 2-liter flask to 2,000 ml with distilled water and mix thoroughly.

The final concentrations of radium and hydrogen ion in this stock solution are: (Ra⁺²) = 50 pCi/ml and (H⁺) = 0.75 M.

5.6 *Radium standard solution II*, 1 ml = 10 pCi: Transfer 50 ml of the radium standard stock solution to a 250-ml volumetric flask

and dilute to volume with distilled water. Add a small, clean disk or foil of 22-carat gold (surface area $\cong 4$ cm²) to the solution to remove polonium-210. This disk should remain in the standard solution continuously.

5.7 *Sulfuric acid wash solution*: Dilute 5 ml of concentrated H₂SO₄ to 1,000 ml with distilled water and add 3 to 4 drops of Triton X-100 surfactant (Rohm and Haas Co.).

6. Procedure

6.1 Measure 1,000 ml of the sample, previously filtered if necessary, into a 1,500-ml beaker. If the sample contains more than 350 mg/l of calcium, take a proportionately smaller volume and dilute to 1,000 ml. 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, the internal standard modification should be used (sec. 6.8).

6.2 Prepare duplicate standard solutions, each consisting of 5.00 ml of radium standard solution (1 ml = 10 pCi radium-226) diluted to 1,000 ml with distilled water, and a blank solution consisting of 1,000 ml of distilled water. Add a few drops of methyl orange indicator, and adjust the pH to approximately 3.5 by dropwise addition of concentrated HCl (or NH₄OH followed by HCl if the sample has an initial pH below 3.5).

6.3 Heat blank solution, samples, and standard solutions to incipient boiling point, and readjust the pH to approximately 3.5.

6.4 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 heating near the boiling point for an additional 15 to 30 min.

6.5 Allow the precipitate to digest at room temperature for 4 hr or longer, then collect the precipitate on a membrane filter. Police down the beaker carefully to ensure complete transfer of the precipitate to the filter. Wash the precipitate with small volumes of the sulfuric acid wash solution. The barium sulfate precipitate should be evenly

distributed to minimize self-absorption of alpha particles. A fine jet of the wash solution can be used to redistribute the precipitate on the filter and to obtain uniform distribution.

6.6 When the membrane filter is practically dry, mount it in the ring-and-disk holders.

6.7 Determine the alpha activity of the blanks, standards, and samples after allowing the precipitates to age 15 d (or longer). Count each planchet for 100 min.

6.8 For those samples suspected of having excessive absorption loss of alpha radiation, repeat the analysis using the internal standard procedure as follows: Prepare a second sample as in 6.1. Add 5.00 ml of radium standard solution (1 ml=10 pCi). Proceed with the analytical determination as before, and count. The difference between the count rate of the sample containing the internal standard and the count rate of the sample is the basis for calculating the efficiency factor to be used.

7. Calculations

7.1 The "radium as radium-226" efficiency factor (E_a) is calculated using the following equation:

$$E_a = \frac{\bar{c}_n}{d_n},$$

where

\bar{c}_n = average count rate of standard (cpm) corrected for background and blank, and

d_n = disintegration rate of standard (dpm).

7.2 The "radium as radium-226" efficiency factor (E_b), for the internal stand-

ard procedure is calculated using the following equation:

$$E_b = \frac{\bar{c}_{ns} - \bar{c}_n}{d_{ns}},$$

where

\bar{c}_{ns} = average count rate (cpm) of the sample containing the internal standard, and

d_{ns} = known disintegration rate (dpm) of the internal radium standard added to the sample.

7.3 Calculation of radium gross alpha concentration, normal procedure. Use equation:

$$\text{pCi/l of Ra (as radium-226)} = \frac{1000 \bar{c}}{KVE_a}$$

7.4 Calculation of radium-gross alpha concentration, internal standard procedure. Use equation:

$$\text{pCi/l of Ra (as radium-226)} = \frac{1000 \bar{c}}{KVE_b}$$

8. Report

Report concentrations less than 1.0 pCi/l to one significant figure and concentrations above 1.0 pCi/l to two significant figures.

9. Precision

Reproducibility at the two standard deviation level is approximately ± 1.0 pCi/l at concentrations of 0.5 pCi/l and below. Reproducibility is to approximately ± 20 percent at higher concentrations.

Reference

Barker, F. B., and Johnson, J. O., 1964, Determination of radium in water: U.S. Geol. Survey Water-Supply Paper 1696-B, 29 p.