



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**

Radium-226, dissolved Radon emanation method (R-1141-76)

Parameter and code: Radium-226, dissolved (pCi/l): 09511

1. Application

The method is applicable to any water sample.

2. Summary of method

The method is based on the isolation of radon-222 produced by radium-226 and measurement of the alpha activity of the radon and its short-lived daughters. The method is specific for radium-226 in contrast to the precipitation method of Barker and Johnson (1964). The procedure represents an improvement of the emanation method of Rushing (1967) in the substitution of a complexing agent to redissolve precipitated barium sulfate. Formerly a complex procedure for resolution involving a strong acid, ashing, and evaporation was required. Radon is measured in a modification of the alpha scintillation cell of Lucas (1957).

Dissolved radium in filtered water is collected by coprecipitation with barium sulfate. The precipitate is centrifuged and then dissolved in alkaline sodium diethylene triamine pentacetate solution. The solution is transferred to a radon bubbler, and any radon present is removed by purging with helium gas. Fresh radon is then allowed to grow in. After several days the ingrown radon is purged into an alpha scintillation cell, short-lived daughters are allowed to grow in, and the alpha-count rate is then determined. The radium-226 concentration in the original water sample is calculated from the radon determination on the basis of the rate of radon production with time.

3. Interferences

The method is normally specific for radium-226. Radium-223 and radium-224 produce radon-219 and radon-220, respectively. Neither of these interfere directly, but the 10.6 hr lead-212 from radon-220 has alpha-emitting daughters which could interfere. A wait of 2 or 3 d before counting eliminates the interference. The alpha-emitting daughters of radon-219 have no effect if sufficient waiting time is allowed for complete decay of the 36 min lead-211.

4. Apparatus

4.1 *Alpha-counting apparatus*, scaler and high voltage power supply, preamp and amplifier with discriminator.

4.2 *Beaker*, 1,500 ml.

4.3 *Gas delivery system*, for helium gas.

4.4 *Mixer*, wiggle-plate or ultrasonic type.

4.5 *Radon deemanation train and bubbler* (fig. 5).

4.6 *Radon scintillation cell and housing* (fig. 6).

5. Reagents

5.1 *Barium carrier solution*, 50 mg barium/ml: Dissolve 75.81 g barium chloride (BaCl_2) in distilled water and dilute to 1,000 ml.

5.2 *Defoaming emulsion*, Dow Corning Anti Foam H-10 emulsion, or equivalent: Dilute to approximately 4 to 5 percent solution with distilled water before using.

5.3 *DPTA-TEA solution*: Dissolve 10 g of sodium hydroxide pellets in a beaker containing 60 ml of distilled water, and stir in

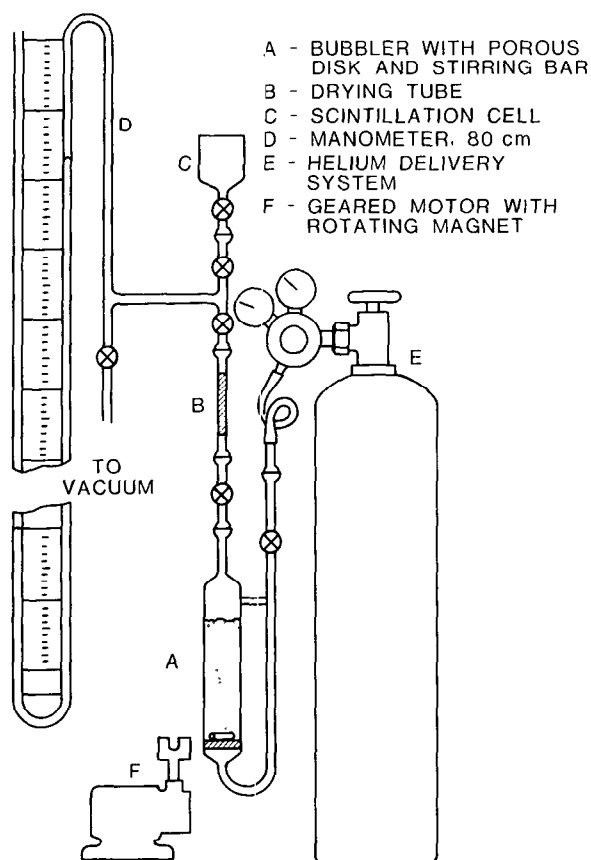


Figure 5.—Radon deemanation train and bubbler.

cold-water bath until dissolved. Add 20 g of purified diethylene triamine penta acetic acid (DPTA), and continue stirring until dissolved. Add 17 ml of 50-percent triethanolamine, mix and dilute to 100 ml. Store in Teflon bottle.

5.4 *Radium standard solution I*, 1 ml = 50.0 pCi: 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 HNO_3 . Rubber gloves should be worn in preparing a standard solution by the following recommended procedure.

5.4.1 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.

5.4.2 Place the bottle (or flask) in a durable plastic sack, and, holding the stopper

firmly in place, shake vigorously to break the vial.

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

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

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

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

5.4.7 Repeat steps 5.4.4 and 5.4.5 alternately, three more times each.

5.4.8 Dilute the solution in the 2-liter flask to 2 liters with distilled water and mix thoroughly.

The final concentrations of radium and hydrogen ion in the stock solutions are: $(\text{Ra}^{+2}) = 50 \text{ pCi/ml}$ and $(\text{H}^+) = 0.75 \text{ mole/l}$.

5.5 *Radium standard solution II*, 1 ml = 1,000 pCi: Dilute 10.00 ml radium standard solution I and 10 ml of concentrated HCl to 500 ml with distilled water.

5.6 *Sulfuric acid wash solution*: Add 5 ml of concentrated H_2SO_4 and 3–5 drops of Triton X-100 to 4 liters of distilled water.

5.7 *Sulfuric acid, concentrated*.

6. Procedure

6.1 Coprecipitation of radium with barium sulfate.

6.1.1 Add 5 ml concentrated hydrochloric acid to 1,000 ml of filtered water sample contained in a 1,500-ml beaker.

6.1.2 Add 1 ml of 50 mg/ml barium carrier to the sample and stir.

6.1.3 Cautiously add 20 ml of concentrated sulfuric acid to each sample with constant stirring. (Use of a 500-ml dispensing flask fitted with a 50-ml delivery head facilitates the acid addition.) Stir well after the acid addition. Allow barium sulfate precipitate to settle overnight.

6.1.4 Carefully remove the supernate by decantation or suction, and quantitatively transfer the balance of the supernate and precipitate to a 40-ml centrifuge tube using a rubber policeman and small quantities of dilute sulfuric acid-Triton-X-100 wash solution.

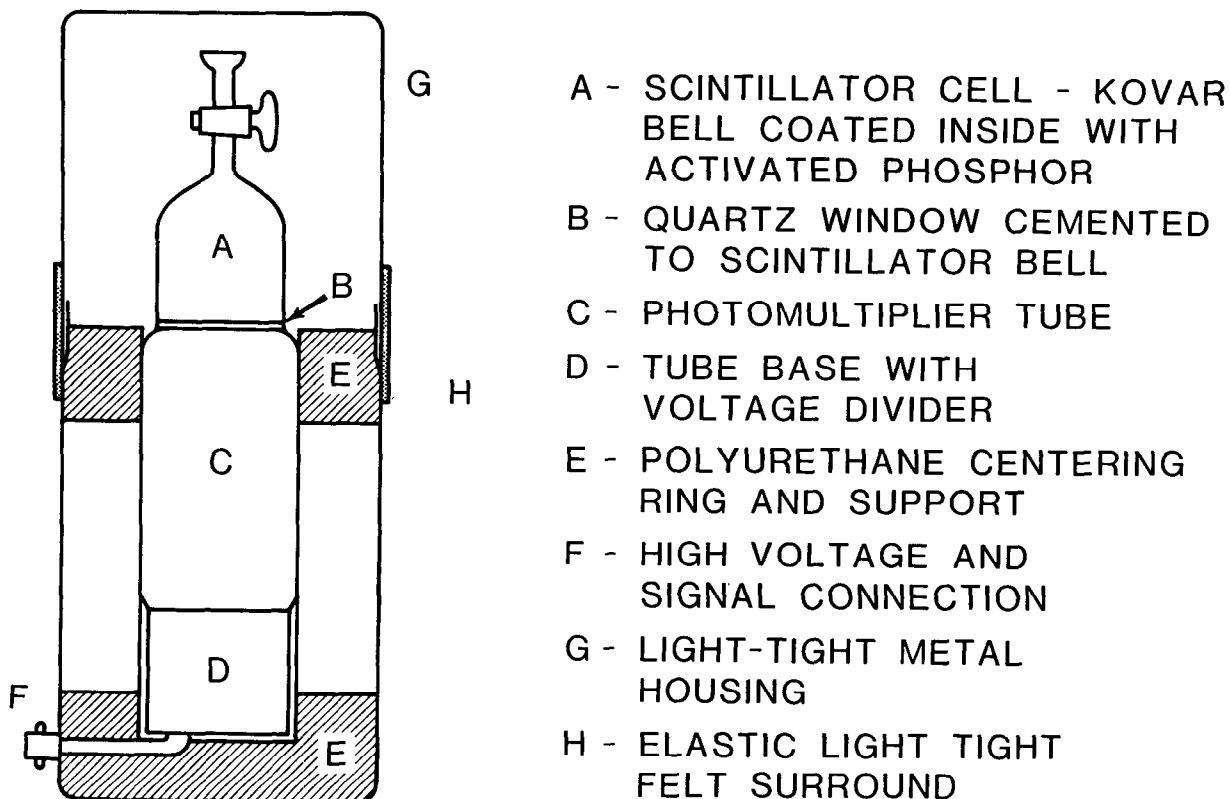


Figure 6.—Radon scintillation cell and housing.

6.1.5 Centrifuge as necessary, decant, and discard supernate.

6.1.6 Add approximately 10 ml of distilled water and 1.5 ml of DTPA reagent to the precipitate in the centrifuge tube. Disperse the precipitate in each tube by using a wiggle-plate mixer or an ultrasonic unit. Place tubes in a wire rack, and immerse rack and tubes to a depth of approximately 1 inch in a boiling-water bath.

6.1.7 Complete dissolution should occur within a few minutes if the barium sulfate "pellet" was adequately dispersed. Occasionally, volume of solution in the centrifuge tubes may decrease by 4–5 ml as a result of prolonged heating, and the precipitate may not dissolve. Addition of distilled water to bring the volume to approximately 20 ml maximum plus additional redispersion and heating will usually result in rapid dissolution of even difficulty soluble precipitates. After the precipitate has dissolved, cool the tubes,

6.2 Deemanations.

6.2.1 Using a funnel with a fine tip, transfer the cooled solution to a clean bubbler. Wash the centrifuge tube several times with distilled water, and add the washings and sufficient additional water to the bubbler to leave approximately 2 cm of airspace at the top. Add 1–3 drops of 4 percent silicone defoaming emulsion to the solution in the bubbler to minimize frothing during purging.

6.2.2 Attach stopcock and "O" ring to bubbler using clamp, leaving outlet stopcock on bubbler assembly in open position. Attach helium line (3–5 psi) to inlet side of bubbler. Slowly open stopcock on inlet until a stream of fine bubbles rises from the porous disk. Maintain a steady flow of bubbles through the sample for approximately 20 min to completely purge all ingrown radon from the solution. Close inlet stopcock and allow pressure under porous disk to equalize momentarily. Close outlet and record the day, hour, and minute. This is zero time for the growth

of radon that will be removed in the second deemanation and counted.

6.2.3 Allow from 2 to 20 d in-growth time for radon-222 depending upon the radium-226 concentration in the original sample, volume of sample used, and so forth.

6.2.4 The second deemanation is made by setting up the bubbler as in 6.2.2 except that both stopcocks are initially closed. Attach bubbler to drying tube with "O" ring and clamp. Evacuate purging assembly, including cell, with vacuum pump for approximately 1.5 to 2 min. Close stopcock at vacuum pump, turn pump off, and momentarily crack vacuum-pump connection. Open stopcock in helium line above bubbler-inlet stopcock and momentarily crack "O" ring connection to purge trapped air from line and bubbler-inlet connection. Clamp and allow system to stand for approximately 2 min. If system leaks, manometer meniscus will flatten or manometer will begin to fall. If meniscus remains stable, proceed to next step.

6.2.5 Carefully open bubbler-outlet stopcock until manometer begins to fall (check porous disk for fine bubbles). Allow vacuum to equilibrate slowly (otherwise there is excessive risk of drawing liquid sample into drying tube). Bubbling will slow appreciably in a few seconds. Slowly open outlet stopcock complete. Then continue with purging by slowly opening bubbler-inlet stopcock, checking porous disk carefully for rising bubbles. (*Flow rate must be closely controlled again at this point, to prevent sudden surge of liquid into drying tube.*) Allow pressure to build up slowly, controlling manometer fall rate to complete purging in 15–20 min. To prevent cell leakage during counting, close the cell stopcock at approximately 4 mm below atmospheric pressure.

6.2.6 Close down purging assembly stopcocks from cell to helium inlet in sequence as rapidly as possible. *Record time.* Remove bubbler from assembly quickly, and crack outlet stopcock momentarily to release helium pressure.

6.2.7 Place cell in light-tight counting chamber. Allow to age 3 or 4 hr before count-

ing. Count overnight (1,000 min) for the average water sample.

6.2.8 Dates, times, counts, and all other pertinent sample information should be recorded on data and calculation sheets.

6.3 Calibration of equipment: One low ($\cong 10$ cpm) and one high ($\cong 1,000$ cpm) count rate disk standards are useful for routine instrument calibration tests and for determining photomultiplier tube plateau curves. Prepare by precipitating each of two standards containing 5 and 500 pCi of radium-226 with 50 mg of barium sulfate respectively as previously described. Mount the precipitate by filtering through a 47-mm 0.45-micrometer membrane filter. Dry and place on the disc of a ring-and-disc assembly. After drying, cover the precipitate on the filter with a Mylar disk coated with an alpha-sensitive phosphor. The dull phosphor-coated side should be placed against the sample. Cover with the ring, press into place, and then seal the assembly with several pieces of cellophane tape to prevent it from separating.

The high count rate standard is used to determine the plateaus for each photomultiplier tube, and the appropriate operating voltage is then chosen accordingly. The low count rate standard is used to check instrument operating conditions at low count rates comparable to those of typical samples.

Frequently operating characteristics of two or more photomultiplier-counting systems are sufficiently similar to enable the use of a single high-voltage power supply.

Minor differences in the counting efficiency of each unit can be adjusted by the use of a focusing potentiometer on each photomultiplier housing.

Long-term instrument backgrounds should be obtained for each counting system and should not generally exceed 0.005 cpm.

Scintillation cell background count rates should be determined periodically for each cell in combination with each instrument. Generally, background count rates are determined using a minimum of 1,000 min. Background count rates for a specific cell may vary considerably from one instrument to an-

other, but should not generally exceed 0.10 to 0.15 cpm.

After long use or after counting a high-radium-content sample, background rates in some scintillation cells may become excessive (>0.15 cpm) for low-level work. In that event the cells must be used only for relatively high-level samples. Original low background may be restored by rebuilding.

6.4 Experimental determination of counting efficiency: The counting efficiency of each scintillation cell varies between cells and between counting instruments. Consequently, for the most accurate work, the counting efficiency of each scintillation cell should be determined in each instrument in which it is used.

The counting efficiency for each cell-instrument unit is determined by counting radon transferred from a "standard bubbler" containing a measured amount of radium-226 standard solution. A minimum of four or five standards or one for each counting instrument enables four or five cells to be calibrated simultaneously. Waiting time for radon in-growth is also considerably reduced as compared to that required if only one standard is available.

Standards are prepared by pipetting 10.0 ml of 10-pCi/ml radium-226 standard solution directly into each of several bubbler tubes. The tubes are fitted with an "O" ring stopcock assembly, and then deemanated to determine the zero in-growth time for radon in the same manner as a sample. Barring any spillage or breakage, the standards will last indefinitely and can be deemanated every 4 or 5 d to provide radon for calibration purposes.

Cell-counting efficiencies are generally about 5.3 cpm/pCi of radon-222 after in-growth of daughters for 3 hr, but this may vary considerably depending upon factors including the age of the cell, phototube condition, and moisture in cells. Erratic results are sometimes obtained as a result of improper cell or instrument grounding, loose connections, noisy power lines, and so forth.

7. Calculations

7.1 Radon counting efficiency factors (E). The calculation requires corrections for radon in-growth and radon decay. The radon in-growth and decay curves and their relation to the time intervals that appear in the equation are shown in figure 1. Substitute the experimental data obtained for each cell-instrument unit (sec. 6.4) into a modified form of equation 4.

$$E = \frac{\bar{c}_n}{d_n(1 - e^{-\lambda_1 t_1})(e^{-\lambda_1 t_4})},$$

where

λ_1 = decay constant of radon-222
($1.259 \times 10^{-4} \text{ min}^{-1}$),

t_1 = time interval for buildup of radon between the previous deemanation of the standard (point A, fig. 1) and the present deemanation (point B),

t_4 = time interval between deemanation standard (point B) and midpoint of the counting

$$\text{time,} = t_2 + \frac{t_3}{2},$$

where

t_2 = time interval between deemanation of the standard, (point B) and the beginning of the count time (point C),

t_3 = half the time interval between the beginning (point C) and the end (point D) of the counting time, and

\bar{c}_n and d_n are as defined in equation 2.

7.2 Calculation of radium-226 concentration: Efficiency (E) used for an individual sample is that determined for the cell and instrument used to count the sample. An in-growth factor is introduced because of in-growth of radon with time after the first deemanation. Use a modified form of equation 3 when counting time is less than 3,600 minutes.

pCi/l of radium-226

$$= \frac{1000 \bar{c}}{KVE(1 - e^{-\lambda_1 t_1})(e^{-\lambda_1 t_4})},$$

where

t_1 = time interval for in-growth of radon between first deemanation (step 6.2.1) and second deemanation (step 6.2.5) of the sample, and

t_4 = time interval between second deemanation of the sample (step 6.2.5) and midpoint of the sample

$$\text{counting time,} = t_2 + \frac{t_3}{2}$$

The other symbols are as defined in section 7.1.

When counting time exceeds 3,600 minutes, use equation 3 including the term for correction for decay during the count. pCi/l of radium-226

$$= \frac{1000 \bar{c}_1 t_3}{KVE(1 - e^{-\lambda_1 t_1})(e^{-\lambda_1 t_2})(1 - e^{-\lambda_1 t_3})}$$

where

t_2 = delay before counting, point B to C, figure 1, and

t_3 = time interval of count, point C to D.

The other symbols are as defined in 7.1 and 7.2.

Radon decay and in-growth factors are easily and accurately calculated with an electronic calculator having natural log and e^x functions. The table of "Radon fraction ($e^{-\lambda t}$) remaining after radioactive decay for specified times," for commonly used time intervals (table 1) may also be used.

8. Report

Report concentrations less than 0.10 pCi/l to one significant figure and values above 0.10 pCi/l to two significant figures.

Table 1.--Radon fraction ($e^{-\lambda t}$) remaining after radioactive decay for specified times

[Radon $T_{1/2} = 3.823$ d]

Time	Days	Hours	Minutes	Time	Minutes
1	0.834,18	0.992,47	0.999,87	31	0.996,10
2	.695,85	.985,00	.999,75	32	.995,98
3	.580,46	.977,59	.999,62	33	.995,85
4	.484,21	.970,23	.999,50	34	.995,73
5	.403,91	.962,93	.999,37	35	.995,60
6	.336,93	.955,68	.999,24	36	.995,48
7	.281,07	.948,49	.999,12	37	.995,35
8	.234,46	.941,35	.998,99	38	.995,23
9	.195,58	.934,27	.998,87	39	.995,10
10	.163,15	.927,24	.998,74	40	.994,98
11	.136,09	.920,26	.998,62	41	.994,85
12	.113,53	.913,33	.998,49	42	.994,73
13	.094,70	.906,46	.998,36	43	.994,60
14	.079,00	.899,64	.998,24	44	.994,48
15	.065,90	.892,87	.998,11	45	.994,35
16	.054,97	.886,15	.997,99	46	.994,22
17	.045,86	.879,48	.997,86	47	.994,10
18	.038,25	.872,86	.997,74	48	.993,97
19	.031,91	.866,29	.997,61	49	.993,85
20	.026,62	.859,77	.997,48	50	.993,72
21	.022,20	.853,30	.997,36	51	.993,60
22	.018,52	.846,88	.997,23	52	.993,47
23	.015,45	.840,50	.997,11	53	.993,35
24	.012,89	.834,18	.996,98	54	.993,22
25	.010,75	-----	.996,86	55	.993,10
26	.008,97	-----	.996,73	56	.992,97
27	.007,48	-----	.996,61	57	.992,85
28	.006,24	-----	.996,48	58	.992,72
29	.005,21	-----	.996,36	59	.992,60
30	.004,34	-----	.996,23	60	.992,47

9. Precision

On the basis of limited data the precision at the 0.10 pCi/l level is estimated at ± 20 percent. Above 0.10 pCi/l the precision is estimated at ± 10 percent.

References

Barker, F. B., and Johnson, J. O., 1964, Determina-

tion of radium in water: U.S. Geol. Survey Water-Supply Paper 1696-B, 29 p.

Lucas, H. F., 1957, Improved low-level alpha scintillation counter for radon: Rev. Sci. Instr., no. 28, 680-683.

Rushing, D. E., 1967, Determination of dissolved radium in water: Am. Water Works Assoc. Jour. no. 59, 593-600.

Radium-228, dissolved

Determination by separation and counting of actinium-228 (R-1142-76)

Parameter and code: Radium-228, dissolved (pCi/l): none assigned

1. Application

The method is applicable to all natural-water samples. Applications to samples containing reactor effluent or other contaminants have not been evaluated.

2. Summary of method

The method is based on the chemical separation and subsequent beta counting of actinium-228, the daughter of radium-228. Radium-228 is not determined directly because of the difficulty of counting its weak beta emission in the presence of other alpha-emitting radium isotopes and their beta-emitting daughters (Johnson, 1971).

3. Interferences

No chemical interferences have been detected. Because of chemical similarity, radionuclides of the actinide elements and the rare-earth elements may accompany the actinium precipitate. Significant concentrations of these would be expected only in areas where nuclear fission or nuclear research is carried on.

Radiochemical interferences are unlikely to occur in natural waters. Decontamination factors for other natural radionuclides appear to be 5,000 or greater. Exhaustive tests for artificially produced radionuclides have not been made, but little or no interference has been detected for cesium-137, strontium-90, and yttrium-90. Lanthanum-140 appears to be the most probable interference, but this and other rare-earth nuclides would be en-

countered only in waters contaminated by reactor effluent.

Success of the method at low levels of radioactivity depends largely upon use of reagents essentially free of radioactive contamination. Purity of the yttrium reagent is especially important.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Centrifuge tubes, 40- or 50-ml capacity, heavy-walled.*

4.3 *Drying lamp, infrared, mounted in ringstand.*

4.4 *Hotplate.*

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 *Planchets, 50-mm diameter, concentric-ring type.*

4.7 *Stirring rods, Teflon.*

5. Reagents

5.1 *Ammonium hydroxide, concentrated.*

5.2 *Ammonium sulfate solution, 200 mg/ml: Dissolve 200 g of ammonium sulfate in distilled water and dilute to 1 liter.*

5.3 *Ammonium sulfide solution, 2 percent: Dilute 10 ml of 20-23 percent aqueous ammonium sulfide solution to 100 ml.*

5.4 *Barium carrier solution, 1 ml = 16.00 mg Ba⁺²: Dissolve 28.46 g of BaCl₂·2H₂O in distilled water, add 2 ml of concentrated nitric acid, and dilute to 1,000 ml.*

5.5 *Binder solution*: Dissolve about 1 g of "Duco" cement in 100 ml acetone.

5.6 *Citric Acid, 1 M*: Dissolve 210.1 g of citric acid monohydrate in distilled water and dilute to 1,000 ml.

5.7 *EDTA reagent, 0.25 M EDTA* containing 20 mg/ml NaOH: Dissolve 20 g of NaOH in about 750 ml distilled water. Heat, and slowly add 93 g of disodium ethylenediaminetetraacetate while stirring. When dissolution is complete, cool, and dilute to 1,000 ml.

5.8 *Lead carrier solution I*, 1 ml=15.00 mg Pb²⁺: Dissolve 23.97 g of Pb(NO₃)₂ in distilled water; add 2 ml of concentrated nitric acid, and dilute to 1,000 ml.

5.9 *Lead carrier solution II*, 1 ml=1.50 mg Pb²⁺: Dilute 100 ml of lead carrier solution I to 1,000 ml.

5.10 *Methyl orange indicator solution*.

5.11 *Nitric acid, concentrated*.

5.12 *Sodium hydroxide, 10 N*: Dissolve 400 g of NaOH pellets in distilled water and dilute to 1 liter. Store in a polyethylene or Teflon bottle.

5.13 *Sulfuric acid, 18 N*: Cautiously add 500 ml concentrated H₂SO₄ while stirring into about 400 ml distilled water; cool, and dilute to 1,000 ml.

5.14 *Radium-228 standard*: The preparation of the standard solution is complicated by the fact that a standard of radium-228 is not readily obtainable. Generally the radium-228 must be obtained from thorium metal or pure compounds sufficiently old to permit equilibrium in-growth of radium-228. In 40-year-old material the radium-228 daughter has reached 99 percent of equilibrium concentration. The following procedure is used to accurately prepare standardized thorium-232 and radium-228 from thorium oxide approximately 50 yr old.

5.14.1 Weigh out a 1.0000 g sample of thorium dioxide.

5.14.2 Transfer the sample to a 250-ml Erlenmeyer flask containing 20 ml of acid mixture (15.7 N HNO₃, 0.05 N HF). Carefully heat and stir the mixture until the ThO₂ dissolves. Transfer the solution to a 200-ml volumetric flask and add a little barium ni-

trate solution containing 5–15 μg of barium. Make up to volume with 1 N nitric acid. Activity of radium-228 in the solution is calculated as follows:

$$\text{Radium-228 (dpm/ml)} = 246W (1 - e^{-0.1205t}),$$

where

W = thorium concentration in mg/ml, and

t = years since thorium dioxide was prepared.

At equilibrium 1 mg thorium = 246 dpm radium-228.

5.15 *Yttrium carrier solution*, 1 ml=18 mg Y³⁺: Add 22.85 g of Y₂O₃ to a 250-ml Erlenmeyer flask containing 20 ml of water. Swirl, place on a hotplate, and heat to boiling. Slowly and cautiously add concentrated nitric acid, while stirring, until a homogeneous solution is obtained. (Usually about 30 ml of nitric acid is required. It is sometimes necessary to add more water.) Add an additional 70 ml of concentrated nitric acid and dilute to 1 liter. Note: The yttrium oxide must be as free as possible of beta activity (usually due to isotopes of actinium). Yttrium oxide suitable for carrier preparation has been obtained from American Potash and Chemical Corp., West Chicago, Ill.

5.16 *Yttrium-strontium carrier solution*, 1 ml=0.9 mg Sr²⁺ and 0.9 mg Y³⁺: Dissolve 434.8 mg of Sr(NO₃)₂ in distilled water; add 10 ml of yttrium carrier solution, and dilute to 200 ml.

6. Procedure

6.1 Use 1–4 liters of sample, on the basis of the expected radium-228 content, and evaporate to 1 liter, if necessary. Add 5 ml of citric acid for each liter of original sample, and then add a few drops of methyl orange indicator. If the solution is yellow, add nitric acid until the red color is obtained.

Prepare standards by dilution of appropriate volumes of the "old" thorium-radium solution to 1 liter. A disintegration rate of approximately 1,000 dpm is appropriate. Carry the standards through the procedure in the same way as a sample.

6.2 Add 10 ml of lead carrier solution I, 2 ml of barium carrier solution, and 1 ml of yttrium carrier solution. Heat to incipient boiling, and maintain at this temperature for about 30 min with frequent stirring.

6.3 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 15 ml of ammonium sulfate solution for each liter of solution; keep the sample at a temperature of about 90°C for 30 min and stir frequently. Remove from the hotplate and allow to settle for at least 2 hr; then siphon or decant most of the supernatant liquid and discard.

6.4 Transfer the precipitate to a 40-ml centrifuge tube; centrifuge, and discard the supernatant liquid.

6.5 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, adding a little additional 10 N NaOH if the precipitate does not dissolve readily.

6.6 Add 1 ml of strontium-yttrium carrier solution. Stir thoroughly; add a few drops of 10 N NaOH if any precipitate forms.

6.7 Add 1 ml of ammonium sulfate solution and stir thoroughly; then add glacial acetic acid dropwise until barium sulfate precipitates, and 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.

6.8 Add 20 ml of EDTA reagent, heat, and stir until the barium sulfate precipitate dissolves. Repeat steps 6.6 and 6.7.

6.9 Dissolve the barium sulfate precipitate in 20 ml of EDTA reagent, and add 1 ml of yttrium carrier solution and 1 ml of lead carrier solution. If any precipitate forms it should be dissolved by adding a few drops of 10 N NaOH. Transfer the solution to a Teflon or polyethylene container. Record the date and time. Age for 36 hr or longer. Cover the sample to prevent evaporation.

6.10 Transfer the aged solution to a centrifuge tube, and add 0.3 ml of ammonium sulfide solution. Add 10 N NaOH dropwise while stirring vigorously, until lead sulfide precipitates; then add about 10 drops excess. Stir intermittently over a period of about 10 min. The lead sulfide should settle as a fine-granular precipitate.

6.11 Centrifuge the solution, and transfer the supernatant liquid to clean centrifuge tubes. Discard the residue.

6.12 Place the centrifuge tube in a hot-water bath and slowly add 10 N NaOH to the liquid while stirring, until yttrium hydroxide precipitates; add 1 ml excess and stir intermittently for several minutes. Record the date and time of the precipitation. Centrifuge as soon as the yttrium hydroxide has largely settled. Discard the supernate.

6.13 Wash the precipitate thoroughly with 5 ml of water containing about 10 drops of 10 N NaOH, centrifuge, and discard the wash solution.

6.14 Transfer the precipitate to a 5-cm 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.

6.15 Count the sample in a low-background beta counter for a sufficient length of time to obtain satisfactory counting statistics. Record date and time that count begins. For most natural waters a counting period of about 300 to 500 min is desirable because of the low concentration of radium-228.

7. Calculations

7.1 Radium-228 (actinium-228) efficiency factor: The calculation requires a factor for in-growth of the actinium daughter and for decay in the time interval between separation from the radium parent and beginning of count.

The chemical recovery factor is included in overall efficiency and is not separately identified. Use equation 4 omitting the f_n term.

$$E = \frac{\bar{c}_n}{d_n (e^{-\lambda_n t_n}) (1 - e^{-\lambda_1 t_1}) (e^{-\lambda_2 t_2})}$$

where

λ = decay constant of radium-228
(0.1205 yr⁻¹),

λ_1 = decay constant of actinium-228
(0.001835 min⁻¹),

t_n = elapsed time between certification of
the standard and time of count in
years,

t_1 = time interval between final purifica-
tion of barium-radium sulfate
precipitate (step 6.9) and separa-
tion of actinium daughter (aging
time in minutes) (step 6.12), and

t_2 = time interval between separation of
actinium daughter (step 6.12)
and counting in minutes.

7.2 Calculation of radium-228 concentra-
tion: Use equation 3 omitting the f term.
Correction for decay of radium-228 is seldom
required. In addition to in-growth and decay
times for actinium-228 cited under 7.1 a cor-
rection for decay during counting is required.

$$\frac{\text{pCi/l of radium-228}}{KVE} = \frac{1,000 \bar{c} \lambda_1 t_3}{(e^{-\lambda t_n}) (1 - e^{-\lambda_1 t_1}) (e^{-\lambda_1 t_2}) (1 - e^{-\lambda t_3})}$$

where

t_s = decay time of radium-228 between
sampling and analysis in years,
and

t_3 = counting time in minutes.

The other symbols are defined in section 7.1.

8. Report

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

9. Precision

The limited data available suggest that
precision of the method is approximately
 ± 20 percent for a concentration of 1 pCi/l
and ± 10 percent at the 10 pCi/l level or
above.

Reference

- Johnson, J. O., 1971, Determination of radium-228 in
natural water: U.S. Geol. Survey Water-Supply
Paper 1696-G, 26 p.

Radoruthenium, dissolved, as ruthenium-106 Distillation method (R-1150-76)

**Parameter and code: Radoruthenium as ruthenium-106, dissolved (pCi/l):
none assigned**

1. Application

This method is applicable to analysis of nonsaline waters which do not contain high concentrations of organic matter. Using a maximum sample volume of 100 ml, the detection limit is approximately 4 pCi/l. Because of this rather high detection limit, the method is of value primarily for water samples which have substantial fission product activity. The sensitivity may be improved by preconcentrating the ruthenium and by counting the sample more than the recommended 150 min.

2. Summary of method

Ruthenium salts form the tetroxide in acid solution when a strong oxidizing agent is present. This oxide melts near room temperature and can be easily volatilized from concentrated perchloric acid solution, which boils at approximately 200°C. Distillation of the tetroxide provides an excellent separation from almost all potential sources of interference.

The method used is essentially that described by Glendenin (1951). The water sample is evaporated to small volume, and stable ruthenium carrier is added. Nitric acid is added to oxidize organic matter, phosphoric acid is added to prevent volatilization of molybdenum, bromide and iodide are added as halogen holdback carriers, and sodium bismuthate is added to oxidize the halide ions to their respective nonvolatile oxyacids (Wyatt and Rickard, 1961). Finally, perchloric acid is added to oxidize ruthenium to the tetroxide and to provide a high boiling point for the solution. Ruthenium tetroxide is then distilled, with the aid of air bubbles through the solution, into a cold sodium hydroxide solution. Ethyl alcohol is added to precipitate the ruthenium as mixed oxides.

The ruthenium oxides are separated from the supernate by centrifugation, redissolved in hydrochloric acid, and then reduced to ruthenium metal-oxide mixture by addition of magnesium turnings. After dissolving the excess magnesium, ruthenium is recovered by filtration through a tared filter and counted on a low-background beta counter. Recovery is determined gravimetrically. The corrected activity is compared with that of standards similarly prepared to determine the ruthenium-106 activity of the sample.

The restriction of the method to freshwaters and low-sample volumes is necessary to avoid large amounts of solids in the distillation flask. The range of usable sample volumes as a function of dissolved solids has not been evaluated.

The restriction of the method to freshwaters and low-sample volumes is necessary to avoid large amounts of solids in the distillation flask. The range of usable sample volumes as a function of dissolved solids has not been evaluated.

3. Interferences

Because the analytical method separates pure ruthenium, only ruthenium isotopes can interfere. On the basis of half-life, ruthenium-103 is the only interference of practical significance. The ruthenium-103 contribution to the total count is less than ruthenium-106 contribution (for equal numbers of atoms) because of lower counting efficiency. The ruthenium-103 contribution

decreases with time and may be completely eliminated by several months decay. Alternatively, the relatively low-energy betas from ruthenium-103 may be eliminated by counting the sample through an absorber which does not significantly affect the higher energy betas from rhodium-106 (ruthenium-106).

Any organic matter present in the sample should be destroyed by boiling with a concentrated nitric-perchloric acid mixture before proceeding with the perchloric acid distillation. To prevent explosive decomposition of the distillation mixture, nitric acid should be present as long as any unoxidized organic material remains.

Large amounts of insoluble matter in the distillation flask may cause serious bumping and impair the recovery of ruthenium.

4. Apparatus

4.1 *Compressed air*, 1–2 psi supply for bubbling air through distillation flask.

4.2 *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.

4.3 *Burner*, Bunsen, small.

4.4 *Centrifuge*, capable of accepting 40-ml tubes.

4.5 *Centrifuge tubes*, 40-ml, heavy-wall.

4.6 *Distillation apparatus*. See figure 7.

4.7 *Filter disks*, Versapore, 47 mm, 5 micrometer (Gelman Instrument Co., Ann Arbor, Mich. 48106).

4.8 *Hotplate*.

4.9 *Vacuum desiccator*.

4.10 *Vacuum-filtration apparatus* for 47-mm filters.

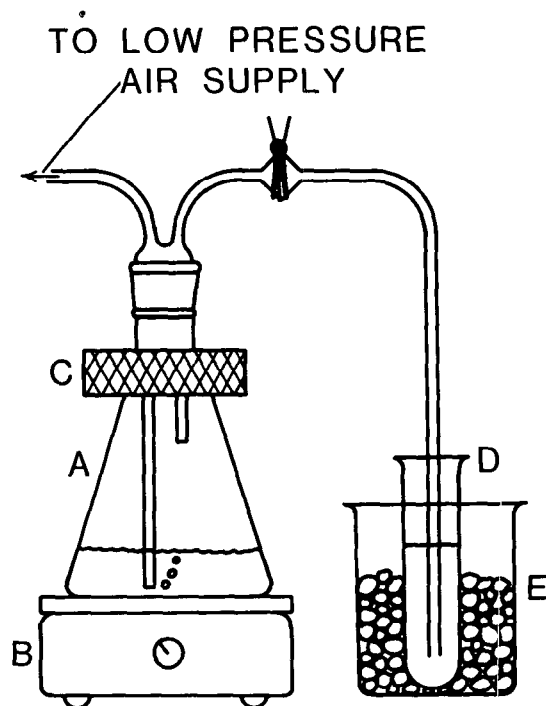
5. Reagents

5.1 *Bromide-iodide solution*, 1 ml = 10 mg Br and 10 mg I: Dissolve 4.7 g NaI and 5.2 g NaBr in 400 ml distilled water.

5.2 *Diethyl ether*.

5.3 *Ethanol*, 95 percent.

5.4 *Hydrochloric acid*, concentrated and 6 M.



- A - FLASK WITH GROUND GLASS JOINT (125ml)
 B - HOTPLATE
 C - ANNULAR LEAD WEIGHT
 D - HEAVY WALL PYREX CENTRIFUGE TUBE (40ml)
 E - ICE BATH

Figure 7.—Apparatus for distillation of ruthenium tetroxide.

5.5 *Magnesium metal turnings*.

5.6 *Nitric acid*, concentrated.

5.7 *Perchloric acid*, 70 percent.

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

5.9 *Ruthenium carrier solution*: Suspend 5 g of purified RuCl_3 in approximately 250 ml of 6 M HCl and agitate for several hours or overnight on a mechanical shaker. Filter the resulting solution through a fine filter. The solution is standardized by direct reduction of aliquots with magnesium metal, followed by filtration and weighing of the

mixed ruthenium oxide and metal produced. Care should be exercised to dissolve excess magnesium with HCl and to thoroughly wash the precipitate before drying.

5.10 *Ruthenium standard*: Prepare standard deposits of ruthenium-106 on filter paper starting with ruthenium standard solution of 100 pCi in 5 ml. Follow steps 6.12 through 6.16 in the "Procedure" section. Correct the activity determined for decay.

5.11 *Sodium bismuthate*.

5.12 *Sodium hydroxide, 6 M*.

6. Procedure

6.1 Estimate the volume of sample on the basis of dissolved solids. The volume is selected to avoid excess precipitation of salts in the evaporation step. The distillation flask holds 50 ml without danger of losing sample. Sample volumes in excess of this are evaporated to 50 ml in a Teflon evaporating dish.

6.2 Transfer the water sample into the distillation flask, and evaporate down to approximately 5 ml. Add an accurately measured amount of ruthenium carrier between 20 and 30 mg. Record pipet volume to 0.01 ml.

6.3 Evaporate to less than 5 ml. (Precipitation will usually occur, but the residue must not go dry.) Cool the flask and contents.

6.4 Add the following reagents in order: 1 ml concentrated nitric acid, 1 ml concentrated phosphoric acid, 2 ml bromide-iodide reagent, 0.5 g sodium bismuthate, and 10 ml 70 percent perchloric acid. Mix thoroughly.

6.5 Place the lead-ring weight around the flask. Moisten the ground-glass joint with phosphoric acid, and attach the delivery apparatus to the flask. Place the distillation apparatus on a hotplate, and immerse the end of the delivery tube in a 40-ml centrifuge tube containing 12 ml of 6 M NaOH. The centrifuge tube is kept immersed in an ice bath.

6.6 Connect the air supply to the still, and adjust the flow rate to a few bubbles per second. Heat the flask slowly to the boiling point, and then heat strongly to distill the

ruthenium. Note: It is best to perform the distillation behind an explosion shield.

6.7 Continue the distillation until the dense white fumes of perchloric acid have been carried over for a few minutes. Total time required for the distillation is usually 20-30 min.

6.8 Lower the centrifuge tube from the delivery tube, and remove the still from the hotplate. Disconnect the air supply and allow the still to cool. When cool, rinse the contents of the delivery tube into the centrifuge tube with a little distilled water from a washbottle.

6.9 Carefully warm the centrifuge tube to near boiling over a small burner. Remove from the flame and add, in small amounts, 3 ml of 95 percent ethanol, reheating to incipient boiling after each small addition. It is important to swirl the solution constantly while heating.

6.10 Cool the solution, and centrifuge to recover the precipitated ruthenium oxides. The supernate should be colorless and may be discarded.

6.11 Suspend the precipitate in 10 ml of distilled water to which 1 ml of 6 M NaOH has been added. Heat (with swirling) to boiling. Centrifuge and discard the supernate.

6.12 Suspend the precipitate in a few milliliters of 6 M HCl and reheat to boiling (swirl vigorously). Continue heating for a few minutes to dissolve all solid material. Set aside to cool.

6.13 Add about 5 ml distilled water to the ruthenium solution; then add small portions of magnesium turnings to reduce the ruthenium to the mixed oxide-metal precipitate. The solution may have to be heated to boiling as the reaction nears completion (supernate has light-blue color) to speed the process.

6.14 Add (slowly, at first) about 5 ml of concentrated HCl, and then heat to boiling for a few minutes to dissolve any excess magnesium.

6.15 Filter the suspension through a tared 47-mm Versapore filter using a vacuum-filtration apparatus. (The Versapore filter should be washed and dried by the same procedure as the sample (see below) prior to

ting). Wash the precipitate with three 10- to 30-ml portions of boiling water, two or three 10-ml portions of 95 percent ethanol, and with three 10-ml portions of diethyl ether to dry and distribute the precipitate over the filter pad.

6.16 Remove the dry filter and place in a heated (100°C) vacuum desiccator for 5-10 min (no longer). Remove, cool in a desiccator, and weigh. Mount in a ring-and-disk assembly, covering the precipitate with a thin plastic kitchen-type wrap.

6.17 Count the sample for three 50-min periods in a low-background beta counter.

7. Calculations

7.1 Ruthenium-106 efficiency factor (E): Counting efficiency for ruthenium-106 is determined by measurement of the count rate of standards prepared by direct precipitation of ruthenium metal from aliquots of the ruthenium-carrier solution spiked with known amounts of ruthenium-106. Ruthenium is reduced by metallic magnesium, filtered, dried, weighed, and counted as in the procedure above. Since recovery is usually in excess of 90 percent for the entire analytical procedure, the counting efficiency on the directly prepared standards is a reasonably accurate measurement of the counting efficiency of the samples. A typical value is 1.0 cpm/pCi.

7.2 Calculation of ruthenium-106 concentration: Use equation 1. The ruthenium recovery factor (f) is determined from the initial and final weights of ruthenium carrier.

$$\begin{aligned} & \text{pCi/l of ruthenium as ruthenium-106} \\ &= \frac{1000\bar{c}}{KVEf(e^{-\lambda t})}. \quad (1) \end{aligned}$$

8. Report

Report ruthenium-106 values of less than 10 pCi/l to one significant figure. Values greater than 10 pCi/l are reported to two significant figures.

9. Precision

Typical ruthenium-106 values for the precision of this method are ± 4 pCi/l or ± 20 percent, whichever is larger, at the 95-percent confidence level.

References

- Glendenin, L. E., 1951, Improved determination of ruthenium activity in fission, *in* Coryell, C. D., and Sugarman, N., Radiochemical studies: The fission products (Book 3): New York, McGraw-Hill Book Co., Paper no. 260, p. 1549.
- Wyatt, E. I., and Richard, R. R., 1961, The radiochemistry of ruthenium: Natl. Acad. Sci., Natl. Research Council Nuclear Sci. Ser. NAS-NS 3029, 78 p.

Strontium-90, dissolved

Chemical separation and precipitation method (R-1160-76)

Parameter and code: Strontium-90, dissolved (pCi/l): 13503

1. Application

The method is applicable to all natural freshwaters and saltwaters. It is applicable to reactor wastes and may be applicable to industrial wastes, provided that recovery tests are made to assure that organic matter does not hold back strontium.

2. Summary of method

This method is based on the work of Hahn and Straub (1955) and of Johnson and Edwards (1967). Dissolved radiostrontium is determined by beta counting after a lengthy separation procedure that removes other fission products. Stable strontium carrier is added to the sample, and a carbonate precipitation is made to collect strontium-90 accompanied by some fission products. The carbonate precipitate is dissolved, and strontium nitrate mixed with calcium nitrate is precipitated with fuming nitric acid. Calcium is removed by washing with acetone, and strontium nitrate is further purified by solution and reprecipitation.

The precipitate may still contain traces of fission products such as transition metals, rare earths, niobium, zirconium, yttrium, and barium. Radium may be present. These are all removed by the addition of iron and barium carriers which are precipitated as the hydroxide and chromate respectively.

Final purification is effected by precipitating strontium as the oxalate. Yttrium-90, the radioactive daughter of strontium-90, has been completely removed at this point, and a new equilibrium begins. The yttrium isotope is also a beta emitter, and the sensitivity of

the analysis is improved by counting after 21 d to allow in-growth of yttrium-90.

If strontium-89 is present, it is counted as strontium-90. Approximately 45 percent of the original strontium-89 activity is retained 21 d after the initial precipitation. Strontium-90 may be determined independently by chemically separating the yttrium-90 daughter, and relating its activity back to strontium-90. The composition of a mixture of the three isotopes, strontium-90, strontium-89, and yttrium-90, may be determined approximately by plotting the growth of radioactivity with time as shown in Johnson and Edwards (1967).

3. Interferences

Interferences from both fission products and natural radioactivity are negligible (Glendenin, 1951). As indicated above, strontium-89 is counted as strontium-90.

4. Apparatus

4.1 *Filter disks*, 25-mm Whatman No. 42, or equivalent.

4.2 *Filtration apparatus* for 25-mm membrane filters.

4.3 *Hotplate*.

4.4 *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.

4.5 *Ring-and-disk mounting assemblies for filters*, including 21-mm diameter rigid copper backing disks.

5. Reagents

- 5.1 *Acetic acid*, 6 M.
- 5.2 *Acetone*, anhydrous.
- 5.3 *Aluminum foil*, 3.5 mg/cm² or less.
- 5.4 *Ammonium acetate*, 6 M solution.
- 5.5 *Ammonium hydroxide*, concentrated and 6 M.
- 5.6 *Ammonium oxalate*, saturated solution.
- 5.7 *Barium carrier solution*, 1 ml=3.00 mg Ba⁺: Dissolve 1.33 g of BaCl₂·2H₂O in distilled water. Add a few drops of concentrated nitric acid and dilute to 250 ml.
- 5.8 *Diethyl ether*.
- 5.9 *Ethanol*, 95 percent.
- 5.10 *Iron carrier solution*, 1 ml=5 mg Fe⁺: Dissolve 500 mg of pure iron wire in a slight excess of nitric acid, and dilute to 100 ml.
- 5.11 *Nitric acid*, fuming, concentrated, 6 M and 1 M.
- 5.12 *Phenolphthalein indicator solution*.
- 5.13 *Sodium carbonate solution*, 1 M and 0.1 M.
- 5.14 *Sodium chromate solution*, 1.5 M.
- 5.15 *Strontium carrier solution*, 1 ml=4.00 mg Sr⁺: Dry "anhydrous" strontium nitrate overnight at 105°C, and cool in a desiccator. Weigh out 9.66 g of the dried salt, and dissolve in distilled water. Add 2 ml of concentrated nitric acid, and dilute to 1 liter. A more exacting procedure is described by Glendenin (1951, p. 1461), but the added work is not warranted unless the strontium nitrate contains radioactive impurities which contribute significantly to the reagent blank.
- 5.16 *Strontium-90 standard solution*: Strontium-90 standard solutions calibrated to ±1.5 percent are commercially available. In purchasing standards it is essential that the concentration of the stable isotopic carrier be known. Dilute the standard to approximately 5 pCi/ml as described by Barker and Robinson (1963, p. A28). It is generally necessary to add both acid and inactive strontium carrier at the time of dilution. The final solution should be approximately 0.1 N in hydrogen ion (HCl or HNO₃) and should have a chemical strontium carrier concen-

tration of 0.1 to 10 mg/l. Strontium-90 standard activity (A), after a decay time (t_n), for an initial activity (A₀), can be calculated by use of the following equation:

$$A = A_0 e^{-\lambda_n t_n},$$

where

λ_n = decay constant of strontium-90 (1.999 × 10⁻³ months⁻¹), and

t_n = elapsed time (in months) between certification of standard and time of count.

5.17 *Thymolphthalein indicator solution.*

6. Procedure

A reagent blank should be run with each set of samples to check for contamination of reagents, and to permit an accurate blank correction to be made. Occasional spiked samples (samples containing a known amount of added standard) should also be run through the entire procedure as checks.

6.1 To a 1,000-ml or other suitable aliquot of filtered water sample in a 1,500-ml beaker add 20 mg of strontium carrier (5 ml of 4-mg Sr⁺/ml). Heat to boiling on a hotplate. Make the solution basic to thymolphthalein indicator (blue color) by dropwise additions of concentrated ammonium hydroxide, and add an additional 6 ml.

6.2 Add 15 ml of 1.0 M sodium carbonate. Stir thoroughly, cover the beaker with a watch glass, and digest on a steam bath for 1 hr. Add more ammonium hydroxide, if required, to maintain the blue color of thymolphthalein. (Add more indicator if the color fades.)

6.3 Remove the beaker from the steam bath, and allow the precipitate to settle while the solution cools to room temperature.

6.4 Carefully decant or draw off as much as possible of the supernatant solution without disturbing the precipitate. Transfer the insoluble material to a 50-ml Pyrex centrifuge tube, and police the beaker with 0.1 M sodium carbonate. Add washings to the centrifuge tube. Centrifuge and discard the supernatant liquid.

6.5 Cautiously add 1 N nitric acid dropwise until the carbonate precipitate is com-

pletely dissolved. Dilute to 5 ml with distilled water. (Note: There may be a small residue of silica or insoluble metal oxide remaining.) Very cautiously add 25 ml of fuming nitric acid (work in the hood, use plastic gloves, safety goggles or face shield, and avoid inhaling the vapors!). Cool, stir, and centrifuge.

6.6 Using the above safety precautions, pour off the nitric acid as completely as possible, cool the tube below room temperature using cold water or ice bath, and cautiously add 25 ml of anhydrous acetone to the residue. Stir thoroughly and centrifuge, again discarding the supernate.

6.7 Repeat step 6.6.

6.8 Dissolve the nitrates in 5 ml of distilled water, and place the tube in a boiling-water bath until the odor of acetone is gone. (Caution: be sure acetone is completely removed.)

6.9 Cool below room temperature, and again precipitate strontium nitrate by adding 25 ml of fuming nitric acid. Swirl, cool, and centrifuge. Discard the supernate.

6.10 Dissolve the precipitate in 10 ml of distilled water and add 5 mg of ferric carrier (1 ml of 5-mg Fe^{+3} per ml) and 15 mg of barium carrier (5 ml of 3-mg Ba^{+2} per ml). Add concentrated ammonium hydroxide with constant stirring until ferric hydroxide begins to precipitate. Then add several drops excess. Centrifuge, and decant the supernate into a clean centrifuge tube. This operation removes the yttrium daughter of strontium-90. Record the time and date.

6.11 Add phenolphthalein indicator, and add 6 *N* nitric acid dropwise until the pink color disappears. Add 1 ml of 6 *N* acetate acid and 2 ml of 6 *M* ammonium acetate. Place the samples in a boiling-water bath and add 1 ml of 1.5 *M* sodium chromate while agitating. Leave in the water bath for 5–10 minutes.

6.12 Cool to room temperature, centrifuge, and decant the supernate into a 100-ml beaker. Discard the precipitate.

6.13 Add 2 ml of concentrated ammonium hydroxide, and heat to boiling. Add 5 ml of saturated ammonium oxalate solution

and stir. Allow the precipitate to settle and the solution to cool to room temperature.

6.14 Filter through a tared 25-mm filter paper (Whatman, No. 42) supported on a sintered glass disk of a microanalytical filtration assembly. Wash the precipitate with three 5-ml portions of distilled water and then successively with small volumes of 95 percent ethanol and diethyl ether. Dry in a desiccator. Weigh as strontium oxalate monohydrate, and determine the gravimetric yield.

6.15 Mount the filter on a copper disk, 21-mm diameter. Cover with aluminum foil (3.5 mg/cm² or less). Store the sample for 21 d to permit in-growth of yttrium-90 to 99.5 percent of equilibrium activity. If it is desired to break down the activity into the three radioactive isotopes, it is necessary to start the counting within a few days of step 6.15 so that the decay of strontium-89 and in-growth of yttrium-90 may be observed.

6.16 Count the sample for 100 min on a low-background, anticoincidence shielded beta counter.

7. Calculations

7.1 Strontium-90 efficiency factor (*E*) and fractional chemical recovery (*f_n*): Use equation 2. Determine *f_n* from the weight of strontium oxalate.

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

where

λ = decay constant of strontium-90
(1.999×10^{-3} month⁻¹).

7.2 Calculation of strontium-90 concentration: Use equation 1, making the decay correction if necessary. Determine *f* from the weight of strontium oxalate precipitate.

$$\text{pCi/l of strontium-90} = \frac{1,000 \bar{c}}{KVEf (e^{-\lambda t})}. \quad (1)$$

According to Hahn and Straub (1955), the chemical recoveries range from approximately 72 to 80 percent. Accurate determination of chemical recovery requires knowledge of the natural strontium content of the

sample. Normally this is less than 1 mg/l and may be neglected. In a few cases, particularly with waters from an area extending through parts of Wisconsin and Illinois, the strontium content may equal or exceed the strontium carrier added, and natural strontium must be determined for the calculation of chemical recovery.

7.3 Calculation of strontium-90, yttrium-90 and strontium-89. The count rate is determined at intervals over a timespan of approximately 30 d starting as close to zero time as possible. A typical counting schedule thereafter would be at 24 hr, 48 hr, 100 hr, 200 hr, and 400 hr. The count rates are plotted against time, and the curve thus obtained is compared against type curves for different isotopic ratios of strontium-90 to strontium-89 (Johnson and Edwards, 1967) to obtain the ratio for the sample.

8. Report

Report strontium-90 equivalent activities to ± 0.5 pCi/l or to ± 10 percent, whichever is greater.

9. Precision

Minimum detection level is 0.5 pCi/l and this is also the precision at activities below 5 pCi/l. At higher strontium-90 activities the precision is ± 10 percent.

References

- Barker, F. B., and Robinson, B. P., 1963, Determination of beta activity in water, U.S. Geol. Survey Water-Supply Paper 1696-A.
- Glendenin, L. E., 1951, Determination of strontium and barium activities in fission, in Coryell, C. D., and Sugarman, N., eds., Radiochemical studies: The fission products, National Nuclear Energy Series IV, 9, Paper no. 236: New York, McGraw-Hill, p. 1460-69.
- Hahn, R. Z., and Straub, C. P., 1955, Determination of radioactive strontium and barium in water: Am. Water Works Assoc. Jour., v. 47, p. 335-340.
- Johnson, J. O., and Edwards, K. W., 1967, Determination of strontium-90 in water: U.S. Geol. Survey Water-Supply Paper 1696-E, 10 p.

Tritium

Liquid scintillation method, Denver lab (R-1171-76)

Parameters and codes: Tritium dissolved (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The technique is generally applicable to the determination of tritium artificially introduced into water by such activities as tracer experiments, nuclear power, waste disposal, and thermonuclear weapons testing. The technique is not sufficiently sensitive to be applicable to the determination of very low natural tritium levels.

2. Summary of method

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a simple multichannel analyzer (three or four channels at most) where sorting into energy takes place. The counts in each channel are displayed on a scaler and may be read out on paper tape, punched tape, or magnetic tape.

Liquid scintillation counting is primarily used for the counting of beta emitters although it can also be used for alpha-emitting isotopes.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a large volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a

secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much of the tritium data reported in the literature was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietary scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. Since the composition of the proprietary mixtures is not available, these are listed by trade name in the "Reagent" section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many substances, including water, interfere in the energy transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and the ratio of liquid scintillator mixture to

water sample. As the fraction of water sample in the water scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The maximum on the curve of activity versus volume of tritiated water (in a constant overall volume) is a rounded plateau. Therefore, the proportion of water sample to scintillating liquid mixture is not critical and is easily reproducible in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed.

A detailed description of the method is given by Schroder (1971).

3. Interferences

Distillation is used to remove both quenching substances and radionuclides that could contribute to excess count. Distillation is fully effective in removing inorganic salts and high-boiling organic compounds. Organic materials that vaporize at a lower temperature than water and are condensable under the same conditions as water vapor may be carried over in the vacuum distillation. If these materials contribute either quenching or beta radioactivity the possibility of interference exists, although it would appear remote.

Further protection against interferences is provided by the energy discrimination in the liquid scintillator analyzer and the external standard-ratio test.

4. Apparatus

4.1 *Autopipet*, 25-ml maximum capacity.

4.2 *Counting equipment*. Liquid scintillation spectrometer; counting systems capable of meeting the following specifications:

Counting efficiency—not less than 24 percent with optimum sample-scintillator mixture and polyethylene vials.

Background—not to exceed 5 cpm at sea level in tritium channel.

Sample capacity—at least 100 samples.

Operation—programmable and automatic.

Internal check—an external standard and ratio computation capability required.

Readout—automatic printout.

4.3 *Pipets*, 8 ml.

4.4 *Vacuum-distillation apparatus*. Consists of a 50-ml round-bottom flask as the distillation flask and a 125-ml round-bottom flask as the condenser flask. The distillation flask is heated with a rheostat-controlled mantle, and the condenser flask dips into a Dewar containing isopropanol-dry ice. The two flasks are connected by a 20-mm diameter U-tube, 10-cm long with ground-glass connectors and stopcock for application of vacuum. Heating tape is coiled around the U-tube connecting the two flasks.

5. Reagents

5.1 *Scintillator*, Instagel (Packard Instrument Co.) for low-temperature counting (1° – 4° C). A preblended gel-forming scintillator designated 3A70* (Research Products International) for room-temperature counting.

5.2 *Tritium standard solution*: Appropriate standards are prepared by the dilution of NBS standard tritiated water with "dead" water, that is, water containing less than 1 Tu.

5.3 *Water, "dead."* The tritium blank introduced by reagents must be tested at intervals by analyzing "dead" water (water with no measurable tritium content) in exactly the same procedure as for a normal water sample. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 Counting.

6.1.1 Distill 25 ml of water sample for direct counting, or approximately 10 ml of

electrolyzed water sample, using the vacuum distillation apparatus. The U-tube is preheated to assure dryness.

6.1.2 Pipet 8.00 ml of the distillate from the preceding step into a 25-ml polyethylene vial, and add 14 ml of scintillator mix. The choice of scintillator depends on the type of liquid scintillation spectrometer to be used for counting. Instagel is used with the instruments that operate at cold temperature (3°C), and 3A70* is used with the instruments that operate at room temperature. Cap the vial and mix. Heat the Instagel-sample mixture on a hotplate at approximately 100°C for 2 or 3 min. This clarifies the mixture. The 3A70*-sample mixture does not require heating. The above operation is carried out under subdued red light to filter out the blue region of the spectrum. This minimizes excitation of fluorescence background in the sample.

6.1.3 Prepare three blanks and two standards in the same manner as the samples. Place one standard in the 2d counting position in the spectrometer and one in the 10th position. Place blanks at intervals throughout the run of 10–14 samples.

6.1.4 Place three sealed standards (tritiated toluene in glass-sealed scintillator solution) in the group. One standard goes in the first counting position to permit monitoring the instrument before counting the samples. The remaining sealed standards are placed near the blanks.

6.1.5 Allow prepared samples to remain in the dark in the liquid scintillation spectrometer for several hours before counting begins. This allows decay of fluorescence and chemiluminescence. A minimum of 8 hr standing is required with Instagel and 12 hr with 3A70*.

6.1.6 Count each vial five times for 100 min. Total counting time for one sample is 500 min. Counting time is reduced for very active samples. One million counts is cutoff setting.

6.1.7 Program the instrument to perform the external-standard ratio analysis on samples, standards, and blanks at the

end of the counting run (see instrument instruction manual). This procedure is a check for quenching. The ratio of low-energy counts in channel A of the spectrometer is established for both tritium and an external standard placed near the sample vial. The value of R in the following equation should be constant to within ± 0.2 .

$$R = \left[\frac{\text{Counts in A}}{\text{Counts in B}} \text{ tritium} \right] \left[\frac{\text{Counts in B}}{\text{Counts in A}} \text{ standard.} \right]$$

Individual samples that fall outside this range must be reanalyzed. If all values of R fall outside this range, the scintillator has deteriorated and must be replaced.

7. Calculations

Several statistical schemes have been presented for the calculation and verification of tritium data, each intended to optimize a particular analytical situation. In the present analytical procedure the repeated counting of individual samples has the effect of averaging out short-term fluctuations. Statistical checks have shown that highest precision, in this analytical situation, is attained by the use of longer term average values for the samples and standards.

Counting efficiency and background values are determined with tritium standards whenever a new lot of scintillator is used. Counting-efficiency data and background data from standards and blanks run with each set are also determined. The new data from each set are averaged into the data from the preceding sets, thus creating a moving average value for counting efficiency and background. As new efficiency and background data appear they displace older data entered into the moving average. Data from four or five valid runs (no quenching or other aberration) enter into the moving average used at any given time.

7.1 Tritium efficiency factor (E). Use equation 2:

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

where

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

d_n = disintegration rate of standard (dpm), corrected for blank ($\bar{S} - \bar{B}$),

λ = decay constant of tritium (4.685×10^{-3} month $^{-1}$),

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

where

\bar{S} = moving average count rate (cpm) of the standards, and

\bar{B} = moving average count rate (cpm) of the blanks.

7.2 Calculation of tritium concentration:

Use equation 1. The chemical recovery factor (f) is an enrichment factor when electrolytic enrichment is applied to the sample. Since electrolysis is not used the value of f is unity.

$$\text{pCi tritium/l} = \frac{1,000\bar{c}}{KVEf(e^{-\lambda t})}, \quad (1)$$

where f is electrolytic enrichment factor determined by standard included in the run,

$$f = \frac{\text{cpm/ml after electrolysis}}{\text{cpm/ml before electrolysis}}$$

7.3 Conversion of tritium concentration in pCi/l to tritium units. Tritium concentration in Tu =

$$\frac{\text{pCi tritium/l}}{3.22}$$

8. Report

Concentrations in both tritium units and picocuries per liter are reported to two significant figures down to the minimum detection level (MDL). The latter can only be estimated because of the very pronounced effect of altitude on the background count. At sea level the MDL is estimated at 60 Tu, and at 5,000 ft (1,500 m) it is estimated at 150 Tu for the direct count method.

9. Precision

Precision is dependent on altitude in the same way as MDL. At 500 Tu reproducibility is approximately ± 20 percent. Precision improves with increasing concentration.

Reference

- Schroder, L. J., 1971, Determination of tritium in water by the U.S. Geological Survey, Denver, Colo.: U.S. Geol. Survey Rept. USGS-474-134, 22 p.; Avail. *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA 22151.