

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*, wigggle-plate or ultrasonic type.

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

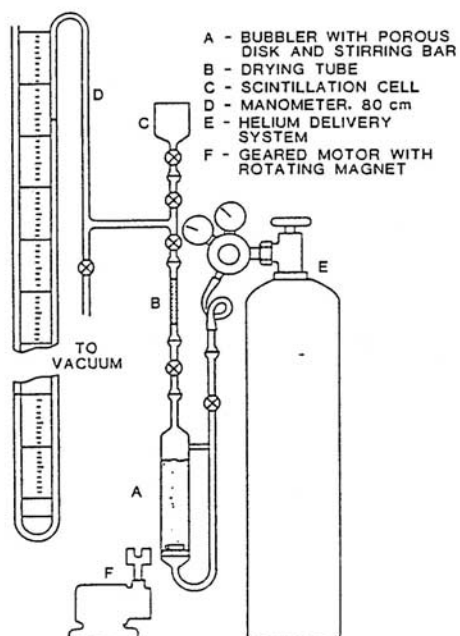


Figure 5.—Radon deemanation train and bubbler.

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

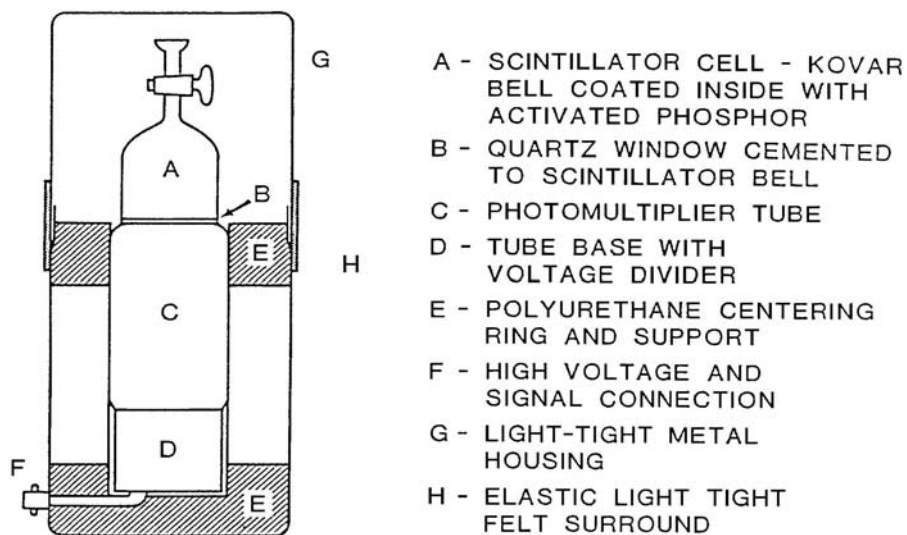


Figure 6.—Radon scintillation cell and housing.

## 5. Reagents

5.1 *Barium carrier solution*, 50 mg barium/ml: Dissolve 75.81 g barium chloride ( $\text{BaCl}_2$ ) 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 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  $0.100 \times 10^{-6}$  curie of radium-226 in 5 ml of 5 percent  $\text{HNO}_3$ . 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  $\text{H}_2\text{SO}_4$  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.

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 difficultly 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 counting. 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 ( $\approx 10$  cpm) and one high ( $\approx 1,000$  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 another, 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.

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

where

$\lambda_1$  = decay constant of radon-222 ( $1.259 \times 10^{-6} \text{ min}^{-1}$ ),  
 $t_1$  = 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 ex 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<sub>1/2</sub> = 3.823 d]

Time	Days	Hours	Minutes
1-----	0.834,18	0.992,47	0.999,87
2-----	.695,85	.985,00	.999,75
3-----	.580,46	.977,59	.999,62
4-----	.484,21	.970,23	.999,50
5-----	.403,91	.962,93	.999,37
6-----	.336,93	.955,68	.999,24
7-----	.231,07	.948,49	.999,12
8-----	.234,46	.941,35	.998,99
9-----	.195,58	.934,2?	.998,87
10-----	.163,15	.927,24	.998,74
11-----	.136,09	.920,26	.998,62
12-----	.113,53	.913,33	.998,49
13-----	.094,70	.906,46	.998,36
14-----	.079,00	.899,64	.998,24
15-----	.065,90	.892,87	.998,11
16-----	.054,97	.886,15	.997,99
17-----	.045,86	.879,48	.997,86
18-----	.038,25	.872,86	.997,74
19-----	.031,91	.866,29	.997,61
20-----	.026,62	.859,77	.997,48
21-----	.022,20	.853,30	.997,36
22-----	.018,52	.846,88	.997,23
23-----	.015,45	.840,50	.997,11
24-----	.012,89	.834,18	.996,98
25-----	.010,75	-----	.996,86
26-----	.008,97	-----	.996,73
27-----	.007,48	-----	.996,61
28-----	.006,24	-----	.996,48
29-----	.005,21	-----	.996,36
30-----	.004,34	-----	.996,23
31-----			.996,10
32-----			.995,98
33-----			.995,85
34-----			.995,73
35-----			.995,60
36-----			.995,48
37-----			.995,35
38-----			.995,23
39-----			.995,10
40-----			.994,98
41-----			.994,85
42-----			.994,73
43-----			.994,60



44 -----	.994,48
45 -----	.994,35
46 -----	.994,22
47 -----	.994,10
48 -----	.993,97
49 -----	.993,85
50 -----	.993,72
51 -----	.993,60
52 -----	.993,47
53 -----	.993,35
54 -----	.993,22
55 -----	.993,10
56 -----	.992,97
57 -----	.992,85
58 -----	.992,72
59 -----	.992,60
60 -----	.992,47

## 9. Precision

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

## References

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