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Method 903.1: Radium-226 in Drinking Water (Radon Emanation Technique)

SECTION 7 RADIUM-226 IN DRINKING WATER
RADON EMANATION TECHNIQUE
METHOD 903.1

1.0 Scope and Application

1.1 This method covers the measurement of radium-226 in a drinking water sample and would be employed after the gross alpha or the gross radium alpha screening technique had indicated possible non-compliance with the alpha radioactivity limits set forth in the Safe Drinking Water Act, PL 93-523. 40 FR 34324.

1.2 This method is specific for radium-226, and is based on the emanation and scintillation counting of radon-222, a daughter product of radium-226.

1.3 The detection limit for this method assures measuring radium-226 concentrations as low as 0.1 pCi/L.

2.0 Summary of Method

2.1 The radium-226 in the drinking water sample is concentrated and separated by coprecipitation on barium sulfate. The precipitate is dissolved in EDTA reagent, placed in a sealed bubbler and stored for ingrowth of radon-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived radon-222 daughters are in equilibrium with the parent (4h), the scintillation cell is counted for alpha activity.

2.2 The absolute measurement of radium-226 is effected by calibrating the scintillation cell system with a standard solution of this nuclide.

3.0 Sample Handling and Preservation (see Sec. 3, Method 900.0).

4.0 Interferences

4.1 There are no radioactive interferences in this method.

5.0 Apparatus - See Appendix D for details and specifications.

5.1 Scintillation cell system. (Figure 1.)

5.2 Radon emanation apparatus:
a) Radon bubbler - (Figure 2.)
b) Scintillation cell - (Figure 3.)

5.3 Electric hot plate

5.4 Analytical balance

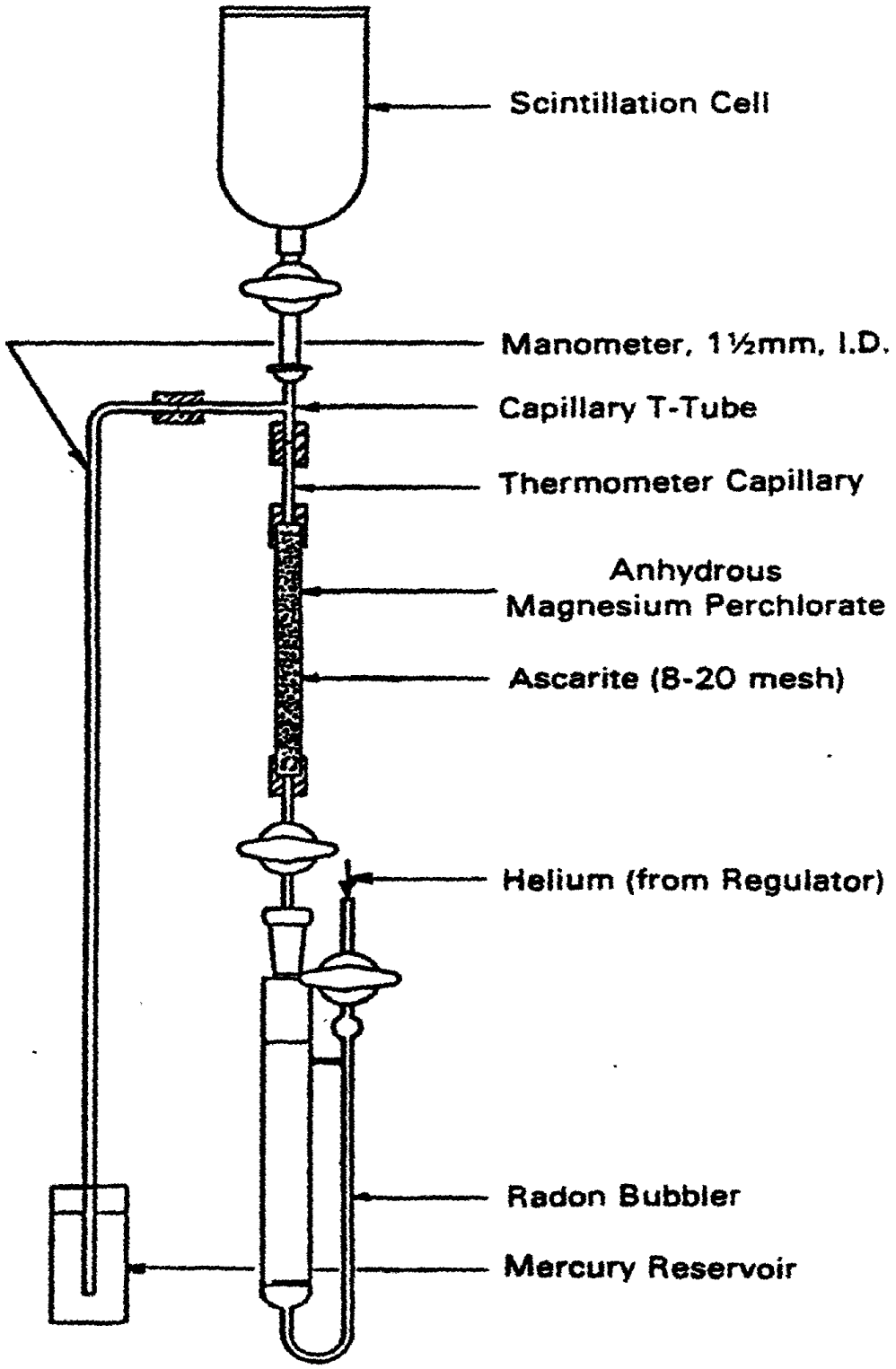

Figure 1. Randon Emanation apparatus with scintillation cell

5.5 Centrifuge

5.6 Glassware

6.0 Reagents

6.1 Distilled or deionized water.

6.2 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. gr. 0.90. 56.6%.

6.3 Ascarite, drying reagent: 8-20 mesh.

6.4 Barium carrier, 16 mg/mL, standardized: (see Sec. 6, Method 903.0).

6.5 EDTA reagent, basic, (0.25M): Dissolve 20g NaOH in 750 mL water, heat and slowly add 93g disodium ethylenedinitriloacetate dihydrate, ($Na_2C_{10}H_{14}O_8N_2.2H_2O$) while stirring. After the salt is in solution, filter through coarse filter paper and dilute to 1 liter.

6.6 Helium, gas.

6.7 Hydrochloric acid, 12N: HCl (conc.), sp. Gr. 1.19, 37.2%

6.8 Magnesium perchlorate, $Mg(C10_4)_2$: reagent grade

6.9 Sodium hydroxide, 10N: Dissolve 40g NaOH in 50 mL water and dilute to 100 mL.

6.10 Standard radium-226 tracer solution: preferably purchased from National Bureau of Standards, Special Publication 260, 1978, SRM 4960. Prepare stock dilution equivalent to 50 pCi radium-226 per mL.

6.11 Sulfuric acid, 18N: Carefully mix 1 volume 36N H_2SO_4 (conc.) With 1 volume of water.

6.12 Sulfuric acid, 0.1N: Mix 1 volume 18N H_2SO_4 with 179 volumes of water.

7.0 Calibrations

7.1 The calibration constant of each scintillation cell must be determined using a standardized radium-226 solution with a labeled cell and a specific photon counter. This is determined as follows:

7.1.1 Place 50 pCi of the radium-226 solution in a bubbler (50 pCi of radium-226 will produce about 6 pCi radon-222 in 18 hours). Attach the bubbler to the radon assembly. (Fig. 1.)

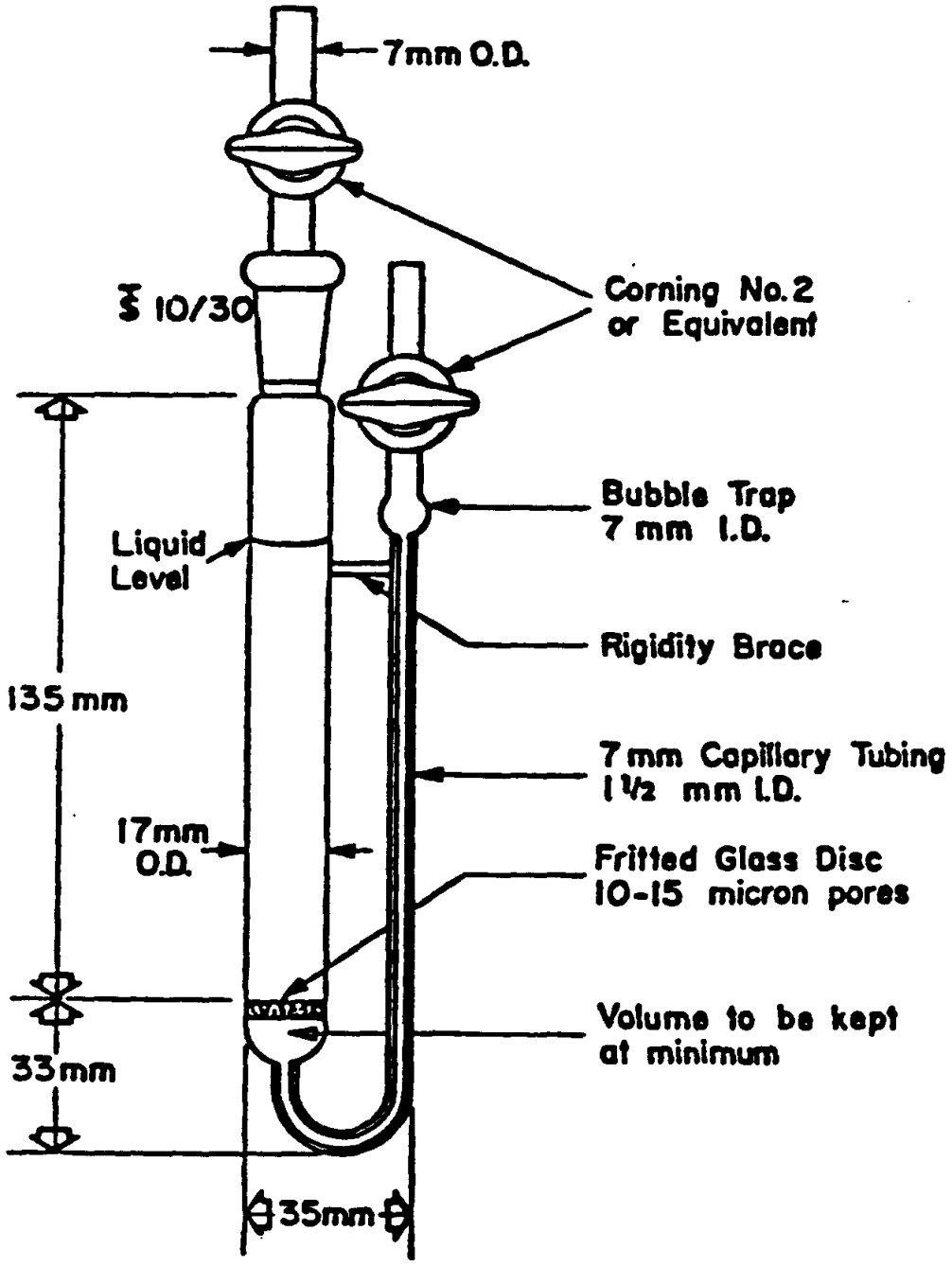

Figure 2. A typical radon bubbler

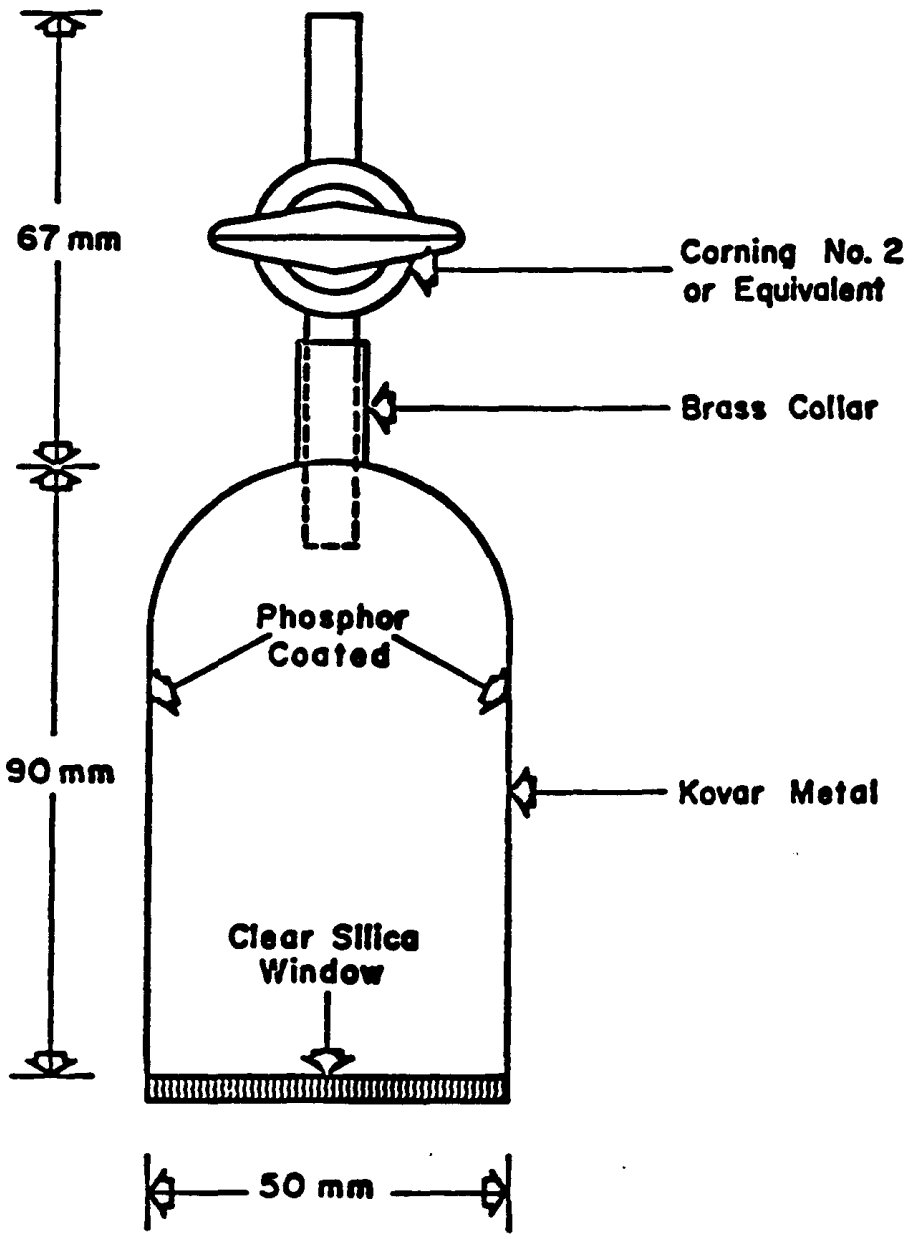

Figure 3. A typical scintillation cell for radon counting

7.1.2 With the scintillation cell disconnected, bubble helium gas through the solution for 20 minutes to remove all radon-222.

7.1.3 Close both stopcocks on the bubbler to establish zero time for ingowth of radon-222. (Refer to 9.2) Set aside for approximately 18 hours.

7.1.4 Evacuate the scintillation cell and attach to the column and bubbler.

7.1.5 Proceed with steps 8.8 - 8.13, Radon Emanation Technique.

7.1.6. The calibration constant is determined from the radium-226 activity in the bubbler and the ingrowth time of radon-222.

7.2. The calibration constant includes the de-emanation efficiency of the system, the counting efficiency of the cell, and the alpha activity contributed by polonium-2l8 and polonium-214, which will be in equilibrium with radon-222 when the sample is counted 4 hours after the de-emanation. A 100-minute counting time will be sufficient for the standard and will eliminate the need to correct for decay of radon-222, which occurs during counting.

7.3 The bubbler used for the radium-226 standardization should not be used for sample analysis. It should be set aside to be retained for future calibrations. Each scintillation cell should be calibrated periodically with the radium-226 standard to ensure instrument quality control.

8.0 Procedure

8.1 To a 1000-mL drinking water sample, add 20 mL 12N HC1 and 2.0 mL barium carrier and heat to boiling.

Note: If there is solid matter in the sample, do not filter before starting analysis. Follow procedure steps through 8.4, then filter solution into a clean centrifuge tube. Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add glacial (17.4N) acetic acid (CH_3COOH) until barium sulfate precipitates, then add 2 mL excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate. Repeat step 8.4 and continue with radium analysis.

8.2 Cautiously and with vigorous stirring, add 20 mL 18N H_2S0_4. Digest 5 to 10 minutes and let precipitate settle overnight. Decant and discard supernate,

8.3 Slurry the precipitate and transfer to a centrifuge tube with a minimum amount of 0.1N H_2SO_4. Centrifuge and discard supernate. Wash twice with 0.1 N $_2$H S$_4$O . Centrifuge and discard washes.

8.4 Add 20 mL basic EDTA reagent, heat in a water bath and stir well. Add a few drops 10N NaOH if the precipitate does not readily dissolve.

8.5 Transfer the solution to a radon bubbler (Fig. 2). Open both the upper and lower stopcocks and de-emanate the solution by **slowly** passing helium gas through the bubbler for about 20 minutes.

Note: the volume of these bubblers is usually greater than 20 mL allowing for at least a 1 cm air space between the bubbler and the stopper. In those instances where the solution volume exceeds the capacity of the bubbler, it will be necessary to continue the boiling in the water bath until the volume is reduced.

8.6 Close the two stopcocks, and record time. Store the solution for 4 to 8 days for ingrowth of radon-222 (Fig. 4).

8.7 At the end of the storage period, fill the upper half of an absorption tube with magnesium perchlorate and the lower half with ascarite.

Note: For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing should be used whenever possible, and the drying tube volume with the ascarite and magnesium perchlorate must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each of the drying agents occupying 4 cm and being separated by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced.

8.8 Attach the tube to the radon bubbler and then attach the evacuated scintillation cell (Fig. 3) to the tube. Open the stopcock on the cell and check the assembly for leaks. Gradually open the outlet stopcock on the bubbler, and when the stopcock is fully open and no further significant bubbling takes place, close the stopcock.

8.9 Adjust the helium gas pressure so that the gas flows at slightly above atmospheric pressure.

8.10 Connect the hose to the bubbler inlet and gradually open the inlet stopcock using the bubbling as a guide. When the stopcock can be fully opened without a significant amount of bubbling, the bubbler is essentially at atmospheric pressure again.

8.11 Open the outlet stopcock very slightly and allow bubbling to proceed at a rate, determined by experience, such that 15 to 20 minutes are required to complete de-emanation.

8.12 Toward the end of the de-emanation, when the vacuum is no longer effective, gradually increase the helium gas pressure. When the system is at atmospheric pressure, shut off the helium gas, disconnect the tubing from the bubbler inlet and close the inlet and outlet stopcocks of the cell and bubbler, and record time. This is the beginning of radon-222 decay and ingrowth of radon-222 daughters.

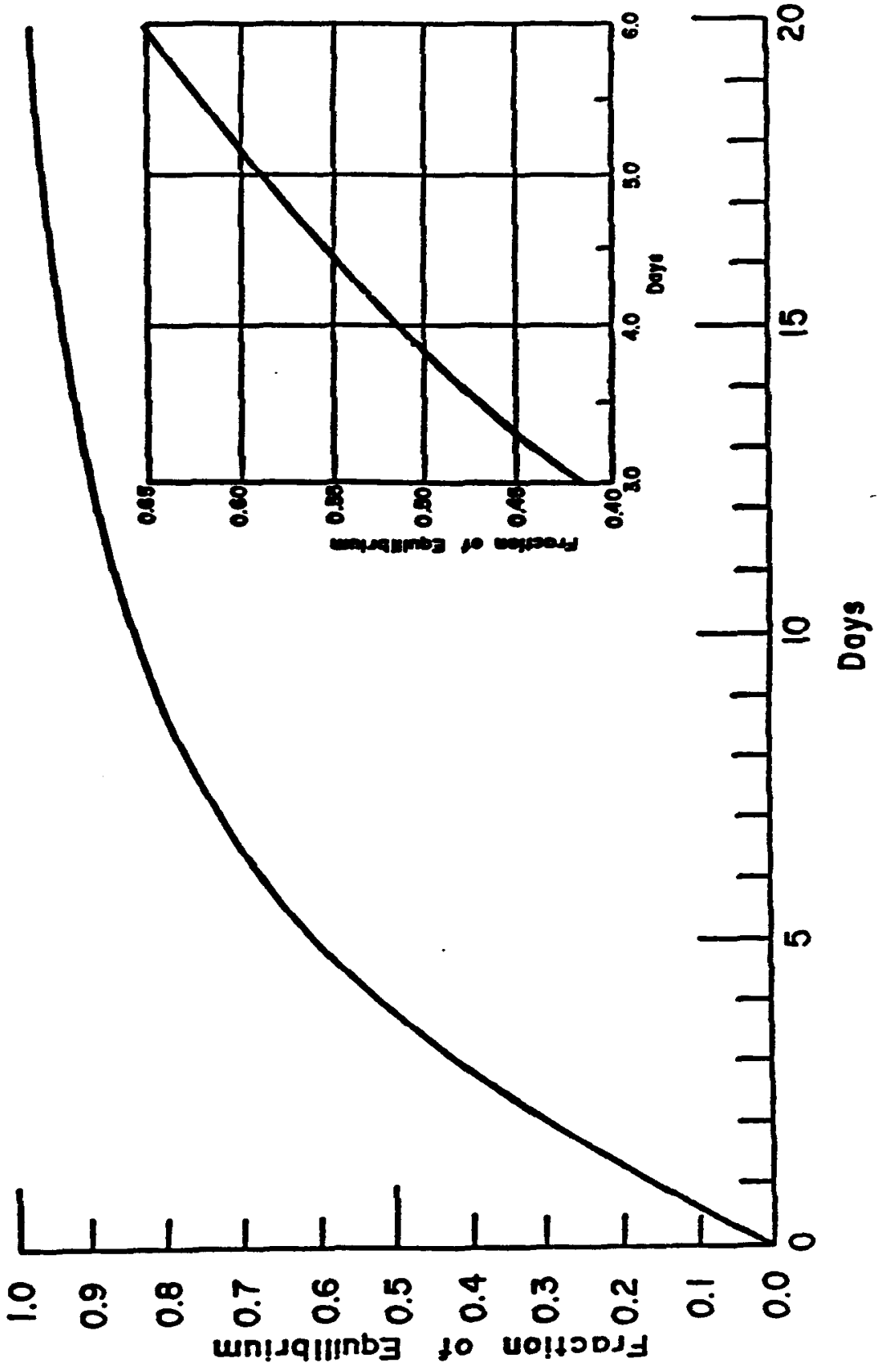

Figure 4. The growth of radon-222 from radium-226

8.13 Store the scintillation cell for at least 4 hours to ensure equilibrium between radon and radon daughters. Count the alpha scintillations from the cell in a radon counter with a light-tight enclosure that protects the photomultiplier tube. Record the counting time to correct for the decay of radon-222.

Note: After each analysis, flush the cell three times by evacuation and filling with helium, and store filled with helium at atmospheric pressure. This procedure removes radon from the cell and prevents the build-up of radon daughter products. Before each analysis, the scintillation cell should be evacuated, filled with helium and counted to ascertain the cell background.

9.0 Calculations

9.1 Calculate the radium-226 concentration, D, in picocuries per liter as follows:

$$D = \frac{C}{2.22\ EV} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{t_3}{1-e^{-\lambda t_3}}$$

where:

C = net count rate cpm

E = calibration constant for the de-emanation system and the scintillation cell in counts per minute / disintegrations per minute of radon-222, (see 9.2),

V = liters of sample used

t_1 = the elapsed time in days between the first and second de-emanations (steps 8.6 and 8.12) and λ is the decay constant of radon -222 (0.181 d^{-1})

t_2 = the time interval in hours between the second de-emanation and counting and λ is the decay constant of radon-222 (0.00755 hr^{-1})

t_3 = the counting time in minutes and λ is the decay constant of radon-222 (1.26 x 10^{-4} min^{-1})

2.22 = conversion factor from dpm / pCi.

9.2 The calibration constant, E, is determined by the following equation:

$$E = \frac{C}{A\ (1-e^{-\lambda t_1})\ (e^{-\lambda t_2})}$$

where:

C = net count rate, cpm

A = activity of radium-226 in the bubbler (dpm)

t_1 = ingrowth time of radon-222 in hours

t_2 = decay time of radon-222 in hours occurring between de-emanation and counting

λ = decay constant of radon-222, (0.00755 $hour^{-1}$).

10.0 Precision and Accuracy

A number of laboratories which participate in the EPA, EMSL-Las Vegas intercomparison program for radium-226 in water used this method in their analyses of water samples received in that program for the period 4/78 through 12/78. Five intercomparison studies for radium-226 in water were conducted during that period. Two of the five studies were "Performance Studies" in which the sample contained other radionuclides. In the other three studies the samples contained only radium-226, radium-228 and their decay products. The radium-226 concentrations in the test samples for the five studies ranged from 3.7 to 9.2 pCi/L, all low level, which should relate well to drinking water supplies. Data from those five studies were used for this precision and accuracy evaluation of the method.

10.1 The number of laboratories that participated in the five studies (labs that were called and indicated that they used this method) ranged from 12 to 17 laboratories per study. The results from one laboratory in one study was rejected as an "outlier" as determined by the T test (ASTM Standards, Part 31, page 15, 1978). All laboratories reported triplicate analyses for each study (one test sample per study). The total number of analyses for the five studies was 207 of which 174 were acceptable results (within 3 sigma of the known value, 1 sigma being 15% of the known value). This calculates to be 84% acceptability of results as determined by this method.

10.2 A statistical evaluation of the data, from the five studies was made according to the methods of Youden[4] and Steiner[5]. The coefficient of variation for within-laboratory error ranged from 6.4% to 19% with an average of 10.2% for the five studies. The coefficient of variation for systematic error between laboratories ranged from 14% to 18% with an average of 16.2% for the five studies. The coefficient of variation for the total error between laboratories based on a single analysis ranged from 16% to 26% with
an average of 19.4% for the five studies. A comparison of the grand average values with the known values in a test for systematic error in a method gave a value for one of the studies higher than the critical value, indicating a bias (low) for the method. However, values for the other four studies were well below the critical values, indicating no bias for the method.

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