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Environmental Monitoring Series

MEASUREMENT OF TOTAL RADIUM AND RADIUM-226 IN ENVIRONMENTAL WATERS

A Tentative Reference Method

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Las Vegas, Nevada 89114

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by

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Effective June 29, 1975, the National Environmental Research Center-Las Vegas (NERC-LV) was designated the Environmental Monitoring and Support Laboratory-Las Vegas (EMSL-LV). This Laboratory is one of three Environmental Monitoring and Support Laboratories of the Office of Monitoring and Technical Support in the U.S. Environmental Protection Agency's Office of Research and Development.

CONTENTS

	Page
1. Principles and Applicability	1
2. Range and Sensitivity	2
3. Interferences	2
4. Precision and Accuracy	3
5. Apparatus	4
6. Reagents	4
7. Procedure	9
8. Calibration	24
9. Calculations and Reporting	24
References	26
APPENDIX A. Factors for Decay of Radon-222, Growth of Radon-222 from Radium-226, and Correction of Radon-222 Activity for Decay During Counting	27
APPENDIX B. Error and Statistical Calculations	30

FIGURES

1. Apparatus for Radon Transfer	5
2. Emanation Tube (Bubbler)	6
3. Lucas Scintillation Cell	7

TENTATIVE REFERENCE METHOD FOR THE MEASUREMENT OF TOTAL RADIUM AND RADIUM-226 IN ENVIRONMENTAL WATERS

1. Principles and Applicability

1.1 Total radium in water is concentrated and separated from sample solids by coprecipitation with barium and/or lead sulfate. The precipitate is purified by washing with nitric acid, dissolving in alkaline EDTA, and reprecipitating as radium-barium sulfate after adjusting the pH to 4.5. This slightly acidic EDTA keeps other naturally occurring alpha emitters and the lead carrier in solution. The precipitate is transferred to a counting dish, dried, weighed to determine chemical yield, and alpha-counted to determine the total disintegration rate of radium isotopes.

For radium-226, the barium-radium sulfates are solubilized, the radon-222 daughter allowed to grow in, then radon-222 is de-emanated from the ingrowth bubbler chamber to a counting cell. The radon-222 is counted for radium-226 determination.

1.2 This method is applicable for measuring radium in environmental waters. It is also applicable to sewage and industrial wastes, provided steps are taken to destroy organic matter and eliminate other interfering ions. The method may be used for absolute measurements by calibrating with a suitable alpha emitter or for relative methods by comparing measurements with each other.

2. Range and Sensitivity

2.1 The minimum limit of concentration to which this method is applicable will depend on sample size, counter characteristics, background and counting time. It is recommended that samples be counted long enough so that samples with activities as low as the detection limit of the method and counting instrument used, will have a counting error (± cpm) of no more than the sample net count rate (when counting error cpm equals sample net cpm, the counting error is 100 percent). For instance, when a 1-liter water sample is analyzed for total radium by this method and is counted for 50 minutes in an alpha scintillation detection system having a background of 0.005 cpm, a counting efficiency of 45 percent, and gives a gross count rate of 0.09 cpm, the sample will have a net count rate of 0.085 cpm and a counting error of ± 0.085 cpm at the 95 percent confidence level. This corresponds to a detection limit of 0.09 ± 0.09 pCi/liter. Also, when a 1-liter water sample is analyzed by this method for radium-226 by radon-222 count in a gas scintillation detector with a background count rate of 0.13 cpm, a counting time of 30 minutes, a counting efficiency of 76 percent, and a gross count rate of 0.39 cpm, the sample will have a net count rate of 0.26 cpm and a counting error of ± 0.26 cpm at the 95 percent confidence level. This corresponds to a detection limit of 0.15 ± 0.15 pCi/liter. Samples having concentrations above the detection limit and counted for the time indicated above will have correspondingly lower counting errors. Since radium is separated from the sample, the detection limit can be improved by analyzing larger samples.

3. Interferences

3.1 If barium is present in the sample it will cause an error in the barium sulfate yield determination. The error will be proportional to the amount of barium present.

3.2 The gaseous alpha-emitting radionuclides, radon-219 and -220 (through the alpha-emitting decay products), can interfere with the test, but can be corrected for if known to be present. Interferences from these radionuclides would be rare in water not contaminated by industrial wastes from some type of uranium operation.

4. Precision and Accuracy

Water samples of 1-liter size containing as little as 1 pCi of radium (as radium-226) can be analyzed for total radium by this method with a precision of less than ± 25% at the 95 percent confidence level, when precipitated samples are counted in an alpha scintillation detection system with a background of 0.12 cpm (blank sample), and counted for 60 minutes at a counting efficiency of 45 percent. Liter size samples containing as little as 5 pCi of radium (as radium-226) can be analyzed with a precision of less than ± 20 percent at the 95 percent confidence level (same counting time, background, and counting efficiency as indicated above).

Water samples of 1-liter size containing as little as 1 pCi of radium-226 can be analyzed for radium-226 by radon-222 gas-alpha scintillation counting by this method with a precision of less than ± 35 percent at the 95 percent confidence level, when counted for 30 minutes at 76 percent counting efficiency. Liter size samples containing as little as 5 pCi can be analyzed with a precision of less than ± 10 percent at the 95 percent confidence level (at 30-minute counting time and 76 percent counting efficiency).

The overall accuracy is a combination of the accuracy of the standard used (data furnished by the supplier) and the precision and accuracy of the method of measurement. Analytical results, using the "Total Radium by Precipitation" portion of this method, of spiked water samples prepared with as little as 1 pCi/liter of radium-226, should show an accuracy with a deviation from the known of less than ± 10 percent, at the 95 percent confidence level. Analytical results, using

the "Radium-226 by Radon-222 De-emanation" portion of this method, of spiked water samples prepared with as little as 1 pCi/liter of radium-226, should show an accuracy with a deviation from the known of less than ± 15 percent at the 95 percent confidence level.

5. Apparatus

Counting Systems

For radium-226 by radon-222 emanation: an alpha scintillation counting system that will accommodate gas counting cells

For total precipitated radium: an alpha scintillation counting system or a thin window proportional counting system

Filter holder for, and 0.45 micrometer pore size membrane filters (47-mm diameter, cellulose triacetate type)

Filter flask, 2-liter

Suction pump

Four-liter (or one-gallon) polyethylene bottles and labels

Gas de-emanation apparatus (see Figures 1 and 2)

Scintillator-type gas counting cells (see Figure 3)

A cylinder of helium gas provided with a 2-stage regulator and a needle valve

Vacuum pump

Two-liter beakers and 50-ml centrifuge tube

Centrifuge

Platinumware: 50-75 ml crucibles, 500-ml dish, and platinum-tipped tongs

6. Reagents. It is implied in this "guideline" that all reagents are of "reagent-grade" purity whenever such reagents are commercially available.*

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* Reagent Chemicals, "American Chemical Society Specifications," American Chemical Society, Washington, DC. For reagents not listed by the ACS see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, or the "United States Pharmacopeia" for purity tests.

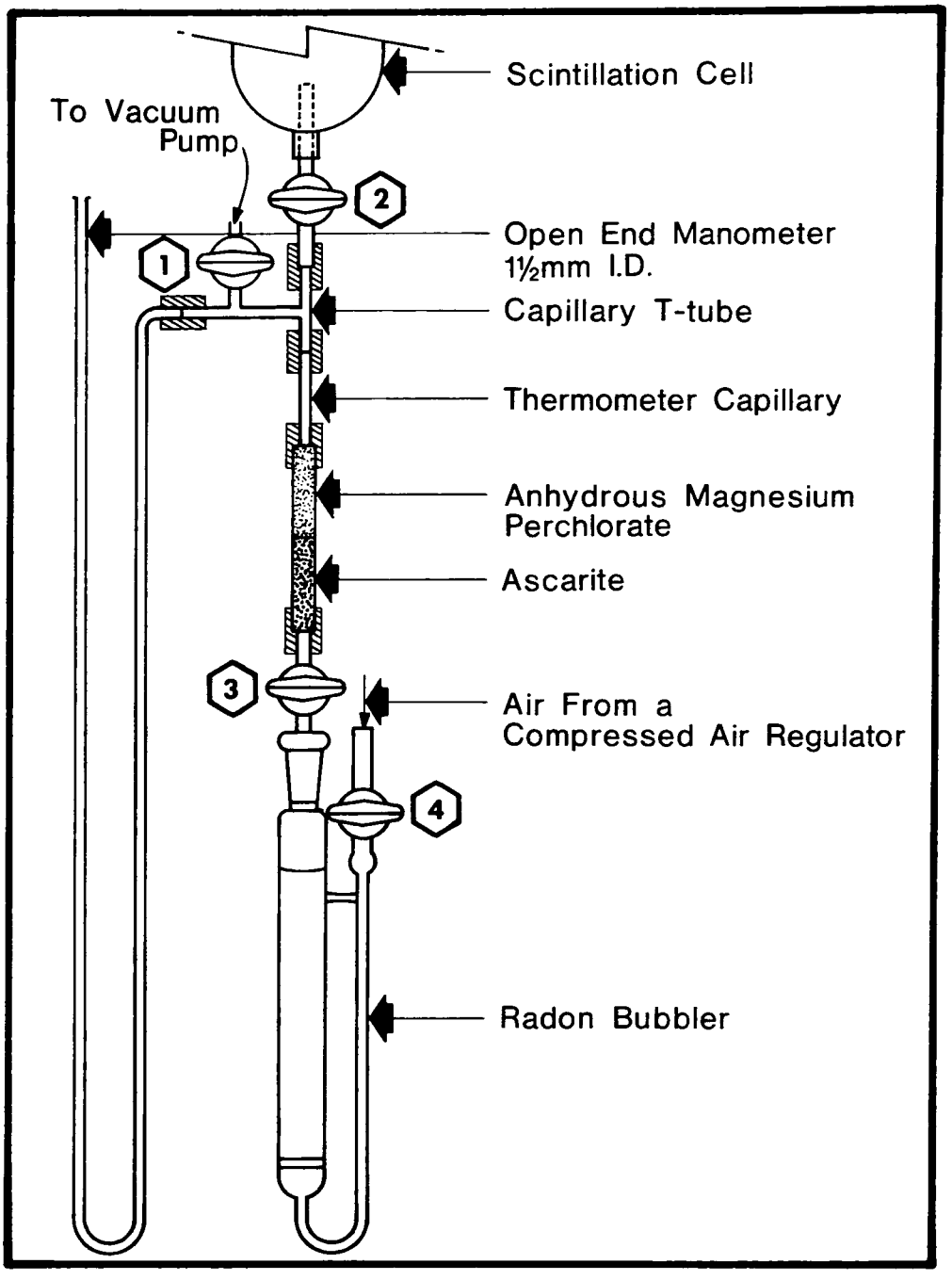


Figure 1. Apparatus for Radon Transfer

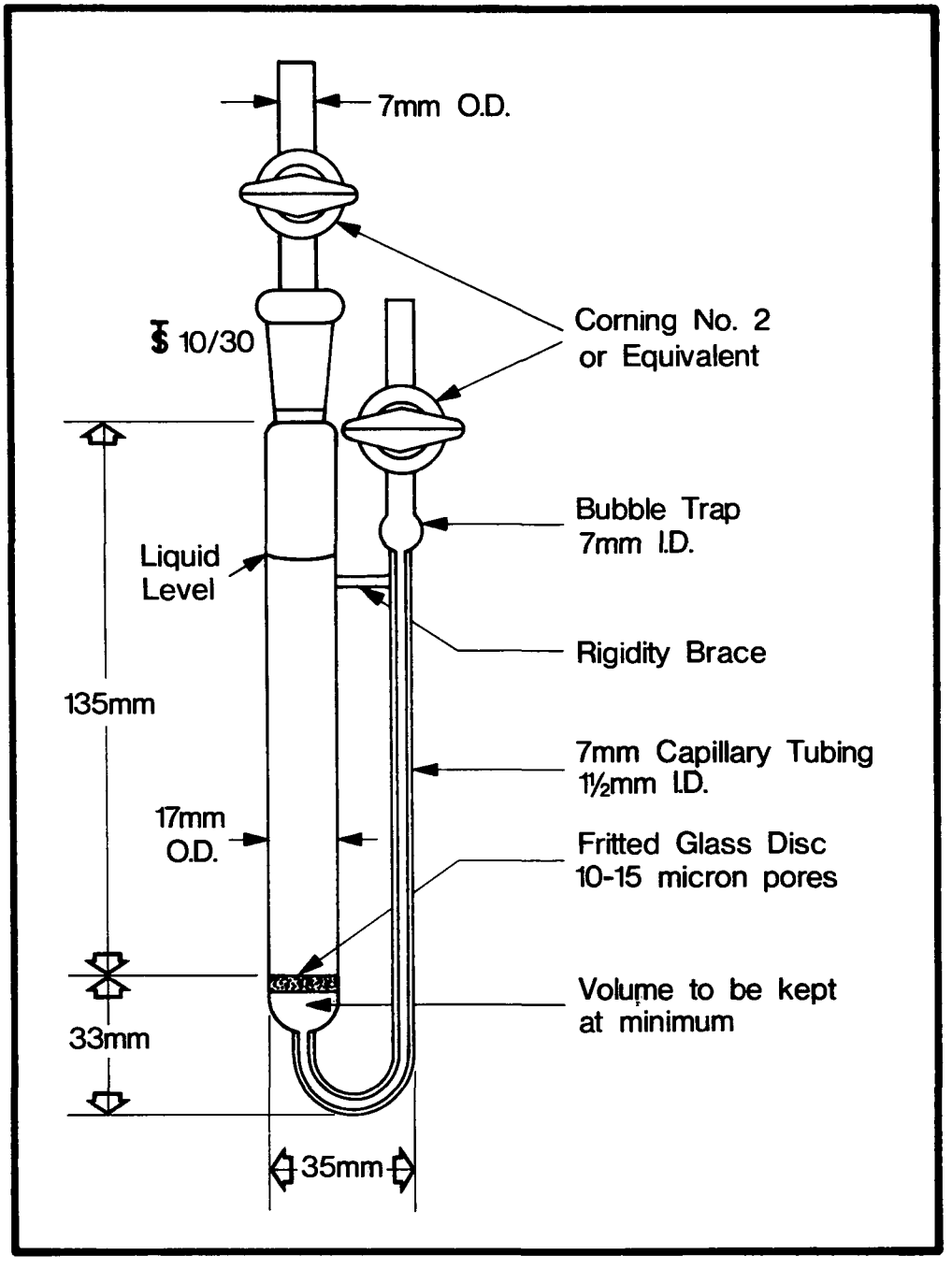
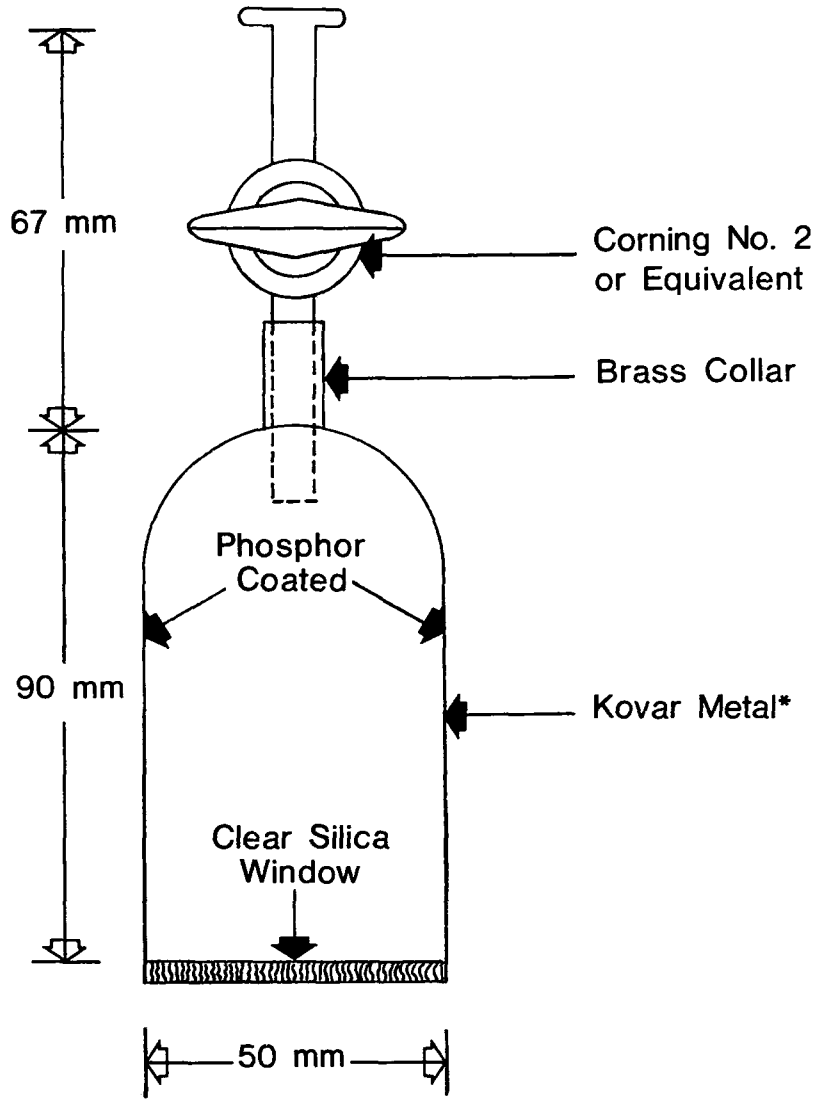


Figure 2. Emanation Tube (Bubbler)



* Cell can be made from 2-inch OD aluminum tubing by 3½-inch long, to which one end is epoxy-cemented a 2-inch diameter by 1/8-inch thick aluminum disc with aluminum or brass collar. Stopcock and quartz window can also be cemented in place by epoxy cement.

Figure 3. Lucas Scintillation Cell

Ammonium hydroxide, concentrated

Citric acid, 1M, dissolve and dilute 210 g of $H_3C_6H_5O_7 \cdot H_2O$ with distilled water to 1 liter

Barium carrier solution: dissolve and dilute 3.555 g of $BaCl_2 \cdot 2H_2O$ plus a few drops of concentrated HCl with distilled water to 1 liter (1 ml equals 2 mg Ba)

Barium chloride solution: dissolve and dilute 17.79 g of $BaCl_2 \cdot 2H_2O$ plus a few drops of concentrated HCl with distilled water to 1 liter (1 ml equals 10 mg Ba)

Lead carrier solution: dissolve and dilute 160 g of $Pb(NO_3)_2$ plus a few drops of concentrated HNO_3 with distilled water to 1 liter (1 ml equals 100 mg Pb)

Methyl orange indicator solution: dissolve and dilute 0.05 g of methyl orange with distilled water to 100 ml

Phenolphthalein indicator solution: dissolve 0.5 g of phenolphthalein in 50 ml ethanol and dilute with 50 ml of distilled water

Bromcresol green indicator: dissolve and dilute 0.1 g bromcresol green sodium salt with distilled water to 100 ml

EDTA solution; dissolve and dilute 93 g of disodium ethylenediaminetetraacetate dihydrate with distilled water to 1 liter

Acetic acid, concentrated (glacial)

Nitric acid, concentrated

Sulfuric acid, 18N, and 0.1N

Hydrochloric acid, concentrated, 6N, 1N, and 0.1N

Phosphoric acid, 85%

Ammonium sulfate solution: dissolve and dilute 10 g of ammonium sulfate with distilled water to 100 ml

Ascarite, 20 mesh (drying agent)

Hydrogen peroxide, 30%

Anhydrous magnesium perchlorate

Sample preservative solution, 6N hydrochloric acid containing 24 mg barium carrier per 150 ml

Radium-226 solutions:

Solution A: Obtain a National Bureau of Standards radium-226 standard, 0.1 μg radium-226 in solution (glass ampul). Prepare a barium-HCl diluting solution containing 7.116 g of $BaCl_2 \cdot 2H_2O$ and 40 ml of concentrated HCl diluted to 2 liters in a volumetric flask (1 ml = 2 mg Ba). Place the radium standard, glass ampul, in a 400-ml beaker containing 200 ml of the barium-HCl diluting solution. Break the ampul with a glass rod, stir to mix, then very carefully transfer the solution to a weighed 1-liter volumetric flask through a funnel provided with a glass wool mat to collect the broken ampul pieces. Rinse the beaker three times with 200-ml portions of the barium-HCl diluting solution and add the washes to the 1-liter volumetric flask. Dilute to the 1-liter mark with the diluting solution. Stopper and mix thoroughly. Weigh the flask plus contents. Solution concentration then is:

$$\text{pCi/g} = \frac{\text{pg of radium-226} \times 0.990 \text{ pCi/pg}}{\text{g of Solution A}}$$

(approximately 100 pCi/g and 2 mg Ba/g)

Solution B: Transfer and accurately weigh approximately 3 g of Solution A into a weighed 100-ml volumetric flask. Dilute to the mark with the barium-HCl diluting solution, stopper, and mix thoroughly. Weigh the flask plus contents. Solution concentration is:

$$\text{pCi/g} = \frac{\text{g of Solution A} \times \text{pCi/g of Solution A}}{\text{g of Solution B}}$$

(approximately 3 pCi/g and 2 mg Ba/g)

7. Procedure

7.1 Sampling

Sampling may be accomplished as described in "Environmental Radioactivity Surveillance Guide," published by the U.S. Environmental Protection Agency as report ORP/SID 72-2. It is recommended that samples be preserved at the time of collection by the addition of 150 ml of

6N hydrochloric acid containing 24 mg of barium carrier (from standard barium carrier solution) per 4 liters (or 1 gallon) of sample collected. Care should be taken in adding the acid-carrier solution to samples in the field because the barium carrier is to be accounted for (recovery to be determined) in the sample analysis. However, if determination is to be made of the radium content in the separate dissolved and suspended fractions of the sample, then those fractions must be separated before the preservative is added, since the preservative may change the distribution of the sample radioactivity. Rather than separating the dissolved and suspended solids fractions of samples in the field, samples can be brought to the laboratory without preservative added. Separation is then done by filtering out the suspended solids on a tared 0.45-micrometer membrane filter. The filter is dried, weighed, and set aside for further analysis. The preservative solution is then added to the filtrate which is then returned to the original sample container and held there for overnight or longer before analysis is begun.

7.2 Analysis for Radium-226 by Radon-222 De-emanation

7.2.1 Calibration of Gas Scintillation Counting Cells

7.2.1.1 Determine the background of each scintillation counting cell before using to count standards or samples. In the apparatus shown in Figure 1, substitute a glass tube adapter provided with stopcocks for a bubbler in the apparatus. Evacuate the counting cell and the apparatus and check for leaks, especially the counting cell, by closing the vacuum source stopcock and observing the manometer reading. If there is no change in the manometer reading after 5 minutes the cell and system can be considered leak-free. With the system and the cell evacuated, open the stopcock to the carrier-counting gas supply and fill the cell and system just to atmospheric pressure. Remove the cell from the apparatus and place it on the phototube in the counting system. Cover the cell and phototube with a light-tight cover and

after a 15 minute dark-adapting period, count the cell activity for at least 30 minutes. (The cover should be provided with a high voltage interlock switch so that there is never high voltage on the phototube when it is exposed to room light. Exposure to room light when high voltage is applied will destroy the phototube.)

7.2.1.2 Before adding standard radium-226 to the bubbler, test the bubbler for flaws in the frit that will cause unwanted larger bubbles (larger bubbles reduce the de-emanation efficiency). Add about 10 ml of distilled water and 5-10 drops of isopropyl alcohol to the bubbler and apply about 5-10 psi of helium gas pressure to the gas inlet of the bubbler. Observe the bubble action. Satisfactory bubble size is evidenced by a milky appearance in the bubbler solution. Reject bubblers that do not show a milky appearance under the conditions of this test (be sure both bubbler stopcocks are open). Remove the test water from the bubbler.

7.2.1.3 Clean and lubricate bubbler stopcocks with silicone grease, and close the gas inlet stopcock. Thoroughly degrease the standard taper joint of each bubbler. Clamp each bubbler to a ring stand or lattice.

7.2.1.4 Accurately transfer 10.0 ml of the radium-226 Solution B (3 pCi/ml) to each of three bubblers (triplicate analyses). Add 0.1N HCl to fill bubblers to about two-thirds full. Add 5-10 drops of isopropyl alcohol to each bubbler.

7.2.1.5 Dry the standard taper joint with lint-free cloth or paper. Heat both parts of the joint with a hot air stream or carefully with a blue gas-air flame from a bunsen burner. Apply sealing wax sparingly to the male part of the joint and join the two parts with a twisting motion to make a complete seal.

7.2.1.6 Attach the gas inlet of the bubbler to the helium gas cylinder outlet with Tygon tubing, adjust the outlet pressure to 5-10 psi, open the bubbler outlet stopcock, open the bubbler inlet stopcock, and purge the standard radium-226 sample for 20 minutes. Note the time at the end of the purge as the beginning of the radon-222 ingrowth period. Isolate the bubbler chamber by closing both bubbler stopcocks. Store the closed bubblers for a measured ingrowth period (for this standard amount of radium-226 a 24-hour period is sufficient time, but be sure to record the ingrowth period). See Appendix A for the decay, ingrowth and decay during counting factors for radon-222. Since the radon is ingrowing during the de-emanation period, the end of the de-emanation period should be noted as the end of the ingrowth period.

7.2.1.7 Place the bubbler in the de-emanation system (Figure 1) with a clean counting cell whose background count has been measured. Evacuate the system, including the cell, but only up to the outlet of the bubbler (inlet and outlet stopcocks of the bubbler should still be closed).

7.2.1.8 Check the cell and the system for leaks by closing the stopcock to the vacuum source and observing the manometer. No change in the manometer reading for 5 minutes is sufficient indication for no leaks.

7.2.1.9 Then with the vacuum stopcock still closed, the de-emanation of the radon gas to the cell can be started. Open the bubbler outlet stopcock and allow a minute or so for the system pressure to equilibriate. Adjust the carrier gas outlet pressure to 5 psi at the diaphragm valve. Open the bubbler inlet stopcock and the carrier gas needle valve and allow gas to flow at a rate that produces a froth a few mm thick until the system pressure just reaches atmospheric pressure. Then close the counting cell stopcock and the carrier gas needle valve.

Close the bubbler stopcocks and remove the bubbler from the system. Store the bubbler for future radium-226 (radon-222) calibrations of the counting cells.

7.2.1.10 Remove the counting cell from the de-emanation system and after 4 hours of equilibrating time (radon-222 with its daughters) place the counting cell in the phototube counting system. Close the counting chamber (to be light-tight), wait 15 minutes, and then start the count. Count for the length of time needed to give the desired reliability (see Section 2.1 and Appendix B).

7.2.1.11 Calculate the counting cell counting efficiency using the ingrowth time (hours), the decay time (between de-emanation and start of count), and the decay during counting. See Appendix A for these factors.

Calculations:

$$E = \frac{R_{STD} - R_b}{\text{pCi of radium-226}} \times \frac{C}{AB}$$

where E = counting efficiency, counts per hour/pCi of radium-226

R_{STD} = counts per hour from the radium-226 standard

R_b = counts per hour background of the cell

A = factor for decay of radon-222, see Appendix A

B = factor for the ingrowth of radon-222 from radium-226, see Appendix A

C = factor for the decay of radon-222 during counting, see Appendix A

The error associated with the results of the analysis should also be reported. See Appendix B for error and statistical calculations.

7.2.1.12 To clean the counting cells for reuse, evacuate with a 10-minute pumping period, then refill with carrier counting gas (helium preferred). Repeat the evacuation and refill steps at least twice (more times are necessary if cell has contained high radon-222 activity).

7.2.1.13 Repeat steps 8-13 for each counting cell. Number each counting cell and record its counting efficiency.

7.2.2 Water-soluble Radium-226

7.2.2.1 The insoluble or suspended radium-226 fraction should have been removed by filtration before the HCl-barium carrier preservative has been added to the sample (see Section 7.1). The insoluble or suspended fraction can be analyzed by the method described in the next section (7.2.3).

7.2.2.2 To 800-ml or 1000-ml fractions (3) of the sample add 20 ml of concentrated HCl and 40 ml of barium chloride solution (10 mg Ba/ml) in a 1- or 2-liter beaker.

7.2.2.3 With each series of samples set up a reagent blank with distilled water and all of the reagents used with the sample, including those added at the time of collection.

7.2.2.4 To each sample and blank, with vigorous stirring, add (cautiously) 20 ml of concentrated H_2SO_4. Cover each beaker and allow the sulfate precipitate to settle overnight.

7.2.2.5 Filter the barium-radium sulfate precipitate onto a membrane filter using dilute H_2SO_4 solution (0.1N) to make the transfer and wash.

7.2.2.6 Transfer the filter to a platinum dish, add 0.5 ml of concentrated HF and 0.2 ml of the ammonium sulfate solution (10%), and evaporate to dryness.

7.2.2.7 Burn off the membrane filter in a 600° C muffle furnace or carefully over a Meker burner.

7.2.2.8 Wet the sulfate precipitate with only 1 ml of 85% H_3PO_4, heat the platinum dish on a hot plate at 200° C, slowly increasing the heat to about 400° C, maintaining that temperature for about 30 minutes.

7.2.2.9 Continue heating the dish over a Meker burner at just below red heat, swirling to coat the dish walls with the hot melt to insure the complete removal of SO_3.

7.2.2.10 Cool the platinum dish and add 6N HCl to about one half the dish volume. Heat on a steam bath for ten minutes, then dilute with distilled water to a few mm from the top of the dish. Evaporate the solution to just a few ml on the steam bath.

7.2.2.11 Add 5 ml of 1N HCl and 5 ml of distilled water, warm and swirl carefully to dissolve the $BaCl_2$. Sample is now ready to transfer to a de-emanation bubbler.

7.2.2.12 Close the gas inlet stopcock of a prepared bubbler (see calibration section for preparation), wet the frit in the bubbler with 2-3 drops of distilled water and quantitatively transfer the sample from the dish to the bubbler using a transfer pipette. Rinse the dish with 3-4 portions of distilled water, adding the rinses to the bubbler until it is about three-fourths full.

7.2.2.13 Apply silicone stopcock grease to the bubbler joint and close the bubbler. Purge the sample solution with helium gas for 20 minutes (see the calibration section, 7.2.1.7). Record the date and time as the beginning of the ingrowth period. Store the sample bubbler for radon-222 ingrowth, for 3 weeks for low radium-226 concentrations.

7.2.2.14 Place the sample bubbler in the de-emanation system (Figure 1) with a clean counting cell whose background count and counting efficiency have been measured and de-emanate the radon-222 from the sample solution to the counting cell and count as described in the calibration section (7.2.1), steps 8-11.

7.2.2.15 Calculate the radium-226 in the sample and in the reagent blank and subtract the reagent blank value from the sample. See Section 9, Calculations and Reporting, step 2.

7.2.2.16 The sample may be stored for a second ingrowth or may be discarded (so also the reagent blank). When sample and reagent blank solutions are discarded, the bubblers should be carefully cleaned for further use. If the sample (or reagent blank) just discarded contained no more than 10 pCi/l of radium-226, the bubbler may be cleaned by rinsing with 200 ml of 0.1N HCl. To insure a complete rinse of the bubbler invert the bubbler, attach a tube from the inlet to a beaker containing the rinse solution, attach another tube from the outlet to a suction flask, and by alternately opening and closing the outlet and inlet stopcocks successively fill the bubbler with the rinse solution and draw the rinse to the suction flask. Bubblers that have held samples containing more than 10 pCi/liter should be cleaned as follows: discard the sample solution; rinse the bubbler with distilled water; fill with a solution of 10 g of disodium ethylenediaminetetraacetate dihydrate (EDTA) plus 10 g of sodium carbonate per liter; place the bubbler in a hot water bath and heat for 1 hour; discard the cleaning solution; and rinse the bubbler with distilled water,

0.1N HCl, and again with distilled water by the technique described above. Degrease the stopcocks and the joint fittings of the bubbler with benzene or toluene and regrease for reuse.

7.2.3 Water Insoluble (Suspended) Radium-226

7.2.3.1 In the analysis of suspended matter for radium-226, organic and siliceous materials must be eliminated without loss of radium-226 and this is accomplished in the following steps.

7.2.3.2 Prepare an alkaline flux mixture as follows: to a 500-ml platinum dish (if only a smaller size dish is available reduce the following amounts proportionately) add 30 mg barium sulfate, 65.8 g potassium carbonate, 50.5 g sodium carbonate, and 33.7 g sodium tetraborate decahydrate. Mix the contents thoroughly, then heat cautiously to expel water of hydration. Then fuse the mixture by heating over a Meker burner, carefully swirling to mix the melt. Cool and grind the fused material in a porcelain mortar to pass through a 12-mesh screen. Store the flux in an airtight bottle.

7.2.3.3 Place a membrane filter, on which a sample of suspended matter has been collected, in a tared platinum crucible or dish. Carefully ignite the filter and residue over a small flame until carbon is burned off. Cool and weigh the dish to determine the weight of the residue.

7.2.3.4 Add alkaline flux to the platinum dish, 8 g of flux for each gram of residue but not less than 2 g of flux. Mix the flux and residue with a glass stirring rod. Run a reagent blank for radium-226 determination starting with a blank membrane filter and all subsequent reagents as is used for the sample.

7.2.3.5 Heat the dish over a Meker burner (carefully to avoid spattering) until melting begins. Continue heating after bubbling stops for 20 minutes more, carefully swirling occasionally to achieve a uniform melt. Remove the dish from the burner and rotate as the melt cools to form a thin layer on the dish wall and bottom.

7.2.3.6 Place the cooled dish in a beaker containing sufficient distilled water to fill and cover the dish. Add to the beaker (cautiously) 20 ml of concentrated H_2SO_4 and 5 ml of diluted H_2O_2 (30% to 3%) proportionately for each 8 g of flux used (increasing or reducing the H_2SO_4 and H_2O_2 accordingly). Cover the beaker and swirl it occasionally to aid in dissolution of the fused residue. Rinse the dish with distilled water into the beaker.

7.2.3.7 Heat the solution on a hot plate to near boiling and add slowly, with stirring, 10 ml of the 10-mg Ba/ml barium chloride solution. Cover the beaker and let stand overnight for precipitation.

7.2.3.8 Continue the analysis as described above for soluble radium-226, Section 7.2.2, steps 5-16. In the calculation account for the volume of the water sample represented by suspended solids fraction used in the analysis and report in pCi/liter.

7.2.3.9 The total sample radium-226 content is, of course, the sum of the soluble and insoluble fractions and should be normalized to a 1-liter quantity of sample and reported in pCi/liter.

7.2.4 Combined Soluble and Insoluble (Suspended) Radium-226

7.2.4.1 Mix the sample thoroughly by vigorous shaking and immediately take three 1-liter aliquots and put in separate 2-liter beakers. Add 20 ml of concentrated HCl and 10 ml of 10 mg Ba/ml barium

chloride solution to each beaker. Stir the mixture thoroughly. Proceed with the analysis in step 3 below.

7.2.4.2 Prepare a reagent blank using one liter of distilled water and all of the reagents used with the sample. Analyze the reagent blank the same as with a sample.

7.2.4.3 Slowly and with vigorous stirring add 20 ml of concentrated H_2SO_4 to each sample and reagent blank beaker. Cover the beakers and let stand overnight for precipitation of the barium-radium sulfate.

7.2.4.4 Filter the barium-radium sulfate precipitate onto a membrane filter completing the transfer of the precipitate with 0.1N H_2SO_4 solution.

7.2.4.5 Continue the analysis as described for Insoluble Radium-226, Section 7.2.3, steps 3-8. Omit the addition of barium carrier in step 7 (since sufficient carrier is already in these samples), digest the solution on a hot plate for 1 hour and then immediately filter, collecting the barium-radium sulfate again on a membrane filter. After step 7 of 7.2.3 continue the analysis as described for Soluble Radium-226, Section 7.2.2, steps 5-16.

7.3 Analysis - Total Radium by Precipitation - a screening analysis for potable water and filtered raw water.

7.3.1 Calibration - determination of a combined counting efficiency, self-absorption factor.

7.3.1.1 Prepare three standard radium-226 samples and two reagent blanks as follows: to separate 1500- or 2000-ml beakers add 1 liter of distilled water; add 3.0 ml of the barium carrier solution (2 mg Ba/ml) to each reagent blank beaker; add 0.25 ml of the standard

radium-226 solution, 100 pCi/ml (Solution A), using a 250-µl pipette; and 2.75 ml of the barium carrier solution (2 mg Ba/ml) to each standard sample beaker (the barium and radium-226 additions can be done more accurately by aliquoting from a weighed polyethylene doll bottle containing the respective solutions (1), a recovery determination is to be made on the added barium carrier, therefore accuracy of barium addition is important).

7.3.1.2 To each beaker add 5 ml of 1M citric acid, 2.5 ml of concentrated NH_4OH, and 2 ml of the lead carrier solution (100 mg Pb/ml). Heat the solutions to boiling and add 10 drops of methyl orange indicator. Stir to mix.

7.3.1.3 While stirring the solution, slowly add 18N H_2SO_4 to obtain a permanent pink color, then add 0.25 ml excess of the 18N H_2SO_4. Boil the solution gently for 5 to 10 minutes then set aside for 3-4 hours allowing the precipitate to settle.

7.3.1.4 Draw off or decant and discard the clear supernate. Transfer the precipitate to a 50-ml centrifuge tube, centrifuge at 2000 rpm for ten minutes and discard the supernate.

7.3.1.5 Rinse down the wall of the centrifuge tube and wash the precipitate three times with 10-ml portions of concentrated HNO_3, stirring the precipitate each time with a glass rod, centrifuging at 2000 rpm for ten minutes, and discarding the wash HNO_3. (Ultrasonic agitation of centrifuged precipitates is an excellent way of stirring up precipitates for washing action without having to transfer a stirring rod to and from the centrifuge tube, resulting in some chance of losing sample material).

7.3.1.6 To each centrifuge tube add 10 ml of distilled water and 2 drops of phenolphthalein indicator solution. Stir up the sulfate precipitate and add 5N NH_4OH, while stirring, until the solution shows a definite red color.

7.3.1.7 Add 10 ml of EDTA reagent solution and 3 ml of 5N NH_4OH (fresh solution) to each tube. Heat the tubes in a boiling water or steam bath for 10 minutes with frequent stirring to dissolve the sulfate precipitate. If the precipitate does not completely dissolve in 10 minutes, add 1 ml more of 5N NH_4OH and continue heating with frequent stirring for 5-10 minutes more. Excessive heating will drive off ammonia and some sulfate may reprecipitate.

7.3.1.8 In the next step, barium-radium sulfate will be selectively precipitated out of solution while the Pb-sulfate carrier is held in solution. This step is very pH dependent, therefore a pH adjusted color reference should be prepared by which to adjust the pH of the samples and reagent blanks. To a clean 100-ml beaker add 10 ml of distilled water, 2 drops of phenolphthalein solution, 10 ml of the EDTA solution, and 4 ml of 5N NH_4OH. Stir the solution and add glacial acetic acid, dropwise, until the alkaline red color disappears. Add 3 drops of bromcresol green indicator solution, stir the solution with a magnetic stirring bar, mount pH electrodes to dip into the solution and add glacial acetic acid dropwise until pH is at 4.5. Transfer this adjusted solution to a clean centrifuge tube.

7.3.1.9 Now add glacial acetic acid to the sample and reagent blank centrifuge tubes, dropwise, and with stirring until the alkaline red color disappears. Add 3 drops of bromcresol green indicator solution to each tube and add glacial acetic acid, dropwise, and with generous stirring between drops to a color adjustment to the reference color (aqua green). With this pH adjustment barium-radium sulfate will precipitate. Note the time and date of this precipitation as zero time for ingrowth of alpha activity.

7.3.1.10 Heat the centrifuge tubes (containing the precipitating mixture) in a hot water bath for 5-10 minutes, cool, and centrifuge at 2000 rpm for ten minutes. Decant and discard the supernate. Wash the precipitate three times with 10-ml portions of distilled water, centrifuging at 2000 rpm for ten minutes and discarding the supernate.

7.3.1.11 Weigh a membrane filter, a counting dish, and an o-ring that fits snugly in the counting dish (o-ring will serve to mount the filter flat in the counting dish).

7.3.1.12 Suspend the precipitate in about 20 ml of distilled water and quantitatively transfer the precipitate to the filter. Transfer the filter to the counting dish and place the o-ring on the filter. Place the dish in a drying oven and dry for one hour at 110° C. Cool and weigh the counting dish.

7.3.1.13 Count the standard sample and reagent blank filters in a thin window proportional counting system or in a phototube counting system after removing the o-ring, placing a ZnS phosphor mylar film over the filter (phosphor side facing the filter), and replacing the o-ring. The phototube counting system has a higher counting efficiency and is therefore the preferred system.

7.3.1.14 Determine the chemical yield of the barium carrier for the standard samples and reagent blanks. Subtract instrument background count from standard samples and reagent blanks. Normalize the net cpm for the reagent blanks to 100% yield and average the normalized counts. Normalize the standard samples net cpm to 100% yield and from those normalized cpm values subtract the average normalized reagent blank cpm. From these corrected net cpm values calculate the combined factor for counting efficiency and sample self-absorption.

$$f = \frac{\text{net cpm}}{2.22 \times \text{pCi radium-226 added}}$$

where f is the combined factor for counting efficiency and sample self-absorption.

7.3.2 Potable Water and Filtered Raw Water Samples.

7.3.2.1 Samples that have been treated (at the time of collection) with barium-acid preservative whose volumes are not accurately known, should be measured for volume and the barium carrier concentration determined (from the known addition). Samples that have not been treated with barium-acid preservative at the time of collection should be measured for volume, treated with 20 ml of concentrated HCl and 3.0 ml of the barium carrier solution (2 mg Ba/ml) for each one liter of sample, and allowed to stand overnight before aliquots are taken for total radium analysis.

7.3.2.2 Place aliquots of samples containing 6.0 mg of barium carrier in 1500 or 2000-ml beakers. Also prepare and analyze at least one reagent blank using one liter of distilled water, 6.0 mg of barium carrier, 20 ml of concentrated HCl, and carry through each step of the analysis. Before proceeding with the following steps neutralize each sample and blank to the methyl orange end-point (red to orange) by adding dropwise, with stirring, concentrated NH_4OH (approximately 16 ml will be required).

7.3.2.3 Perform the analysis on all samples and reagent blanks as described above in the Calibration section (7.3.1) from step 2 through the corrected net cpm determination of step 14. Calculate the total radium, pCi/liter as described in the following Calculation section.

8. Calibration

See Section 7.3.1 for "Total Radium by Precipitation" and Section 7.2.1 for "Radium-226 by Radon-222 Determination."

9. Calculations and Reporting

9.1 Total Radium

$$\text{Total Ra, pCi/liter} = \frac{\text{corrected net cpm}}{afe \times 2.22}$$

where a = ingrowth factor (daughter products, see table below)

f = the combined counting efficiency, self-absorption factor for 6.0 mg of barium carrier, determined in the Calibration section (7.3.1.14)

e = the sample aliquot volume in liters

corrected net cpm = the sample cpm normalized to 100% barium carrier yield and corrected for instrument background and reagent blank cpm contribution

Radium-226 Alpha Activity Ingrowth

Ingrowth (Hours)	Alpha Activity Factor
0	1.00
1	1.02
2	1.04
3	1.06
4	1.08
5	1.10
6	1.12
7	1.14
8	1.16
9	1.18
10	1.20
24	1.49
48	1.90
72	2.25

Since the recommended limit for radium-226 in drinking water is 3 pCi/liter (Public Health Service Advisory Committee 1962 Drinking Water Standards), when a total radium value for a water sample is found to be 3 pCi/liter or greater, a radium-226 by radon-222 analysis should be made. A radium isotopic content can be estimated from a total radium analysis by successive counts of the precipitated radium at increasing ingrowth ages and solving a set of simultaneous equations (2,3,4).

9.2 For radium-226 by radon-222, determine the radium-226 for the sample by the following equation:

$$\text{Radium-226, pCi} = \frac{\frac{R_s - R_{b.1}}{E_1} \times \frac{C_1}{A_1 B_1} - \frac{R_r - R_{b.2}}{E_2} \frac{C_2}{A_2 B_2}}{V}$$

where R_s = observed counts per hour for the sample radon-222

R_r = observed counts per hour for reagent blank radon-222

R_b = observed counting cell background counts per hour ($R_{b.1}$ for sample, $R_{b.2}$ for reagent blank)

E = counting efficiency of the particular cell, counts per hour/pCi of radium-226 (E_1 for sample, E_2 for reageant blank)

V = volume of sample analyzed, in liters

A = factor for decay of radon-222, see Appendix A (A_1 for sample, A_2 for reagent blank)

B = factor for the ingrowth of radon-222 for radium-226, see Appendix A (B_1 for sample, B_2 for reagent blank)

C = factor for the decay of radon-222 during counting, see Appendix A (C_1 for sample, C_2 for reagent blank)

The error associated with the results of the analysis should also be reported. See Appendix B for error and statistical calculations.

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APPENDIX A

Factors for Decay of Radon-222, Growth of Radon-222 from Radium-226, and Correction of Radon-222 Activity for Decay During Counting

Time	Factor for Decay of Radon-222		Factor for Growth of Radon-222 from Radium-226		Factor for Correction of Radon-222 Activity for Decay during Counting
	$A=e^{-\lambda t}$		$B=1-e^{-\lambda t}$		$C=\lambda t/(1-e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours
0.0	1.0000		0.000 00		1.000
0.2	0.9985		0.001 51		1.001
0.4	0.9970		0.003 01		1.001
0.6	0.9955		0.004 52		1.002
0.8	0.9940		0.006 02		1.003
1	0.9925	0.8343	0.007 52	0.1657	1.004
2	0.9850	0.6960	0.014 99	0.3040	1.008
3	0.9776	0.5807	0.022 40	0.4193	1.011
4	0.9703	0.4844	0.029 75	0.5156	1.015
5	0.9630	0.4041	0.037 05	0.5959	1.019
6	0.9557	0.3372	0.044 29	0.6628	1.023
7	0.9485	0.2813	0.051 48	0.7187	1.027
8	0.9414	0.2347	0.058 61	0.7653	1.031
9	0.9343	0.1958	0.065 69	0.8042	1.034
10	0.9273	0.1633	0.072 72	0.8367	1.038
11	0.9203	0.1363	0.079 69	0.8637	1.042
12	0.1134	0.1137	0.086 62	0.8863	1.046
13	0.9065	0.0948	0.093 49	0.9052	1.050
14	0.8997	0.0791	0.100 31	0.9209	1.054
15	0.8929	0.0660	0.107 07	0.9340	1.058
16	0.8862	0.0551	0.1138	0.9449	1.062
17	0.8795	0.0459	0.1205	0.9541	1.066
18	0.8729	0.0383	0.1271	0.9617	1.069
19	0.8664	0.0320	0.1336	0.9680	1.073
20	0.8598	0.0267	0.1402	0.9733	1.077

Factors for Decay of Radon-222, Growth of Radon-222 from Radium-226, and Correction of Radon-222 Activity for Decay During Counting (continued)

Time	Factor for Decay of Radon-222		Factor for Growth of Radon-222 from Radium-226		Factor for Correction of Radon-222 Activity for Decay during Counting
	$A=e^{-\lambda t}$		$B=1-e^{-\lambda t}$		$C=\lambda t/(1-e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours
21	0.8534	0.0223	0.1466	0.9777	1.081
22	0.8470	0.0186	0.1530	0.9814	1.085
23	0.8406	0.0155	0.1594	0.9845	1.089
24	0.8343	0.0129	0.1657	0.9871	1.093
25	0.8280	0.0108	0.1720	0.9892	1.097
26	0.8218	0.0090	0.1782	0.9910	1.101
27	0.8156	0.0075	0.1844	0.9925	1.105
28	0.8095	0.0063	0.1905	0.9937	1.109
29	0.8034	0.0052	0.1966	0.9948	1.113
30	0.7973	0.0044	0.2027	0.9956	1.118
31	0.7913	0.0036	0.2087	0.9964	1.122
32	0.7854	0.0030	0.2146	0.9970	1.126
33	0.7795	0.0025	0.2205	0.9975	1.130
34	0.7736	0.0021	0.2264	0.9979	1.134
35	0.7678	0.0018	0.2322	0.9982	1.138
36	0.7620	0.0015	0.2380	0.9985	1.142
37	0.7563	0.0012	0.2437	0.9988	1.146
38	0.7506	0.0010	0.2494	0.9990	1.150
39	0.7449	0.0009	0.2551	0.9991	1.154
40	0.7393	0.0007	0.2607	0.9993	1.159
41	0.7338	0.0006	0.2662	0.9994	1.163
42	0.7283	0.0005	0.2717	0.9995	1.167
43	0.7228	0.0004	0.2772	0.9996	1.171
44	0.7173	0.0003	0.2827	0.9997	1.175
45	0.7120	0.0003	0.2880	0.9997	1.179

Factors for Decay of Radon-222, Growth of Radon-222 from Radium-226, and Correction of Radon-222 Activity for Decay During Counting (continued)

Time	Factor for Decay of Radon-222		Factor for Growth of Radon-222 from Radium-226		Factor for Correction of Radon-222 Activity for Decay during Counting
	$A=e^{-\lambda t}$		$B=1-e^{-\lambda t}$		$C=\lambda t/(1-e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours
46	0.7066	0.0002	0.2934	0.9998	1.184
47	0.7013	0.0002	0.2987	0.9998	1.188
48	0.6960	0.0002	0.3040	0.9998	1.192
49	0.6908	0.0001	0.3092	0.9999	1.196
50	0.6856	0.0001	0.3144	0.9999	1.201
51	0.6804	0.0001	0.3196	0.9999	1.205
52	0.6753	0.0001	0.3247	0.9999	1.209
53	0.6702	0.0001	0.3298	0.9999	1.213
54	0.6652	0.0001	0.3348	0.9999	1.218
55	0.6602	0.0000	0.3398	1.0000	1.222
56	0.6552	0.0000	0.3448	1.0000	1.226
57	0.6503	0.0000	0.3497	1.0000	1.231
58	0.6454	0.0000	0.3546	1.0000	1.235
59	0.6405	0.0000	0.3595	1.0000	1.239
60	0.6357	0.0000	0.3643	1.0000	1.244

APPENDIX B. ERROR AND STATISTICAL CALCULATIONS

Because of the random nature of radioactivity disintegrations there is an error associated with any measured count of these disintegrations. The variability of any measurement is indicated by the standard deviation. The standard deviation in the counting rate is determined by the following equation:

$$\sigma(R) = \left(\frac{R_o}{t_1} - \frac{B}{t_2}\right)^{\frac{1}{2}}$$

where R_o = gross count rate (sample plus reagent) (cph)
t_1 = counting time for the gross count (hours)
B = reagent blank count rate (cph)
t_2 = counting time for the reagent blank (hours)

The counting error for a given sample expressed in pCi/liter and at the 95% confidence level is shown by:

$$E = \frac{1.96\sigma(R)}{eV}$$

where 1.96 = 95% confidence factor
e = efficiency factor, cph/pCi
V = volume of the aliquot analyzed, in liters

The standard deviation associated with the overall random uncertainty may be estimated by performing replicate analyses on a given sample and is calculated from the following equation:

$$S_n = \left[\sum_{i=1}^{m} (n_i - \bar{n})^2/(m - 1)\right]^{\frac{1}{2}}$$

where n = activity (pCi/liter) of a given sample

$\bar{n}$ = mean activity (pCi/liter of a series of analyses

m = the number replicate analyses

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

A tentative reference method for the measurement of total radium and radium-226 in environmental water sources is described. Samples are collected, preserved with acid-barium carrier treatment, and analyzed for total radium and/or radium-226. For samples analyzed for total radium, the radium is separated from the sample with barium and lead carriers. The barium and radium are then separated from the lead carrier, precipitated as the sulfate, filtered, and counted for alpha activity. For samples analyzed for radium-226, the radium is separated from the sample with barium carrier, dissolved and transferred to a de-emanation bubbler, the radon-222 daughter allowed to grow in, the ingrown radon-222 de-emanated from the solution and transferred to a scintillation counting cell, and alpha counted. Recoveries are determined from the added and found (recovered) barium carrier. Counting efficiencies are determined with prepared standard reference samples. Results are reported in pCi/liter.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
radium isotopes	standards	water pollution	07B
radon isotopes	radiochemistry	de-emanation	14B
barium isotopes			14D
reference standards			18B
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