

Determination of Radon in Drinking Water by
Liquid Scintillation Counting

Method 913.0

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1. Scope and Application

- 1.1 The following procedure is designed for the analysis of radon in drinking water supplies from ground water and surface water sources. Application of this analytical procedure to matrices other than drinking water have not been studied. Caution is advised if this procedure is used for matrices other than drinking water.
- 1.2 Diffusion of radon is affected by temperature and pressure. Samples at other than laboratory temperature should be allowed to equilibrate to room temperature before processing.
- 1.3 Radon will be desorbed from water if the sample is subject to turbulent flow or reduced pressure as is encountered when using pipet tips or syringes with a small orifice followed by a large fill space. Losses can be minimized by using pipet tips with the tip opening enlarged to permit laminar flow of sample into and out of the tip fill space.
- 1.4 Precision and bias of the method is affected by the background in the energy window used for analysis. A procedure is provided for selection of the analytical window which minimizes the background contribution to measurement.

2. Summary of Method

- 2.1 In this procedure 10 mL of the water sample are transferred into a 20 mL glass scintillation vial to which has been added 10 mL of mineral oil scintillation cocktail. Radon diffuses from the sample into mineral oil for which it has a much greater affinity than for water. The sample is then equilibrated for three hours, and then counted for 50 minutes in a liquid scintillation counter using energy discrimination for alpha particles. Results are reported as pCi/L.

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3. Interferences

- 3.1 There are no known chemical interferences from species found in drinking water nor from the dilute concentration of acid which may be present in the standards. Uranium, radium or other radioactive elements would cause positive bias if present in significant quantities.

4. Safety

- 4.1 There are no unusual hazards associated with the reagents used in this procedure. Routine safety precautions ie: lab coat, plastic gloves, safety glasses and use of a hood are required when transferring samples and standards and preparing standards when radium solutions are used.

5. Apparatus and Equipment

- 5.1 Pipet - 5mL mechanical pipet. Gas-tight syringe is not recommended because of the large vacuum produced when filling.
- 5.2 Scintillation cocktail dispenser - Adjustable to deliver 10 mL.
- 5.3 Liquid scintillation counter - A system permitting spectral analysis is recommended.

6. Reagents and Consumable Supplies

- 6.1 Scintillation vials - 20 mL glass vials with caps.
- 6.2 Mineral oil scintillator - High efficiency mineral oil cocktail or equivalent.
- 6.3 Concentrated Nitric Acid - Reagent grade.
- 6.4 Water - Demineralized or equivalent.
- 6.5 Radium solution - Two sources are required for calibration and check standards.
- 6.6 Sample collection bottles - 125 mL narrow mouth with teflon-lined caps.

7. Sample Collection, Preservation and Shipment

- 7.1 Samples are collected from a non-aerated faucet or spigot to minimize desorption of radon as follows.

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- 7.2 Fill a 1 liter glass beaker with water from the source and allow to gently overflow. Open the sample container and submerge inverted into the beaker.
- 7.3 Rotate the sample container so that it fills with water. Cap with a teflon-lined cap while the sample container is still under water to eliminate headspace.
- 7.4 Analysis should begin within three days after receipt of sample in the laboratory.

8. Calibration and Standardization

8.1 Radium Solution Method

- 8.1.1 Prepare 100 mL of radium-226 in water standard such that the final activity will be approximately 35,000 pCi/L. Radium-226 traceable to the National Institute for Standards and Technology (NIST) can be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, NRA/STD, P.O. Box 93478, Las Vegas, Nevada 89193.
- 8.1.2 To a 100 mL beaker add 20 mL of water, 0.5 mL of concentrated HNO_3 and place on an analytical balance. Record the initial mass.
- 8.1.3 Dispense with a pasteur pipet, or other suitable dropper, the required mass of radium solution into the beaker and record the mass. The actual mass of radium solution added is obtained by difference of the final and initial weights.
- 8.1.4 Quantitatively transfer the solution into a 100 mL volumetric flask with a stream of water and dilute to the mark.
- 8.1.5 Transfer 10.0 mL of the diluted standard into the scintillation vial to which has been added 10 mL of mineral oil cocktail. Prepare at least three standards and three backgrounds using a distilled water sample.
- 8.1.6 Set the standards and background samples aside for at least 30 days to allow radon to attain secular equilibrium.
- 8.1.7 Determine the optimal analytical window as outlined in: Selecting Optimal Window, below.
- 8.1.8 After 30 days let the sample dark adapt for 3 hours if necessary and count for 50 minutes.

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Repeat the counting two additional times.

- 8.1.9 From the pooled results calculate a system calibration factor CF as cpm/pCi by the following expression:

$$CF = \frac{S - B}{C \times V}$$

Where:

S = Counting rate of standard (min^{-1})

B = Counting rate of background (min^{-1})

C = Concentration of radium-226 standard (pCi/L)

and V = Volume of standard used (eg. 0.0100L)

8.2 Radon Generator Method

- 8.2.1 The radon generator consists of radium-226 strongly bound to a small amount of ion exchange resin in a 60 milliliter bottle of water. The radium remains fixed to the resin while the radon formed by radioactive decay diffuses into the water phase. The transfer is practically quantitative and the generator can be refilled and reused repeatedly after ingrowth of radon to secular equilibrium (30 days).
- 8.2.2 Agitate the radon in water solution by slowly rotating the bottle and allowing the resin beads to mix the solution. Avoid using generators containing an air bubble.
- 8.2.3 Allow the resin beads to settle, remove cap, and carefully pipet two 5-mL aliquots of solution into a 20 mL glass scintillation vial to which has been added 10 mL of mineral oil cocktail. Prepare three replicates from each of the generators. Shake the vial to extract the radon into the organic phase.
- 8.2.4 Determine the optimal analytical window as outlined in: Selecting Optimal Window, below.
- 8.2.5 Let the standards equilibrate for at least three hours and count the samples for 50 minutes. Repeat the counting two additional times. Prepare and count three background samples.

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- 8.2.6 Correct the results to account for radon decay occurring between sample preparation and the midpoint of the counting period. From the pooled results calculate a system calibration factor as cpm/pCi by the following expression:

$$CF = \frac{S - B}{C \times V \times D}$$

Where:

S and B are the standard and background counting rates

C = The equilibrium radon-in-water concentration of the source.

V = The volume of the water transferred

and D = The decay correction factor ($e^{-\lambda t}$)

8.3 Selecting Optimal Window

- 8.3.1 The following procedure is for use with counters which permit analysis of sample spectra.
- 8.3.2 Count a radon standard for five minutes and generate a sample spectrum. For greater clarity use a log scale for the channel number if possible.
- 8.3.3 The region of greatest alpha activity will be obvious as evidenced by one or two large peaks at the high end of the energy spectrum (see Figure 1). The optimal window is formed by extending the region by 10% on each side of the alpha peaks. This window will be used for subsequent calibration and analysis. The calibration factor should be at least 6 cpm/pCi with the background not exceeding 10 cpm.

9. Quality Control

9.1 Background Samples

One background sample having approximately the same total dissolved solids as the samples is run with every twenty samples. At least two backgrounds should be counted with each batch.

A suitable background sample may be prepared by boiling 2 L of laboratory radium- and uranium-free tap water to remove residual radon if present. Store the cooled tap water in a capped 2 L bottle.

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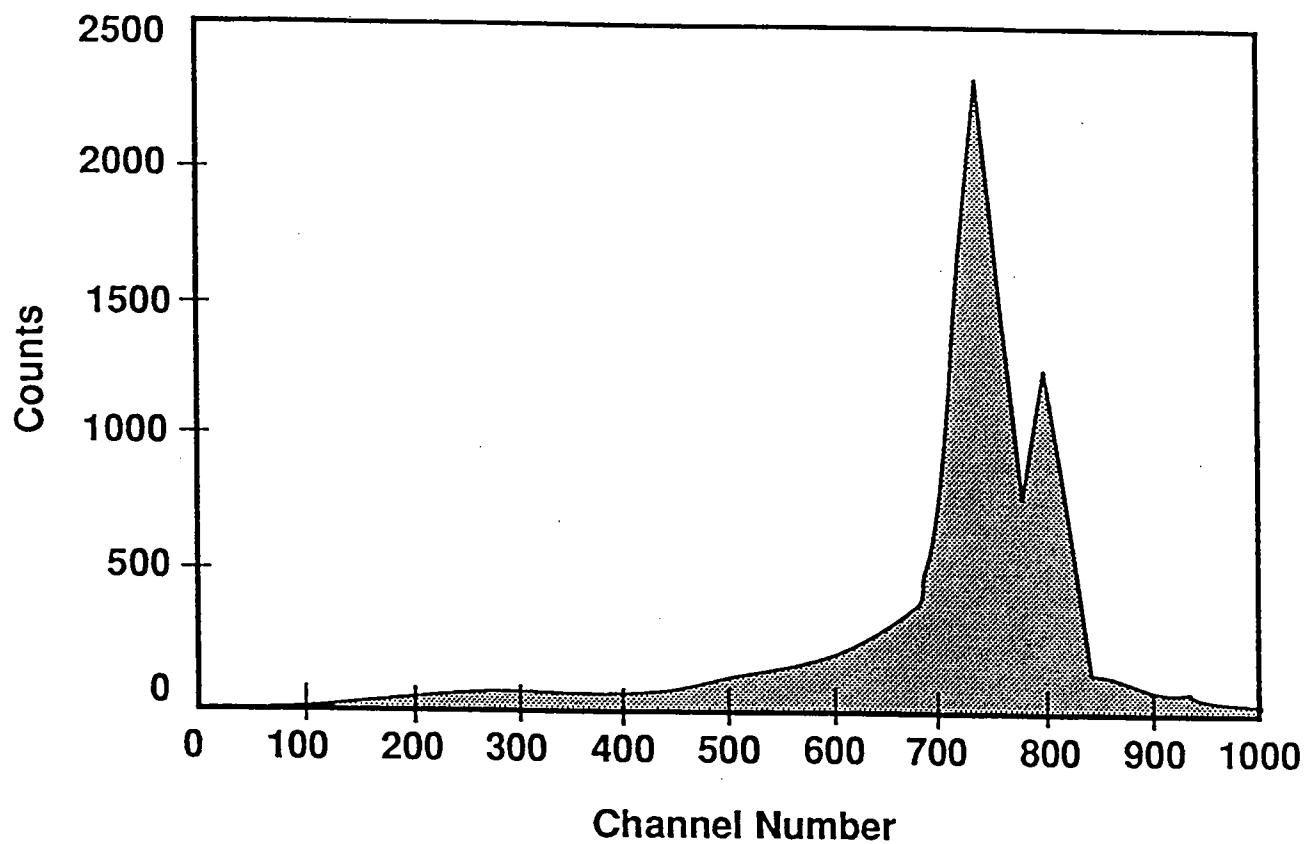


Figure 1. Liquid Scintillation Spectrum of Radon

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9.2 Duplicates

Duplicate analyses are required for one out of every ten samples not including the standards and quality control check standards.

Duplicate analyses should have a relative percent difference (RPD) equal to or less than the percent 2 sigma (2σ) counting error plus 10 percent. Relative percent difference is calculated by taking the absolute value of the following expression:

$$\text{Abs RPD} = \frac{(\text{Analysis 1} - \text{Analysis 2}) \times 200}{\text{Analysis 1} + \text{Analysis 2}}$$

If the RPD exceeds this value, recount the samples. If the new RPD still exceeds $2\sigma + 10$ percent, prepare another duplicate sample or duplicate low-level (100 - 300 pCi/L) standard and analyze. If the RPD for the reanalysis exceeds the limit, check for instrument problems or possible losses in transferring the water to the scintillation vial.

9.3 Quality Control Check Sources (QCCS)

QCCS are prepared from a dilution of radium different than that used to prepare the standards and should have a nominal activity of 5000 pCi/L. Three check sources are analyzed with each batch of samples. One check source is run with the first ten samples, the second is placed approximately in the middle of the batch and the last is run with the last ten samples of the batch.

9.4 Records

Collect and maintain the results from the duplicate pairs and check standards in a bound notebook. The record should include the date, the results, the analyst and any comments relevant to the evaluation of these data.

Plot the results of the check standards on a control chart for that counter.

10. Procedure

- 10.1 Carefully pipet a 10-mL or two 5-mL aliquots of sample into a glass scintillation vial to which has been added 10 mL of mineral oil cocktail.
- 10.2 Cap and shake the samples and set aside in the dark for at least three hours to equilibrate the radon progeny and dark adapt before counting. The time of

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sample collection is the initial time for decay correction.

- 10.3 Count the samples for 50 minutes using the optimized window settings for alpha counting.

11. Calculations

- 11.1 Calculate the concentration of radon-222 in pCi/L from the following equation:

$$\text{pCi/L} = \frac{G - B}{CF \times D \times V}$$

Where:

G = Gross counting rate of the sample

B = Background counting rate

CF = Calibration factor (see 8.1.9)

and D = Decay factor for Rn-222 between time of collection and midpoint of counting period

- 11.2 Calculate the 2 sigma (95% confidence level) counting uncertainty from:

$$2\sigma = \frac{2 \left\{ \frac{G}{T_G} + \frac{B}{T_B} \right\}^{\frac{1}{2}}}{CF \times D \times V}$$

Where:

T_G = The duration of the sample count

and T_B = The duration of the background count

12. Precision and Accuracy

- 12.1 The intralaboratory and interlaboratory precision and accuracy of the method has not been fully evaluated.
- 12.2 At concentrations near zero the counting uncertainty will be the primary factor in the lack of precision of the method. Figure 2 plots the percent 2-sigma (95% confidence level) counting uncertainty as functions of concentrations and counting times.
- 12.3 Interlaboratory differences are estimated to be on the order of 25% based on a 12-laboratory study using the Ra-226/resin radon generators. Figure 3 plots percent recoveries (measured/expected values)

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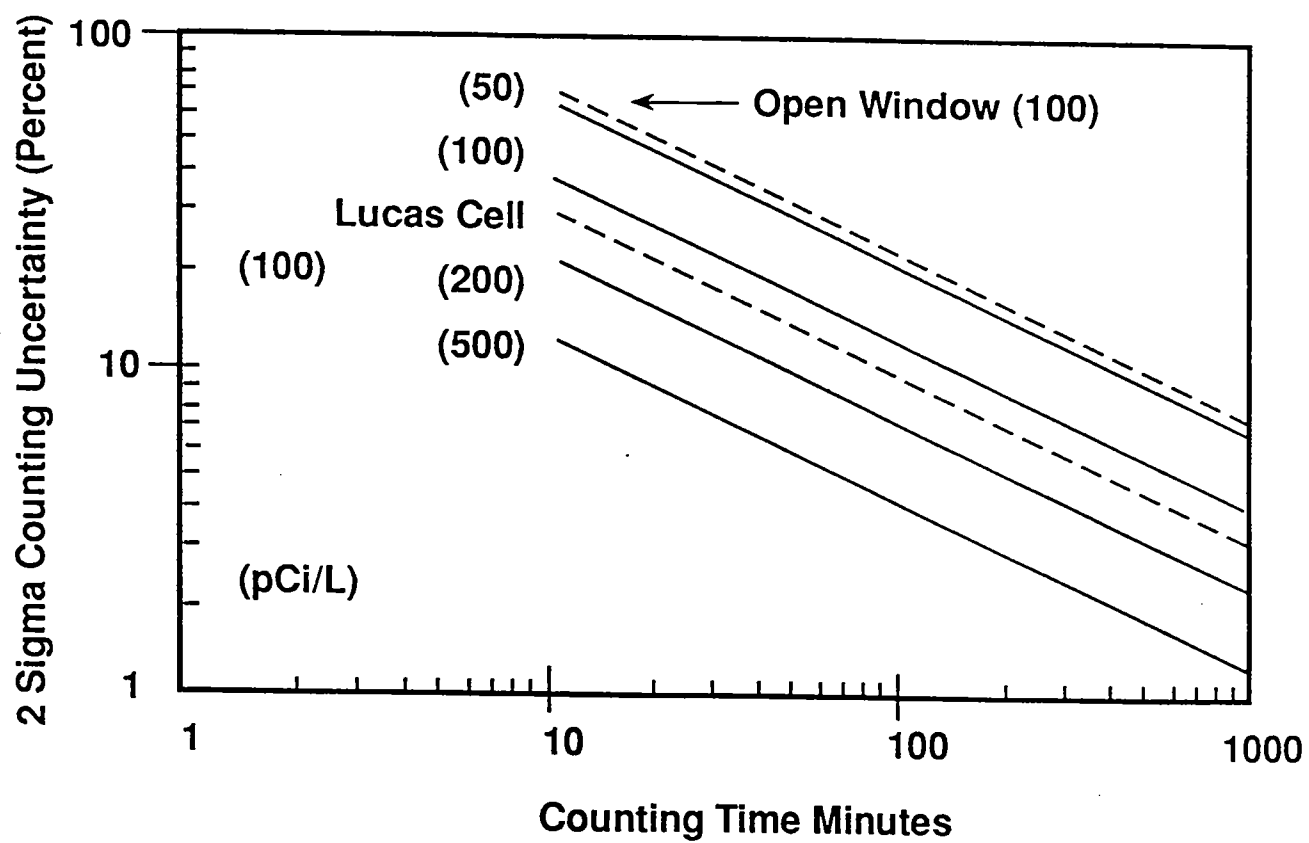


Figure 2. Counting Uncertainty as a Function of Concentration and Counting Time.

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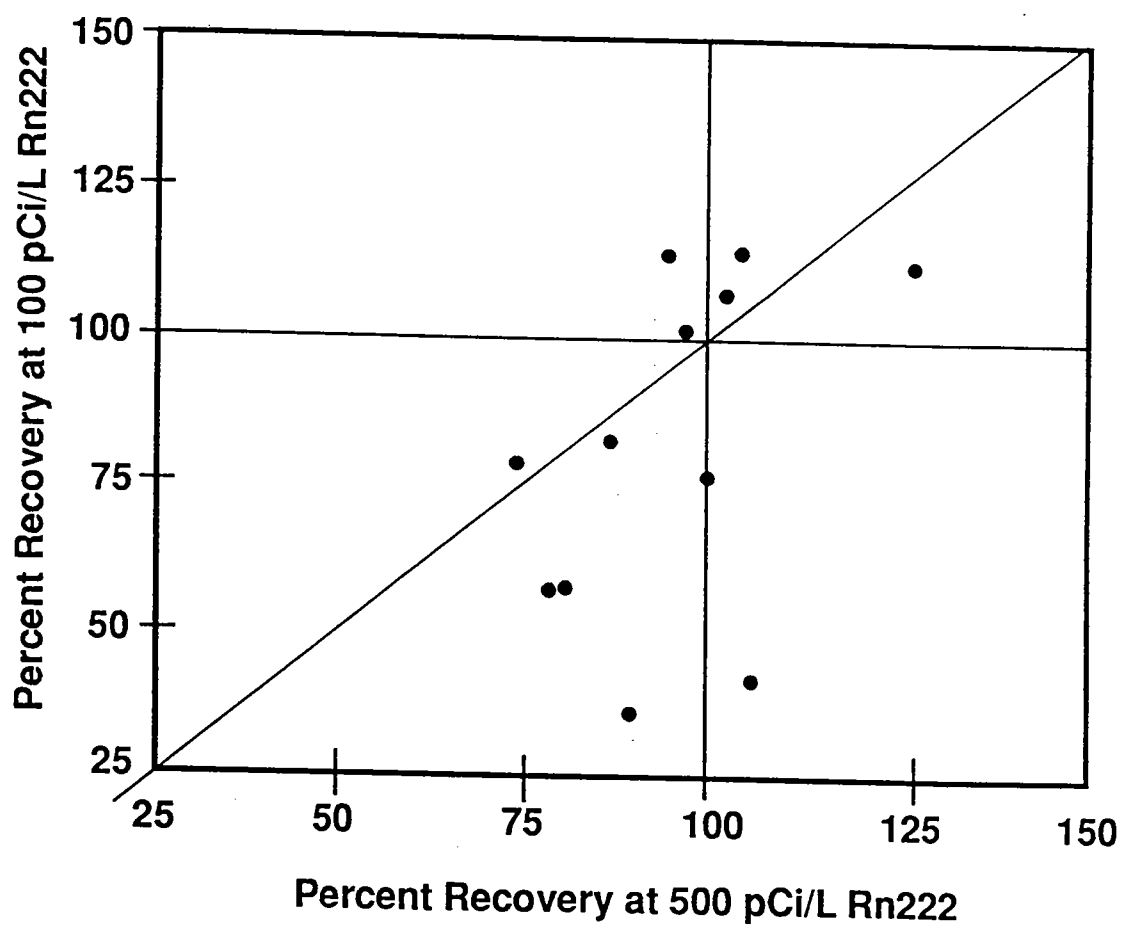


Figure 3. Analytical Recoveries for 12-Laboratory Collaborative Study

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for a 100 pCi/L sample versus a 500 pCi/L sample for each of the 12 laboratories. The four laboratories biased low at the 100 pCi/L level are suspected of using an open window.

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