LABORATORY INTERCOMPARISON OF RADON-IN-WATER STANDARDS

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Abstract

The standardization of instruments used for radon-in-water measurements typically involves handling and disposal of ^{226}Ra in solution. To avoid contact with the Class A carcinogen, radium-free solutions were prepared and tested for use as radon-in-water standards. Filters containing known amounts of ^{226}Ra were sealed in polyethylene and placed in vials filled with distilled water for >30 days to allow the decay products to establish secular equilibrium. Voluntary intercomparisons of the radon-in-water standards were conducted to investigate the accuracy of analyses by commercial, government, and private companies. Various analytical methods were utilized by the participants. Result show that, at radon concentrations of 18,700 and 3850 pCi/L (693 and 143 Bq/L, respectively), most participants reported concentrations within 25% of the known amounts.

Introduction

Naturally occurring radionuclides are frequently measured in groundwaters. Of these radionuclides, radon (^{222}Rn) has sufficient properties, solubility, and half-live (3.8 d) that during household use of groundwater (showering, cooking, or washing dishes and clothes) the dissolved radon can contribute substantially to indoor-air levels (Fitzgerald, 1997). The radon released from the water into the home's air will contribute to the radon concentration in the indoor air.

Liquid scintillation (LS) counting is a recommended method for the measurement of radon in water (Whittaker, 1989). The LS method is inherently easy, rapid, and in common usage. During the efficiency standardization of an LS spectrometer, a solution containing radium (^{226}Ra), a Class A carcinogen, is typically used. Use of ^{226}Ra means that loss of radon

during transfer of the water sample is undetectable, since equilibrium of ^{222}Rn and its decay products is re-establishment in the cocktail. Also, as radioactive equilibrium is maintained in the cocktail during counting, the decay of radon, which occurs in real samples, cannot be monitored. The inability to detect transfer losses and radioactive decay, in standardization cocktails that contain radon in equilibrium with ^{226}Ra, limits the reliability of radon results obtained from groundwater samples that do not contain supporting ^{226}Ra. An alternative method involves creation of a ^{226}Ra-free solution in which radon emanates from a sealed ^{226}Ra source into an encapsulated aliquot of water. This rarely-used method includes sample-transfer proficiency and decay-correction calculations in determination of the method efficiency. Unfortunately ^{226}Ra-free standards for radon-in-water analyses are not readily available. The objective of the present study was to examine results from the analysis of ^{226}Ra-free standards by laboratories that standardize their methods using solutions containing ^{226}Ra.

Methodology

Sealed sources were prepared by pipetting a known volume of a ^{226}Ra-standard solution onto filter papers of 1.27 cm diameter. After drying, each filter paper was sealed inside 0.05-mm (2-mil) thick polyethylene sheeting and placed in a 42-ml glass vial, which was filled with distilled water and capped with a Teflon-lined septum. Concurrently, the ^{226}Ra-standard solution was pipetted into 10 additional vials, which were filled with distilled water, capped, and used as reference solutions.

Solutions containing a sealed ^{226}Ra source of a known activity (A; pCi/L) can be measured to determine the emanating fraction (f) of the source according to the equation:

$$f = \frac{(G - B)}{(2.22*V*\varepsilon*A*D*I)} \quad (1)$$

where G and B are the respective gross and background count rates (cpm), 2.22 is the conversion factor between dpm and pCi, V is the sample volume, and ε is the detector efficiency. The time span for the ingrowth factor (I) extends from initial encapsulation to sample extraction, while the time for the decay factor (D) extends from sample extraction to the midpoint of the measurement.

Prior to sending the vials to participants of the intercomparison, the solutions were allowed to attain full ingrowth (>40 d) of radon and measured to identify any problematical

standards. For each vial, 10 ml of radon-laden water was extracted and injected beneath 10 ml of high-efficiency mineral oil. The LS cocktail was shaken to expedite transfer of the radon into the scintillation fluid. Counting was delayed a minimum of 3 h, to allow radioactive equilibrium of the short-lived radon decay products to be established in the cocktail. Radon activities were determined using 50-min counts on a LS spectrometer, with an absolute efficiency of 64% for radon and for each of its four short-lived (α and β) decay products (ε = 3.2 cpm/dpm). Each sample was counted three times within a week and was decay-corrected to the transfer time. Repetitive counts of the four method blanks resulted in a mean of 0.61 ± 0.07 dpm. While negligible compared to the standards, the blank count rate was subtracted from all LS measurements.

To examine the utility of the ^{226}Ra-free radon-in-water standard, and to investigate the accuracy of radon-in-water measurements, we conducted a voluntary intercomparison. The participants included commercial laboratories, individuals, and state and federal agencies. Each of the sealed ^{226}Ra sources described above was placed in a 42-ml vial filled with distilled water and provided to the participants after full radioactive ingrowth.

Results and Discussion

The 10 vials that contained a known quantity of ^{226}Ra in solution provided a reference value for the LS measurements. There is no decay associated with the activity in the cocktails, and radioactive equilibrium is maintained in the solutions. Further, the radon is dissolved in solution and does not have to penetrate polyethylene, as it does with the sealed sources. Activities measured in the 10-ml vials averaged 99.6% of the value expected based on the NIST certificate that accompanied the standard. Count rates for five determinations of each of the 10 vials (n=50) were within 7% of the known value. For the radium standards, there was no further ingrowth evident during the consecutive counts, implying that the solution pipetted onto the filters is of a known activity and the transfer of the radon-laden water to the LS vials was quantitative. The efficacy of the Teflon-lined septum in retaining radon in the vials is demonstrated by the precision and accuracy of the activity values for the ^{226}Ra-dissolved solutions.

Cocktails were created from water in the vials containing the sealed filters and were measured three times by LS counting. Results (Fig. 1) indicate that after full ingrowth the radon

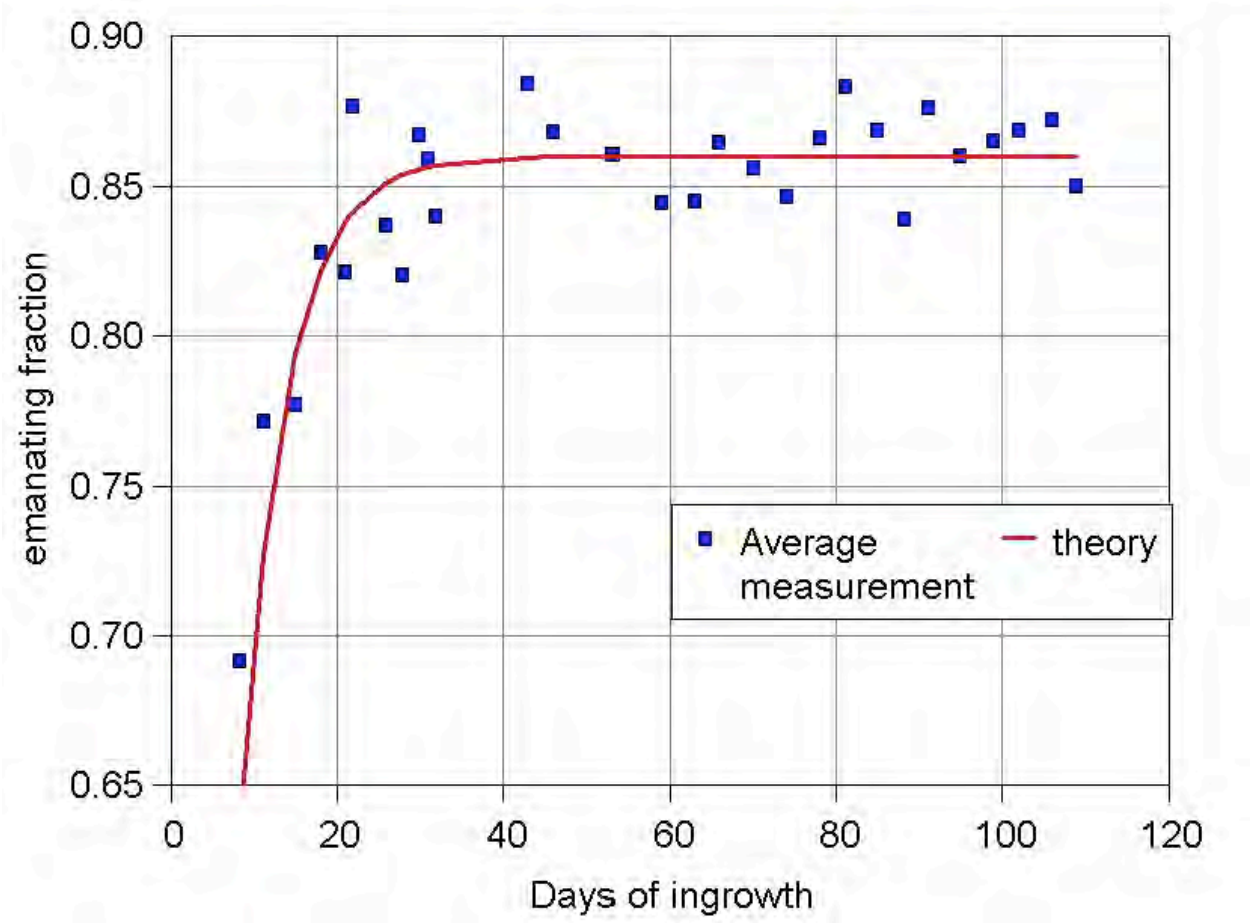

Fig. 1. Decay-corrected activities in the cocktails indicate that secular equilibrium is established within 40 d.

concentration in the solutions averaged 86% of that determined in the ^{226}Ra standards, and was identical to the emanating factor reported (Volkovitsky, 2006) for a polyethylene-encapsulated radium source. Decay during diffusion through the polyethylene and retention of radon in the polyethylene may be responsible for diffusivity below 100%. Errors due to counting statistics were <1% and cannot account for the 14% reduction in activity.

The analytical devices employed by the intercomparison participants included liquid-scintillation counters, alpha-scintillation ("Lucas") cells, electrets, gamma-ray detectors, a continuous radon monitor (CRM), and etching of polycarbonate (Pressyanov, 2008). For those utilizing the liquid-scintillation method, sample volumes were 8, 10 or 15 ml, count times varied from 9 to 100 min, and methods of extraction included needle and large-bore syringes. All participants who utilized a LS counter had standardized the instrument using ^{226}Ra. For the

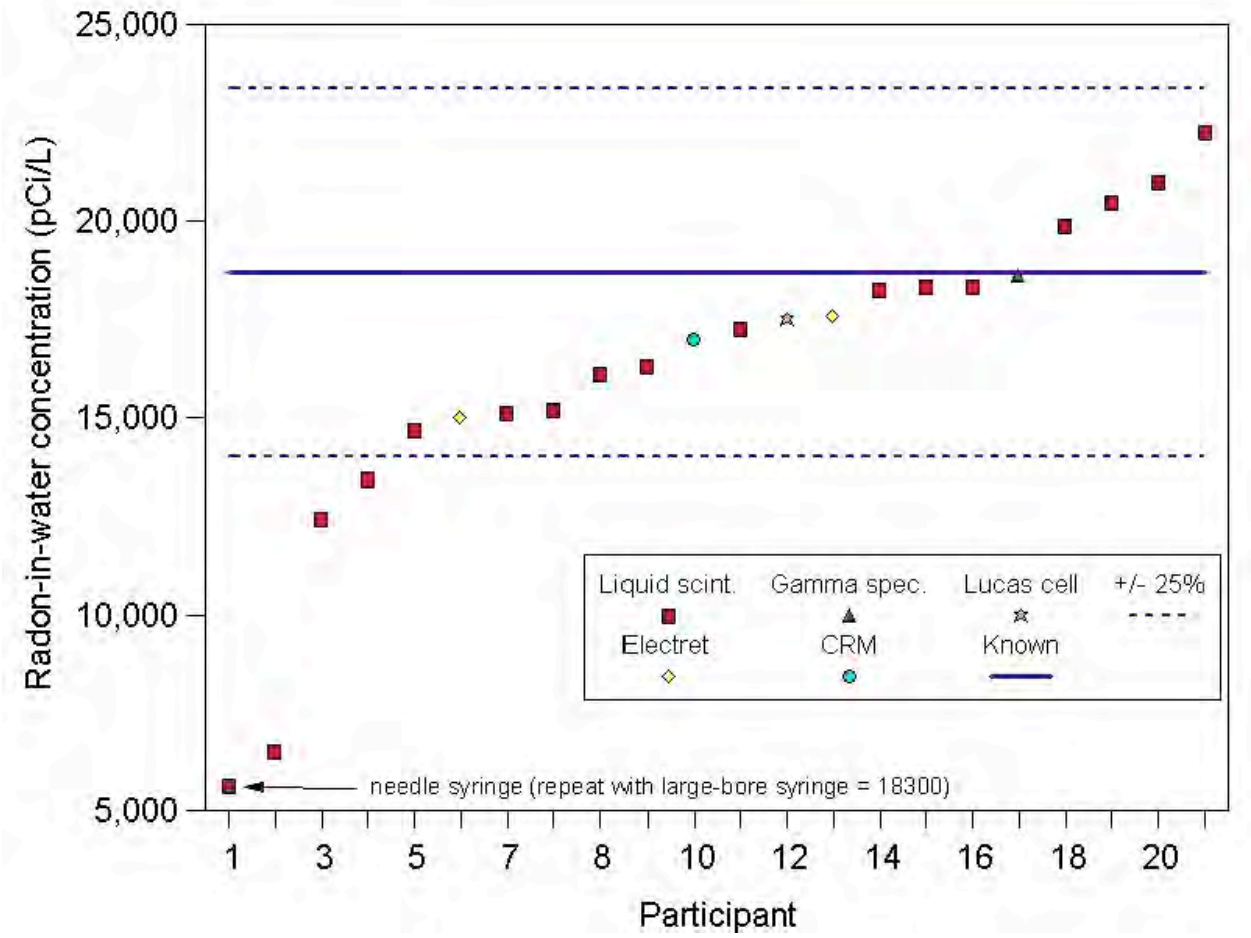

Fig. 2. Results of a radon-in-water intercomparison conducted in 2008 show that 18 of 21 participants reported concentrations within 25% of the known value (18,700 pCi/L).

methods based on electret, gamma-ray, and CRM measurements, the entire volume of the vial was measured for >24h, 2 h, and 20 min. respectively.

As shown in Figure 2, reported waterborne radon concentrations for the first intercomparison varied from 12,400 to 22,300 pCi/L. Results for most (86%) of the participants were within 25% of the known (18,700 pCi/L); the three outliers reported low concentrations. One laboratory initially reported 5670 pCi/L using a needle-syringe extraction, and 18,300 pCi/L for a repeat sample using a syringe containing a large bore for sample extraction. For the second intercomparison, reported waterborne radon concentrations varied from 2760 to 6910 pCi/L (Fig. 3). With the exception of two results, the participants reported concentrations within 25% of the known (3850 pCi/L). Losses occur during sample transfer when the water is exposed to air in

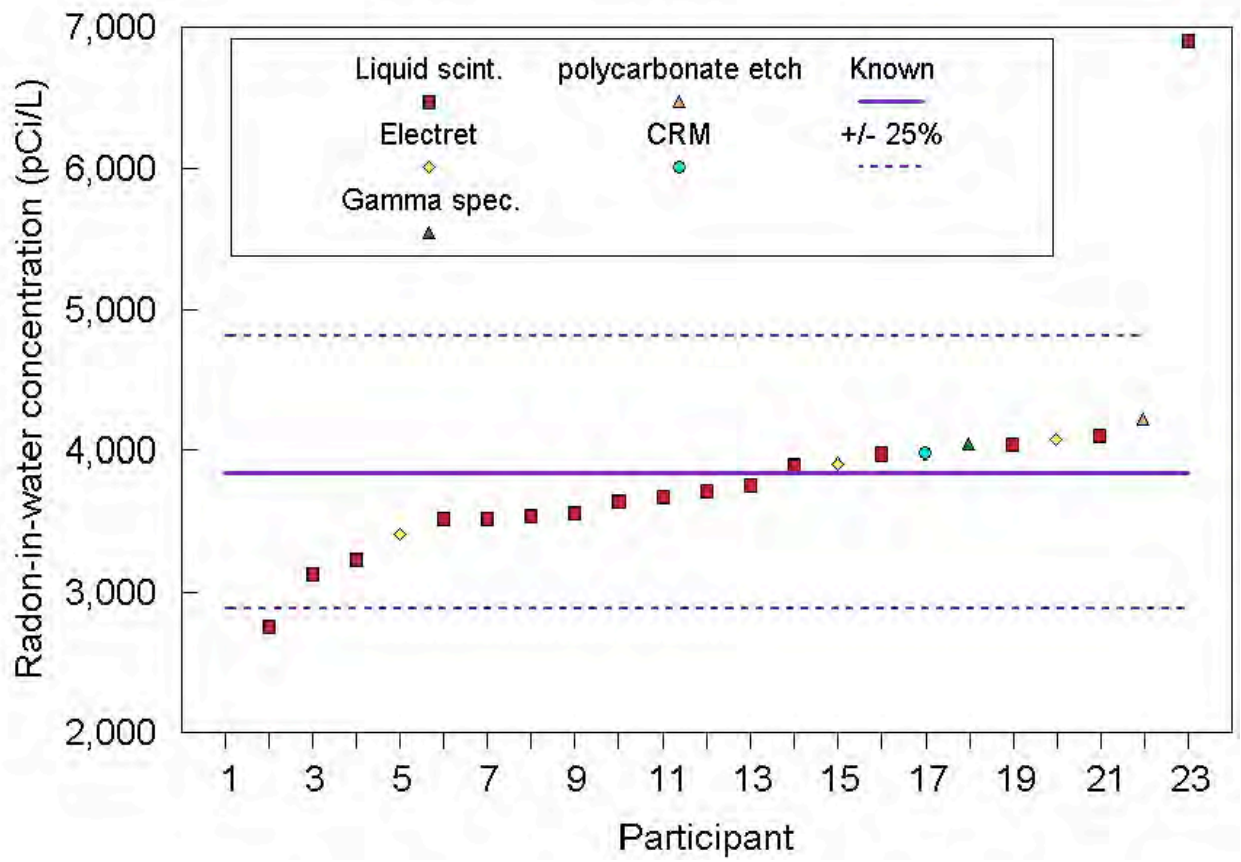

Fig. 3. Results of a 2009 radon-in-water intercomparison conducted in 2009 show that 21 of 23 participants reported concentrations within 25% of the known value (3850 pCi/L).

the syringe. In contrast, reported values above the expected concentration indicate error in the detector efficiency. The inter-method comparison demonstrated that laboratories often provide accurate results; however, results are often skewed toward lower values.

Conclusions

Standards containing radon in water were created. Results of measurements of 10 liquid scintillation cocktails containing ^{226}Ra in solution were nearly identical to the known value. Water in vials that held encapsulated ^{226}Ra sources were found to contain only 86% of the known activity, after full ingrowth had been attained. The uniformity of radon emanation through polyethylene demonstrates that ^{226}Ra-free radon standards can be reliably produced and used repeatedly. The ^{226}Ra-free standards are a functional method to generate samples for proficiency testing of laboratories that conduct radon analyses of water. For both radon-in-water

intercomparisons, a large majority of the participants reported results within 25% of the known activities using an assortment of analytical methods.

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