ORIGINAL ARTICLE

Long-term evaluation of a reusable radon-in-water proficiency test

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Abstract

A proficiency test is an integral part of any analytical procedure; however, there is no known proficiency test in place for radon-in-water analysis. This led us to conduct a long-term study. Successful preparation of a reusable radon (^{222}Rn)-in-water standard containing a 'radium (^{226}Ra)-loaded filter paper (the source)' sandwiched between polyethylene sheeting has been reported. As the source '^{226}Ra-loaded filter paper' is sandwiched between polyethylene sheets, the surrounding water (which is sampled and analyzed) in the bottle remains free of ^{226}Ra. With this type of standards, a previous study reported that at full ingrowth (>30 days), 86% of the ^{222}Rn produced by the source was emanated into the water and remained stable thereafter, and the remaining 14% was retarded by the polyethylene sheeting. We periodically measured radon-in-water in two such standard samples allowing a 40- to 50-day ingrowth interval for more than 6 years (2016–2022). In each measurement, we prepared in duplicate the cocktails in four different ways (in Mineral-oil *vs.* Optifluor in combination with two different ways of 'pipetting or sample drawing' and dispensing into the scintillation vials) and measured the radon-in-water using two different Liquid Scintillation Counting (LSC) assays: full-spectrum (0–2,000 keV) *versus* Region of Interest (ROI) for radon (ROI, 130–700 keV). A substantial number of repeated results unequivocally show that the reusable standards maintained its characteristics satisfactorily for a 6-year long period. Duplicate measurements were precise in almost all cases. We consistently observed significant differences in measured radon concentration between the two different LSC assays and between the two different scintillation fluids, but not between the two sample drawing methods. With full-spectrum assay (0–2,000 keV), both Mineral-oil and Optifluor grossly underestimated the actual radon concentration, and with ROI assay (130–700 keV), Mineral-oil overestimated the radon concentration; therefore, these should be avoided. Preparing the cocktails with Optifluor and measuring by ROI assay (130–700 keV) was the only method that consistently produced results within the acceptance window (±25% of the known), suggesting that a certain way of preparing and measuring the water samples could yield more accurate results for radon. Thus, our findings demonstrate that a proficiency test for radon-in-water using these reusable ^{226}Ra-free radon-in-water standards is a valid and valuable option, and it should be a part of radon-in-water analysis by the laboratories.

Keywords: *kiloelectric volt (keV)*; *Mineral-oil*; *Optifluor*; *proficiency test*; *radon (^{222}Rn)*; *liquid scintillation*

Alpha radiation from the consumption of radionuclides in drinking water is a significant emerging public health concern. According to the World Health Organization (WHO), when the gross-alpha (α) activity in drinking water exceeds 0.5 Bq/L or gross-beta (β) activity exceeds 1 Bq/L, radionuclide-specific activities should be analyzed and brought below the WHO guidance levels of 0.1 Bq/L for ^{228}Ra; 1 Bq/L each for $^{223\text{-}226}$Ra, ^{234}U, and ^{235}U; 10 Bq/L for ^{238}U; 100 Bq/L for ^{222}Rn; and 15 µg/L (ppb) for total uranium (1).

Underground rocks and soils may release radioactive gas radon (^{222}Rn), which can enter the home through invisible cracks and holes in the foundation, increasing its concentration in the indoor air. When ^{222}Rn is inhaled through breathing radon-rich indoor air, it irradiates lung tissue and poses a significant risk of lung cancer in the long run (2). Another route of human exposure to ^{222}Rn is through household water, primarily when it is supplied by a private well. ^{222}Rn-in-water is an under investigated area. Out of 842 Georgia household wells tested for radon by the University of Georgia radon-in-water laboratory, the highest level was 5,365 Bq/L, with 52 wells having levels above 3,700 Bq/L, 102 in the range of 148 to 3,700 Bq/L, 501 between 11.1 and 148 Bq/L, 185 within 3.7 to 11.1

Bq/L, and only two wells were below the reporting limit of 3.7 Bq/L. The primary health consequence from ^{222}Rn in household water is also inhalation and an increased risk of developing lung cancer like ^{222}Rn in indoor air, with a much lower risk of developing stomach cancer through ingestion. When water containing a high concentration of ^{222}Rn is used indoors, radon degasses from the water and increases radon concentrations in the indoor air. This happens when people are performing regular activities like showering and flushing toilets. As a rule of thumb, radon-contaminated household water has the potential to raise radon levels in a home roughly by 1 Bq/L for every 10,000 Bq/L of radon-in-water (3); however, this may vary with the home size and ventilation. Based on a National Academy of Sciences report on radon in drinking water (4), it was estimated that in the United States (US), radon in drinking water causes about 168 cancer deaths (from both lung and stomach cancers combined) per year. An estimated 89% of these 168 deaths occur from lung cancer caused by breathing in radon released from water, and 11% percent from stomach cancer caused by ingesting water contaminated with radon (3, 4).

The United States Environmental Protection Agency (USEPA) recommends Liquid Scintillation Counting (LSC) for analyzing radon-in-water (5), and the state of New York approved this method through its Environmental Laboratory Approval Program (6, 7). Laboratories in the US use several different sampling methods ('Direct Fill' *vs.* 'Submerged Bottle'), pipetting ('Simultaneous Drawing' *vs.* 'Separate Drawing'), scintillation fluids ('mineral oil' *vs.* 'Optifluor'), and volumes of water plus scintillator in the counting vial ('8 mL + 8 mL' *vs.* '10 mL + 10 mL' combinations) when analyzing radon-in-water. The various methods of sample processing make it difficult to compare results from different laboratories for water samples even when they are from the same source and analyzed by the recommended LSC method. Original research by Saha et al. (8) compared different methodological variances in sample collection, sample processing, and LSC analysis of radon-in-water using several household well water samples, and made the following recommendations for optimized sampling and analysis conditions.

1. The 'Direct-Fill' method of sample collection was susceptible to significant loss of radon gas, so the 'Submerged Bottle' method should be used. For the 'Direct-Fill' method, samples are collected by opening and holding the scintillation vial under a gently flowing tap to avoid turbulence. The scintillation vial is allowed to gently overflow, forming a slight dome of water at the opening. The vial is then promptly capped and checked for air bubbles by inverting and gently tapping it. If any air bubbles are found, the vial is emptied, and the filling procedure repeated until air bubbles are no longer observed in the scintillation vial. For the 'Submerged Bottle' method, water is first collected in a bowl by gently flowing the water from a tap against one side of the bowl with minimal disturbance. While the bowl is gently overflowing, the entire scintillation vial with the closed lid is submerged under the water in the bowl. The lid is opened under water, and the vial is filled and then capped while still under water. It is taken out of water and turned upside down. If an air bubble is found, the vial is emptied and refilled again until an air bubble is no longer observed.
2. The 130 –700 kiloelectric volt (keV) assay based on the region of interest (ROI) for radon was better than the 0–2,000 keV assay based on a full spectrum analysis.
3. When Mineral-oil was used as the scintillation fluid, the radon count rates were higher than when Optifluor was used.
4. The liquid scintillation cocktail of 10 mL scintillator plus 10 samples was better than the combination of 8 mL scintillator plus 8 mL sample.
5. 'Separate Pipetting or Drawing' of scintillator and sample resulted in a significant loss of radon. 'Simultaneous Pipetting or Drawing' should be adopted when laboratories use open pipettes; however, this effect could be insignificant if a closed-top (no headspace) sampling syringe was used.

A reliable proficiency test is especially important for radon-in-water because the test results have both health and cost consequences. Radon-in-water is particularly challenging to develop a proficiency test since radon dissolved in water readily escapes over time, making it challenging to attain and maintain a stable concentration for comparison. Kitto et al. (9) prepared an inexpensive, reusable radon-in-water source and used it as a standard sample for laboratories around the US. In that preparation, a fixed amount of ^{226}Ra particles were sandwiched between two polyethylene sheets where radon was allowed to emanate into an encapsulated aliquot of water as described by Volkovitsky (10). With 33 identical samples prepared using this method (10), Kitto et al. (9) observed that at full ingrowth (>30 days), only 86% of the ^{222}Rn produced by the sandwiched ^{226}Ra sources emanated into the water because of retardation by the polyethylene sheeting probably owing to the ability of different plastic materials to absorb radon as reported by various authors (11, 12). The initially measured ^{222}Rn-in-water concentrations in those 33 samples in one laboratory were consistent with <2% standard deviation among them. In a follow-up comparison of one-round measurement of these samples in 21 laboratories, 18 reported concentrations within ±25% of the known, 693 Bq/L (9), indicating their potential for serving as quality control standard samples in

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measurement of radon-in-water. Long-term use of these radon-in-water standards as proficiency test samples and the effect of different sample preparations ('Simultaneous Drawing' *vs.* 'Separate Drawing'), scintillation fluids ('Mineral-oil' *vs.* 'Optifluor'), and LSC assays are yet to be evaluated. In this long-term study at the University of Georgia radon-in-water laboratory, we addressed these unknowns by measuring ^{222}Rn in two such radon-in-water standard samples allowing a 40- to 50-day ingrowth interval for 6 years (2016–2022). This study was a collaborative effort between the University of Georgia radon-in-water laboratory and the New York State Department of Health to develop a proficiency in this field, which is a requirement by accrediting agencies like the International Standard Organization (ISO). Establishment of a proficiency test for radon-in-water has so far been thought to be difficult if not impossible because it is a common belief that as a dissolved gas, radon-in-water would not be stable enough to produce a testable sample, and the magnitude of loss of this gas from the water could be random. The objectives of this long-term study were:

1. To evaluate and determine whether a proficiency test for radon-in-water, using reusable radon-in-water standards containing a '^{226}Ra-loaded filter paper (the source)' sandwiched between polyethylene sheeting, is a viable option.
2. To determine the best methods of radon-in-water sample preparation and LSC analysis to achieve results within the suggested ±25% of the known, which is 139 Bq/L in this study.

Materials and methods

In 2016, we obtained two identical ^{222}Rn (half-life: 3.82 days)-in-water standard samples in 40 mL glass bottles from the co-author Kitto at the New York State Department of Health. The samples were labelled 'Standard-15' and 'Standard-17'. Each sample contained a single (and identical) source composed of a fixed amount of ^{226}Ra sandwiched between polyethylene sheeting. The bottles were filled with water with no headspace left and capped with air-tight lids (Fig. 1). The polyethylene sheets, holding the source in between, keep the sample water free of ^{226}Ra but allow to build up ^{222}Rn, which eventually reached a stable concentration in the surrounding water (9) as described hereunder. When the bottles with ^{226}Ra source were filled with water, completely free of air bubbles, and sealed airtight, the ^{226}Ra source continuously emits ^{222}Rn, which eventually reaches a plateau concentration at 'full ingrowth' (>30 days). This plateau of concentration is attained because the rate of ^{222}Rn addition to the water from the ^{226}Ra source eventually equals the rate of radioactive decay of the ^{222}Rn (half-life: 3.82 days). Full ingrowth is achieved at >30 days, when radon-in-water for both 'Standard-15' and 'Standard-17' should be 162 Bq/L at 100% emanation, but due to retardation by the polyethylene, it measures only at 139 Bq/L equivalent to 86% emanation. Thus, the assigned or known concentration of radon in both 'Standard-15' and 'Standard-17' is 139 Bq/L with the suggested lower (−25% of the known) and upper (+25% of the known) acceptance limits of 104 Bq/L and 174 Bq/L, respectively. As the source '^{226}Ra-loaded filter paper' is sandwiched between polyethylene sheets, the surrounding water (which is sampled and analyzed) in the bottle remains free of ^{226}Ra. Otherwise, it was not technically possible to attain the same, or similar, level of radon build up after each full ingrowth period for a long time (see Results and Discussion).

The University of Georgia Radon-in-Water Laboratory measured radon-in-water in both 'Standard-15' and 'Standard-17' every 40–50 days ensuring full ingrowth for 6 years from 2016 to 2022. During each sampling event, one set of four samples, using two different scintillation fluids in combination with two different methods of sample drawing/pipetting as described later, was prepared

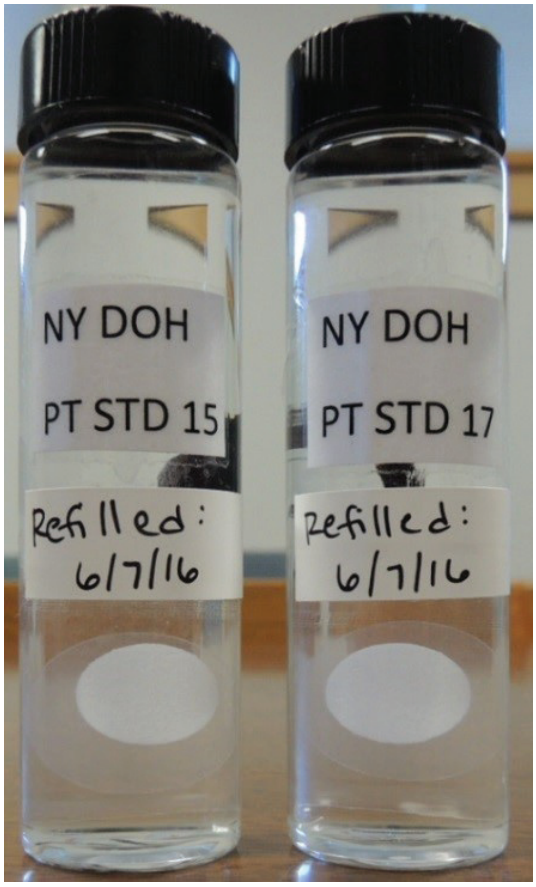

Fig. 1. The ^{222}Rn-in-water 'Standard-15' and 'Standard-17' with the source ^{226}Ra loaded filter paper sandwiched in between polyethylene sheets.

from 'Standard-15', and another set of four identical preparations were prepared from 'Standard-17'. Thus, duplicate preparations of any given combination (out of 4) of scintillation fluid and sample drawing/pipetting were from two different bottles. All eight preparations were analyzed by two different LSC Assays as described later.

Two different scintillation fluids

We compared the efficacy of two different water-immiscible scintillation fluids, namely, 'OptiFluor' (PerkinElmer, Waltham, MA) and 'High Efficiency Mineral-oil Scintillator' (PerkinElmer, Waltham, MA), as both are recommended and used for analyzing radon-in-water in water. According to the manufacturer description of Perkin Elmer:

- 'Optifluor' used in this study is a benzene-based mixture of high flash point and low volatility organic solvents that produced a background count rate of 15 counts per minute (cpm) and 71% quench parameter. It is ideally suited for counting radon-in-water in water when a safer cocktail, with regards to laboratory workers' and environmental safety, is preferred.
- The 'High Efficiency Mineral-oil Scintillator' used in this study contains primarily white Mineral-oil (60–80%) and 1,2,4-trimethylbenzene (20–40%), with a background of 15 cpm and 107.5% counting efficiency. It is the cocktail of choice for the detection of radon-in-water and soil samples.

As Mineral-oil is not biodegradable, it requires special hazardous waste management. In contrast, Optifluor is biodegradable and easily disposed of. Several other scintillation fluids such as Ultima Gold™ AB (water-miscible) and Ultima Gold™ F (water-immiscible) (PerkinElmer, Waltham, MA) are also available for evaluation in analyzing radon-in-water. However, we compared only 'OptiFluor' and 'High Efficiency Mineral-oil Scintillator' because they are commonly used by the laboratories in the US.

Two different methods of pipetting and mixing the sample and scintillation fluid

We compared two different methods of pipetting and mixing sample and scintillation fluid on the recovery of radon. For the first method, called 'Separate Drawing', the scintillation fluid (8 mL) was preloaded into the scintillation vial, and then the sample (8 mL) was pipetted and injected underneath the scintillation fluid in the vial. The second method, called 'Simultaneous Drawing', had the scintillation fluid (8 mL) drawn into a pipette first, then the water sample (8 mL) was drawn into the same pipette underneath the scintillation fluid, and finally both sample and scintillation fluid were dispensed into the scintillation vial. In Simultaneous Drawing, hardly any mixing happened within the pipette. After sample injection in the vials, the vials were immediately capped airtight and shaken vigorously to mix and expedite transfer of radon into the scintillation fluid. Further details and pictorial illustrations of 'Separate Drawing' and 'Simultaneous Drawing' are available elsewhere (8).

Two different LSC assays

Using a Tricarb 2910 Liquid Scintillation Counter (PerkinElmer, Waltham, MA) for counting radon-in-water, we compared radon recovery from two different LSC assays as presented in Table 1. The 'Assay-1' is a full spectrum assay covering the whole range of energy with the ROI from 0 to 2,000 keV. In contrast, the 'Assay-2' is limited within the ROI for ^{222}Rn from 130 to 700 keV, excluding the counts below 130 keV (from 'Bremsstrahlung' radiation). Cutting out the low-energy (below 130 keV) betas also reduces the quenching and background. The efficiency (counts per minute divided by disintegrations per minute) in Assay-2 is 3.0 to 3.1 (or about 66% absolute efficiency for each alpha or beta emission).

Preparation and analysis were carried out by four laboratory personnel over the course of the 6-year study. During each measurement event, all four preparations were made and analyzed for ^{222}Rn in duplicate, and the results allowed us to evaluate both short-term and long-term precision of analysis in each case using Relative Percentage Difference (RPD) and Coefficient of Variation (CV), respectively. The RPD and CV were derived as follows:

$$RPD = \frac{\left|\text{Duplicate} - 1 - \text{Duplicate} - 2\right|}{(\text{Duplicate} - 1 + \text{Duplicate} - 2) \div 2} \times 100$$

$$CV\ (\%) = \frac{\text{Standard Deviation (SD)}}{\text{Grand Mean (GM)}} \times 100$$

The assigned or known concentration of 139 Bq/L along with the suggested acceptance window, from 104 to 174 Bq/L (i.e. ±25% of known concentration), was used

Table 1. The two different LSC assays compared in this study[§]

Regions grid†	Full-spectrum assay		Region of interest (ROI) assay	
	Lower limit (keV)	Upper limit (keV)	Lower limit (keV)	Upper limit (keV)
A	0	2,000	130	700
B	0	2,000	150	1,800
C	0	2,000	0	2,000

[§]Lower and upper limits represent ranges of energy (in kilo-electric-volt) used in the two different LSC assays.

†Predefined counting channels with energy ranges in the Counts Per Minute (CPM) assay.

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Table 2. Various parameters of measurement uncertainty for radon in water for different methods of sample processing and LSC assays

Measurement uncertainty parameters	Simultaneous drawing in Mineral-oil	Separate drawing in Mineral-oil	Simultaneous drawing in Optifluor	Separate drawing in Optifluor
Full-spectrum assay: 0–2,000 keV Bq/L				
Measured range	63–98	79–112	75–99	87–121
Standard deviation	3.1	1.5	1.7	1.5
Standard uncertainty, u_c	3.1	1.5	1.7	1.5
Coverage factor, *k*	3	3	3	3
Expanded uncertainty, U_c	9.3	4.5	5.1	4.5
Region of Interest (ROI) assay: 130–700 keV Bq/L				
Measured range	138–201	152–205	109–180	114–168
Standard deviation	6.5	4.1	7.0	4.2
Standard uncertainty, u_c	6.5	4.1	7.0	4.2
Coverage factor, *k*	3	3	3	3
Expanded uncertainty, U_c	19.5	12.3	21.0	12.6

to evaluate the accuracy of the measured concentrations. The results generated by LSC at the University of Georgia radon-in-water laboratory were compared with results from several other laboratories across the US, which were generated by various methods. These laboratory results were obtained from the coauthor M.E. Kitto, New York State Department of Health.

Various parameters of measurement uncertainty such as standard deviation (SD), standard uncertainty (u_c), and expanded uncertainty (U_c) were calculated using 3 as the value of coverage factor, k, following the National Institute of Standards and Technology (NIST) guidelines (13), which, in turn, is based on the comprehensive ISO Guide to the Expression of Uncertainty in Measurement (14).

Results and discussion

Measurement uncertainty

With full-spectrum assay (0–2,000 keV), the expanded measurement uncertainty (U_c) for radon-in-water varied from 4.5 to 9.3 Bq/L for different methods of sample processing with the measured range of 63 to 121 Bq/L (Table 2). The measured range in ROI assay (130–700 keV) was higher, 109 to 205 Bq/L. The expanded measurement uncertainties (U_c) for different methods of sample processing in ROI assay were also higher, ranging from 12 to 21 Bq/L (Table 2).

Precision of individual duplicate measurement

There were four preparations ('Simultaneous Pipetting/Drawing in Mineral-oil', 'Separate Pipetting/Drawing in Mineral-oil', 'Simultaneous Pipetting/Drawing in Optifluor', and 'Separate Pipetting/Drawing in Optifluor') in duplicate in each of the 34 measurement events, for a total of 136 RPD values (4 × 34 = 136) to evaluate short-term precision of duplicate measurements in both full-spectrum (0–2,000 keV) and ROI (130–700 keV) assays (Table 3). For the full-spectrum assay (0–2,000 keV), out of 136 RPD values obtained from duplicate measurements of four different preparations in 34 measurement events during 2016–2022, 132 were under 15% RPD, 129 were under 10% RPD, and 104 were even under 5% RPD (Table 3 and Fig. 2). Duplicate measurements were remarkably precise for the ROI assay (130–700 keV) as well (Fig. 3). Out of 136 RPD values, 128 were under 15% RPD, 115 were under 10% RPD, and a good majority were under 5% RPD (Table 3). The observed low RPDs for each of the four sample preparations and two LSC assays suggest high preciseness of duplicate measurements based on a substantial number of repeated results despite the duplicates were prepared from two different bottles, and sample preparation and measurements were carried out by four laboratory personnel over the 6-year period from 2016 to 2022.

Table 3. Frequency distribution of Relative Percentage Difference (RPD) values under different thresholds

RPD thresholds	Number of RPD values	
	Region of Interest (ROI) assay (130–700 keV)	Full-spectrum assay (0–2,000 keV)
Below 5% (0–4.99%)	86	104
Below 10% (i.e. 0–9.99%)	115	129
Below 15% (i.e. 0–14.99%)	128	132
Above 15% (i.e. 15 and higher)	8	4
TOTAL: Below 15% + Above 15%	128 + 8 =136	132 + 4 =136

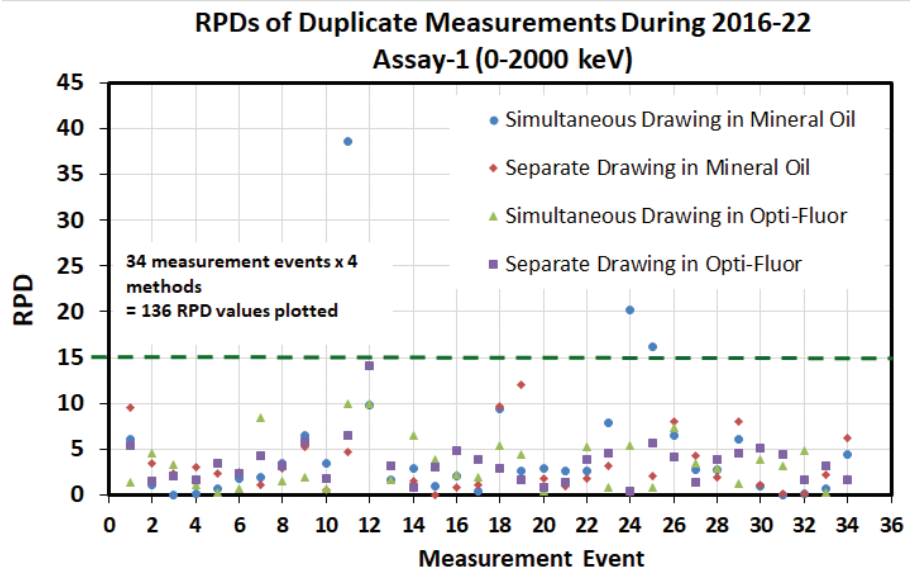

Fig. 2. Relative percentage difference between duplicate measurements of radon in the two ^{222}Rn-in-water 'Standard-15' and 'Standard-17' obtained from full-spectrum assay (0–2,000 keV). Note: 'Measurement Event' on the x-axis denotes 1st, 2nd, 3rd, …, 34th measurements carried out after full ingrowing (40–50 days) in each case.

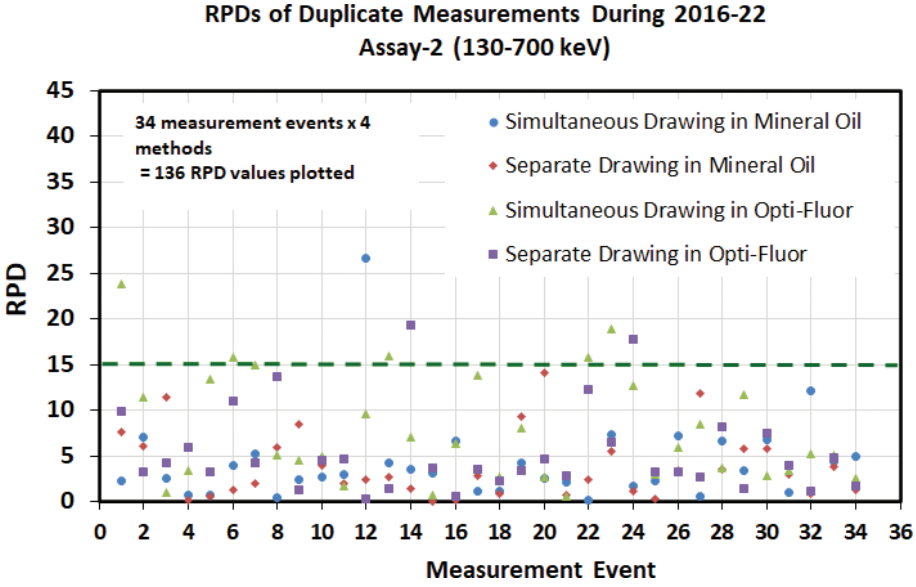

Fig. 3. Relative percentage difference between duplicate measurements of radon in the two ^{222}Rn-in-water 'Standard-15' and 'Standard-17' obtained from Region of Interest (ROI) assay (130–700 keV). Note: 'Measurement Event' on the x-axis denotes 1st, 2nd, 3rd, …, 34th measurements carried out after full ingrowing (40–50 days) in each case.

For long-term precision of the 34 measurement events over the 6 years, there were eight coefficients of variation (CVs) for four different preparations analyzed using full-spectrum and ROI assays. Each of these eight CVs was derived using 68 measured concentrations (34 × duplicate preparations = 68). In Fig. 4, it is evident that the CV was under 10% for all except for simultaneous drawing of sample plus Optifluor under the ROI assay. Even in this case, it was 13.2%, indicating that the long-term precision of the measurements was indeed excellent.

El-Araby et al. (15) analyzed radon using a CR-39 Nuclear Track Detector in 110 ground and drinking water samples from 11 different locations in Saudi Arabia and reported CV of duplicate analysis ranging 5.2 to 10.3% for radon concentrations ranging from 1,650 to 3,820 Bq/m^3. The CV of radon-in-water analysis by LSC in the present study is in agreement with that reported by El-Araby et al. (15). In contrast, analyzing radon-in-water in 59 well water samples from Haryana, India, using a RAD7 radon analyzer with a solid-state alpha detector, Duggal et al. (16)

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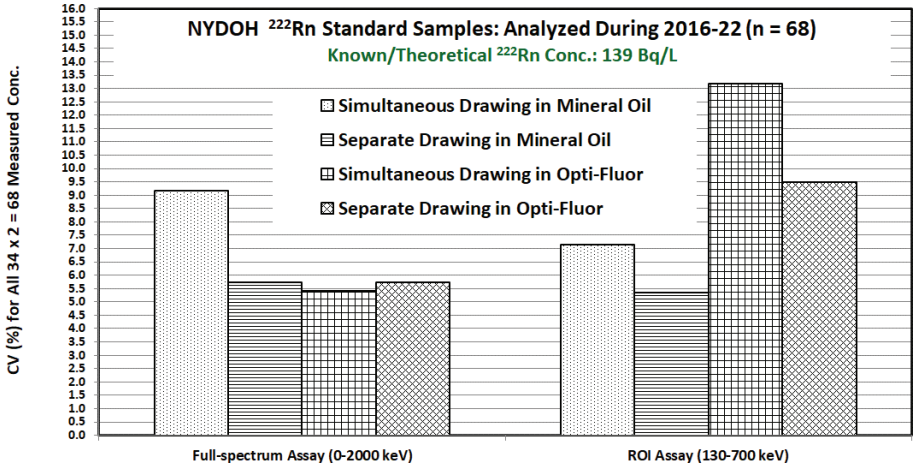

Fig. 4. Coefficient of variation (CV) of radon measurements in the two ^{222}Rn-in-water 'Standard-15' and 'Standard-17' for four different sample preparations under two Liquid Scintillation Counting (LSC) Assays.

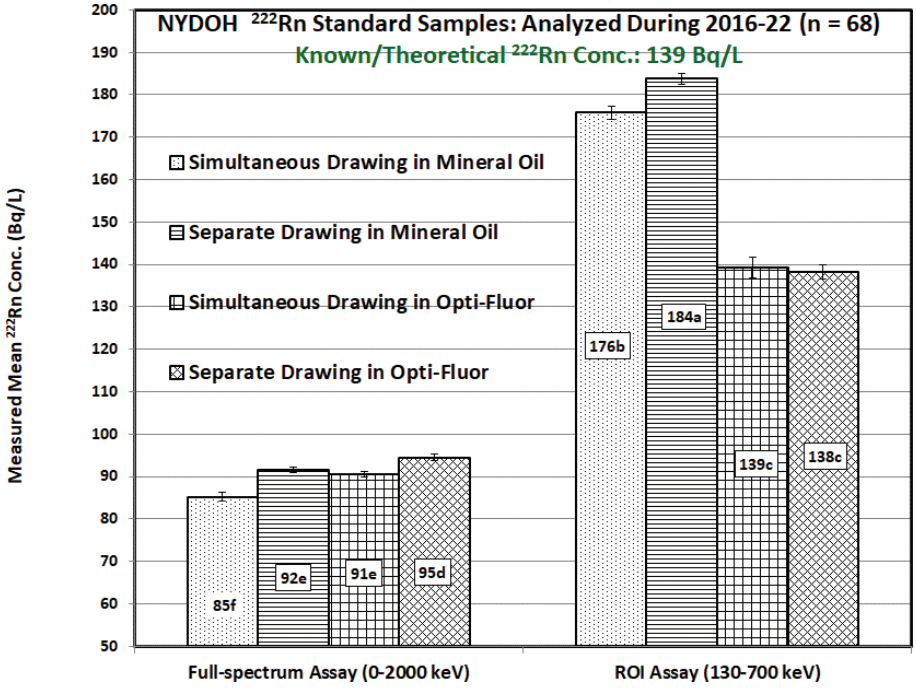

Fig. 5. Mean concentration of radon in the two ^{222}Rn-in-water 'Standard-15' and 'Standard-17' for four different sample preparations under two Liquid Scintillation Counting (LSC) Assays.

Note: The number on each bar is the mean concentration in Bq/L. Within a given group (Full-spectrum Assay or ROI Assay), the mean concentrations followed by the same letter do not differ significantly at 95% confidence interval.

reported CV of duplicate measurements ranging from 5.6 to as high as 43.8% for radon concentration ranging from 1,400 to 22,600 Bq/m^3. In both cases (15, 16), the authors did not report RPD of their replicated analysis.

Accuracy of measurements

Based on the mean results for four different sample preparations from two assays, it is evident that the ROI assay (130–700 keV) gave significantly higher radon count than full-spectrum assay (0–2,000 keV) for any given sample preparation (Fig. 5). Higher background counts coupled with higher quenching in full-spectrum assay (0–2,000 keV) might be responsible for the observed lower results. In contrast, the ROI assay (130–700 keV) excluded the counts below 130 keV, which was, indeed, from 'Bremsstrahlung' radiation. Cutting out the low-energy (below 130 keV) betas also reduced quenching and background (17), thereby yielding higher results. Under full-spectrum assay (0–2,000 keV), all preparations gave similar mean

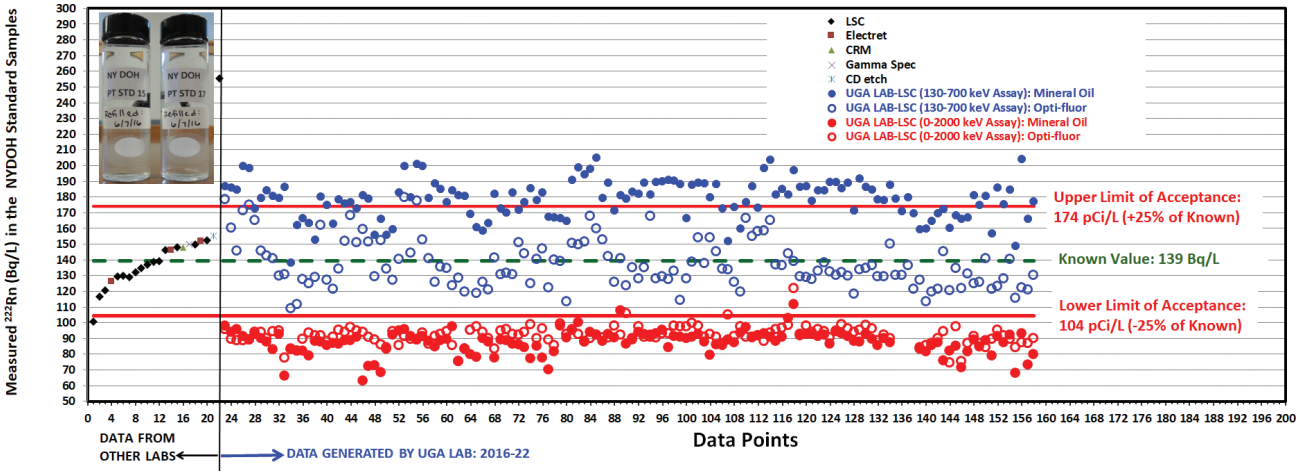

Fig. 6. Radon levels in the two ^{222}Rn-in-water 'Standard-15' and 'Standard-17' in 34 consecutive measurements at around 40–50-day interval at the University of Georgia (UGA) laboratory to compare:

- Two different LSC assays: Full-spectrum assay (0–2,000 keV) *versus* Region of Interest (ROI) assay (130–700 keV)
- Two different scintillation fluids: Mineral-oil *versus* Optifluor.

Note: The UGA laboratory results (data points 23 onward on the x-axis) generated by LSC have been plotted together with the results of an earlier study (obtained from the coauthor M.E. Kitto, New York State Department of Health) from different laboratories across the United States generated by various methods (data points 1–22 on the x-axis).

results except 'Simultaneous Drawing in Mineral-oil', which was significantly lower than the rest (Fig. 5). With ROI assay (130–700 keV), the two Mineral-oil preparations gave significantly higher radon count than the two Optifluor preparations. There was no significant difference in radon counts due to simultaneous and separate drawing of water and scintillation fluid for Optifluor; however, separate drawing gave significantly higher counts than simultaneous drawing for Mineral-oil. The most remarkable observation was that the Optifluor preparations gave mean radon concentration very close to the known or theoretical concentration of 139 Bq/L, whereas Mineral-oil preparations gave mean radon concentration significantly higher than known or theoretical concentrations (Fig. 5). The aforementioned results are in good agreement with the findings reported by Saha et al. (8) from a study with household well water samples; however, a possible explanation of such observations is not currently available in literature, which needs further research.

In Fig. 6, 21 out of the first 22 results from other laboratories (9) were within the acceptance window. The methods used by other laboratories producing these first 22 results (Fig. 6) included LSC (18, 19), Electret (19), Continuous Radon Monitor (CRM), Gamma ray (germanium) detectors (20), and Compact Disk (CD) etch detector (21). A concise description of these methods is available elsewhere (9). While this provided some preliminary evidence that methods other than LSC may also be suitable for measurement of ^{222}Rn in both standard and routine samples, the suitability is yet to be confirmed based on repeated measurements over a substantially long period of time as demonstrated for our proposed method.

As evident in Fig. 6, all results from the University of Georgia (UGA) laboratory generated by the full-spectrum (0–2,000 keV) assay were lower than the lower limit of acceptance (75% of the known), which means they all failed. Among the results generated by ROI (130–700 keV) assay, the data points for the samples prepared in Mineral-oil were mostly higher than the upper limit of acceptance, which means they also failed in most cases. In sharp contrast, all results from Optifluor under ROI assay were acceptable, and at least half of them were very close to the known or theoretical radon-in-water concentration. Therefore, the full-spectrum assay with both Mineral-oil and Optifluor can grossly underestimate the actual radon-in-water concentration, and with ROI assay (130–700 keV), Mineral-oil can over-estimate the radon-in-water concentration. Both should be avoided. This 6-year study shows that these samples can serve as a reusable proficiency test sample when measured in Optifluor with the ROI assay, and this could be part of a nationally coordinated proficiency program and adopted by laboratories testing radon-in-water. Carefully prepared samples of this type could also serve as a very important quality assurance milestone for the laboratories, if properly maintained and analyzed periodically allowing full ingrowing for at least 30 days.

Conclusion and implications

Repeated analyses of two reusable ^{226}Ra-free radon-in-water standards, prepared using a ^{226}Ra loaded filter paper sandwiched in between polyethylene sheeting (9, 10), regenerated at 40- to 50-day ingrowth over a period of

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6 years (2016–2022), consistently yielded excellent precision (based on duplicate analyses) regardless of the sample preparation methods or LSC assays evaluated. The accuracy (closeness of measured concentration to the theoretical concentration) was also excellent all along over the 6-year study period when prepared in Optifluor and analyzed using ROI assay (130–700 keV). This approach is recommended for laboratories analyzing radon-in-water using LSC. As a scintillator for radon-in-water, it is widely believed that Mineral-oil is better than Optifluor; however, our results show that the opposite is true.

The reported results provided necessary evidence that these standards can serve as reusable proficiency test samples when measured in Optifluor with the ROI assay. A proficiency test for radon-in-water was thought to be difficult if not impossible because it was a common belief that as a dissolved gas, radon-in-water would not be stable enough to produce a testable sample, and the magnitude of loss of gas from the water could be random. However, these findings from our 6-year study clearly show that developing and implementing a proficiency test for radon-in-water is indeed possible, thereby filling the gap in this critical aspect of analyzing radon-in-water. In this study, we evaluated and discussed the results based on the acceptance window of ±25% (of the known) as used in a previous small-scale study (9). Once a nationally/internationally coordinated proficiency test is made available, it is likely that participating laboratories will be reporting results with progressively higher accuracy leading to a lower interlaboratory standard deviation and a narrower acceptance window in the proficiency test reports. This is a common trend of any new method in analytical chemistry, and we expect analysis of radon-in-water would follow the same trend.

Testing radon-in-water is a serious endeavor because the reported results can have both health and cost consequences. Without a documented proficiency test, there is a lack of confidence in the accuracy of the results from routine samples. Significantly lower and higher than the actual radon concentration could lead the homeowner to feel falsely safe and to spending for unnecessary mitigation, respectively. The results presented and discussed here merit the attention of all potential stakeholders dealing with radon-in-water such as researchers, policy makers, and testing and mitigation industries toward achieving excellence in this under-investigated, but important area.

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