Evaluation of radon concentration measurements in water using the radon degassing method

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Abstract

This study was the first to determine the effectiveness of radon concentration measurement in water using the degassing method as a screening method based on the liquid scintillation counter method. The degassing method used two radon monitors (AlphaGUARD and RAD7) and two monitor-attached degassing devices (AquaKIT and RAD H_2O). These were effective screening methods based on the WHO guideline value of 100 Bq L^{-1}. The screening values confirmed that a combination of the AlphaGUARD and AquaKIT was preferred. The results are useful for radon measurement for exposure control in drinking water and environmental in-situ field measurement.

Keywords Degassing · Radon · Exposure control · In-situ field measurement

Introduction

Radon (^{222}Rn) is a naturally occurring radioactive gas that is inert, colorless, and odorless. Radon and its parent nuclide, ^{226}Ra, belong to the uranium decay series and have a half-life of 3.82 days [1]. The dissolution water/gas partition coefficient, K, of radon is 0.260 at 20 °C [2]. Environmental measurement of groundwater radon concentration has been used as a tracer and precursor in several hydrogeological and geological applications, such as earthquake predictions and geochemical explorations. [3].

According to the United Nations Scientific Committee on the Effects of Radon on the Environment (UNSCEAR), estimates of the radon transfer coefficient from water to indoor air-derived from existing published data elucidated a mean value of 10^{-4} [4]. Currently, the World Health Organization (WHO) Guidelines for Drinking Water Quality do not provide recommended radon levels because it is considered more appropriate to measure radon concentrations in indoor air than in drinking water [5]. However, the WHO's 2004 guidelines on radon in drinking water state that radon levels in drinking water should be controlled if it exceeds 100 Bq L^{-1} (hereinafter referred to as the WHO guideline value) in public water supplies [6]. The implementation of the EC Directive 2013/51/EURATOM on October 22, 2013 has also led to limit values being set for the concentration of radon in water for human consumption [7].

Theory

The liquid scintillation counting (LSC) method is the most common method for radon detection, which extracts radon in water into an organic scintillator and measures the radon concentration [8]. However, the use of organic scintillators (harmful organic solvents) should be avoided because they

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are difficult to transport by airplane to different parts of the world for measurements. In addition, the LSC method is not suitable for in-situ measurements, which are often conducted for environmental measurements. Therefore, degassing devices that can transfer radon from the aqueous phase to the air phase through aeration have attracted attention for use with conventional radon-in-air monitors which measure radon concentrations in the air [9]. Using a radon-in-air monitoring device equipped with this degassing system can measure the radon concentration in water without using an organic scintillator.

On the other hand, Kozak et al. [10] reported that the AlphaGUARD and AquaKIT (AlphaGUARD (ionization chamber) equipped with an AquaKIT system (Bertin Technologies SAS, France)) [11] provided good results compared to the LSC method. However, the results of the RAD7 and RAD H_2O (RAD7 (semiconductor detector) equipped with a RAD H_2O system (Durridge Company, USA)) [12] were lower than those of the LSC method [13–15]. Higuchi et al. [14] found that RAD7 and RAD H_2O with leak prevention detected radon concentrations of 9.0–89 Bq L^{-1} under a relative humidity of $\leq 6\%$ in the inner chamber of the RAD7 device. Furthermore, Takakaze et al. [16] found that RAD7 and AquaKIT (RAD H_2O in the RAD7 and RAD H_2O was replaced with the AquaKIT) detected radon concentrations of 41–129 Bq L^{-1} under a relative humidity of $\leq 6\%$ in the inner chamber of the RAD7 device.

The degassing method is recommended by the International Organization for Standardization (ISO) [9] to measure radon concentration in water. However, the United States Environmental Protection Agency (US EPA) do not adopt the degassing method to measure radon in water because it requires advanced techniques [17, 18]. Only the LSC method is recognized by both the ISO [9] and US EPA [18].

After an accident at Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Station which contaminated a wide range of soil and food products with radioactive materials, testing procedures were initiated using the index values of food etc. published by the Nuclear Safety Commission as provisional regulation values. For this purpose, the Japanese Ministry of Health, Labor, and Welfare (MHLW) established a screening method that reliably identifies samples with radioactive concentrations lower than the provisional regulation value [19]. As a result, it has become possible to perform the following assessments: (1) confirming the effectiveness of a given screening device; and (2) confirming screening values to identify specimens that are reliably lower than the provisional regulation values. In addition, when the result of the screening device measurement is a value higher than the screening value, further precise measurements are performed to determine the test result.

Therefore, considering these imminent problems regarding the quality of drinking water, in this study, we measured the radon concentration using the AlphaGUARD and AquaKIT and compared the results with those of the LSC method. In this study, a desiccant was also attached to reduce the damage caused by exposing the inside of the AlphaGUARD to high humidity. This study aimed to compare the screening values of the degassing system with previous studies [14, 16] and provide recommendations regarding the effectiveness of each method.

Experimental

A degassing method using the AlphaGUARD and AquaKIT (BertinInstruments, France) was used to measure radon concentrations in water (Fig. 1) and was compared to an LSC method as the reference. Groundwater previously sampled at Kobe Pharmaceutical University in Kobe Japan had a radon concentration of ~ 200 Bq L^{-1}, our research team reported [20]. The groundwater was diluted with tap water to various concentrations to make experimental samples. One test sample was measured using the degassing method, and three reference samples were measured using the LSC method.

Figure 1 shows the AlphaGUARD and AquaKIT in which the AquaKIT, a filter, and the AlphaGUARD were placed in a closed loop. The AquaKIT consisted of degassing and security vessels. A tube containing 5 g of desiccant (Drierite, W. A. Hammond Drierite Co. Ltd., 10–20 mesh) was connected to the glass tube of the security vessel to reduce humidity inside of the AlphaGUARD.

The experimental sample (0.1 L) was poured into the degassing vessel as a test sample. The pump was used to aerate the sample and transfer the radon to the entire AlphaGUARD at an air flow rate of 0.3 L min^{-1} for 10 min. After stopping the pump, the radon concentration was measured four times for 5 min each (20 min total). The radon concentration, C_{R1} (Bq L^{-1}), was the average of the four original display values
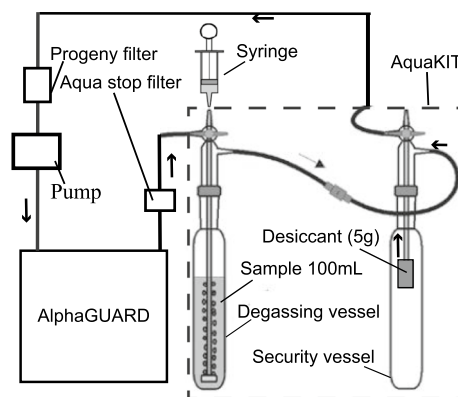

Fig. 1 Schematic diagram of the AlphaGUARD and AquaKIT. The AquaKIT consists of degassing and security vessels. This figure is modified from Takakaze et al. [16] and AlphaGUARD manual [11]

measured with the AlphaGUARD, which was calibrated using the standard radon gas in a radon exposure chamber located at Hirosaki University in Aomori, Japan [21]. The calibration constant of the AlphaGUARD was determined to be $f_1 = 0.932$. The background value, C_{B1} (Bq L^{-1}), of the device was measured using nitrogen gas without radon. From this C_{R1}, we calculated the radon concentration in the water, C_{R2} (Bq L^{-1}), using Eq. (1) [11].

$$C_{R2} = \frac{(C_{R1} - C_{B1})}{f_1}\left(\frac{V_A}{V_W} + K\right) \tag{1}$$

where K is the water/gas partition coefficient of radon, V_W (L) is the volume of the water sample (0.1 L), and V_A (L) is the air volume of the system. The V_A was obtained by subtracting the volume of the desiccant (0.014 L) and V_W from the volume of the system (1.122 L) [11]. The K was calculated using the mole fraction solubility at the sample water temperature using the formula given by Gevantman [2].

The values of C_{R2} were indicated by high values for the reduced humidity of the AlphaGUARD using the desiccant. Radon and radon progeny nuclides (main nuclide: ^{218}Po) were present in the detector. Radon progeny nuclides became positively charged ions due to their metallic nature. Decreased humidity reduced the number of water particles attached to the ions, and the counting efficiency of alpha rays emitted from the ions was thought to increase due to reduced shielding by the water particles. Therefore, the correction coefficient was determined to be $f_2 = 1.30$ using water samples with a radon concentration of ~150 Bq L^{-1}. The radon concentration, C_R (Bq L^{-1}), of the test sample was converted from C_{R2} by f_2 using Eq. (2).

$$C_R = \frac{C_{R2}}{f_2} \tag{2}$$

In the LSC method, three reference samples were prepared using the experimental sample. The reference sample (10 mL) was added to a highly efficient mineral oil scintillation cocktail (10 mL; PerkinElmer Inc., USA) in a 20 mL glass LSC vial (PerkinElmer Inc., USA). The vials were shaken for 30 s to extract radon from the water into the scintillator and left for ~4 h until radon and its descendants achieved radiation equilibrium. The average counting ratio of the three reference samples was measured using the integral counting method of the LSC method (2300TR, PerkinElmer Inc., USA) for 60 min. The radon concentration, C_S (Bq L^{-1}), was converted from the average counting rate of the three reference samples [8].

Screening method

To determine the screening criteria of the WHO guideline value (100 Bq L^{-1}), numeric values for the following two criteria were established based on the MHLW screening method [19]. In the first criterion, the limit of detection (LOD) must be < 25 Bq L^{-1} (i.e., one-quarter of the WHO guideline value, 100 Bq L^{-1}). In the second criterion, an effective screening value was established. Using experimental data, a linear regression (black line in Fig. 2) and a 99% prediction interval (99% PI; grey zone in Fig. 2) were determined. In this study, the 99% prediction interval was
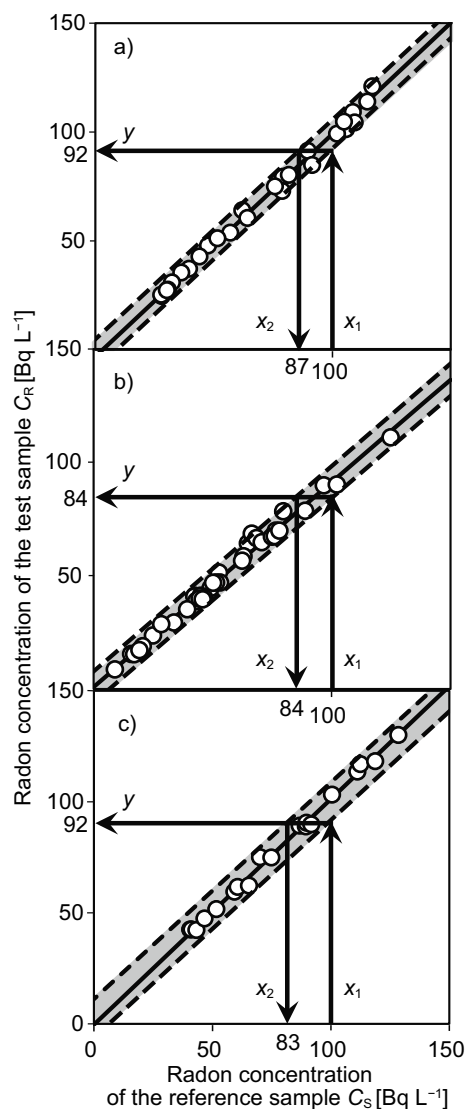

Fig. 2 Assessment of the screening value of the three degassing methods. The black line is regression line, and the grey zone is the 99% prediction interval. **a** the AlphaGUARD and AquaKIT, x_1: the WHO guideline value, y: the test screening value, x_2: the reference screening value, **b** the RAD7 and RAD H$_2$O, **c** the RAD7 and AquaKIT

calculated in IBM SPSS Statistics V.22.0.0 (SPSS Inc., Chicago, IL, USA). The y value in Fig. 2a is a candidate value of the screening value used for acceptance or rejection when the degassing method was used for screening. When $Cs = x_1$ in Fig. 2a (the WHO guideline value of 100 Bq L^{-1}), C_R is mostly (99.5%) larger than the y value, and the sample is rejected. When $Cs = x_2$ in Fig. 2a, C_R is mostly (99.5%) smaller than the y value, and the sample is accepted. If the y and x_2 values are > 50 Bq L^{-1} (i.e., half of the WHO guideline value), the screening method is established. If the degassing method met the above two criteria, the y value can be used for acceptance or rejection as the screening value.

Results and discussion

A total of 59 experiments were conducted in the radon concentration range of 7–117 Bq L^{-1}.
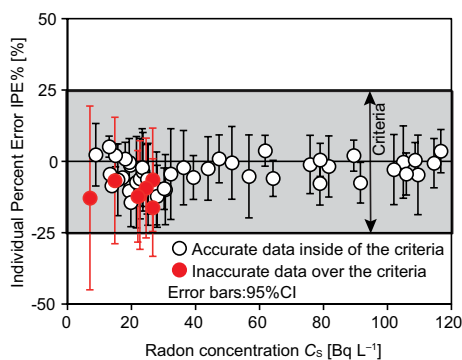

Fig. 3 Assessment of lower limit of quantification (LOQ) based on Individual Percent Error (IPE %)

Lower limit of detection (LOD) and quantification (LOQ)

The LOQ was determined using the difference between the values obtained by the degassing and reference methods. The criteria for quantitative measurement were met at the 95% confidence interval (95% CI) of Individual Percent Error (IPE%), which existed between −25 and 25% [22, 23]. Figure 3 shows the relationship between the C_S and IPE% values of the AlphaGUARD and AquaKIT used to determine the accuracy. When the 95% CI of IPE% (the error bars in Fig. 3) is within the criteria (the grey zone in Fig. 3) [22, 23], the verification measurement is considered accurate. The verification measurement of the AlphaGUARD and AquaKIT showed a minimum quantifiable value of 28 Bq L^{-1}. The LOD, considered to be 1/3 of the LOQ [24], was 9.3 Bq L^{-1}. Similarly, Table 1 shows the LOQs and the LODs of other degassing methods obtained in a previous study [16]. All degassing methods in Table 1 met the first criterion of the screening method because the LOD was < 25 Bq L^{-1}.

Effectiveness of the degassing method as a screening method

The data exceeding the above-estimated LOQ was used as the analysis data. Using these data, a linear regression (black line in Fig. 2) and a 99% prediction interval (99% PI; grey zone in Fig. 2) were determined. Figure 2a shows the results of the AlphaGUARD and AquaKIT. Figure 2b shows the results from the RAD7 and RAD H_2O method, which were taken from Takakaze et al. [16] (see Fig. 4 in [16]). The results were below 100 Bq L^{-1}. In order to determine the screening value of the reference value (100 Bq L^{-1}), results exceeding 100 Bq L^{-1} were necessary. Therefore, three results above 100 Bq L^{-1} were added to the experimental

Table 1 Comparison of the three degassing methods

	AlphaGUARD & AquaKIT	RAD & RAD H_2O[9]	RAD & AquaKIT[9]
Radon monitor	AlphaGUARD (Free-air ionization chamber)	RAD7 (Semiconductor detector)	RAD7 (Semiconductor detector)
Degassing unit	AquaKIT	RAD H_2O	AquaKIT
Sample water	100 mL	250 mL	100 mL
Need for leak prevention	unnecessary	requirement	unnecessary
y in Fig. 2	92 Bq L^{-1}	84 Bq L^{-1}	92 Bq L^{-1}
x_2 in Fig. 2	87 Bq L^{-1}	84 Bq L^{-1}	83 Bq L^{-1}
LOQ	28 Bq L^{-1}	9 Bq L^{-1}	41 Bq L^{-1}
LOD	9.3 Bq L^{-1}	3 Bq L^{-1}	14 Bq L^{-1}
Screening	Valid		
Method	LOD < 25 (Bq L^{-1})		
Evaluation	The y and x_2 values in Fig. 2 > 50 (Bq L^{-1})		

results from Takakaze et al. [16]. Figure 2c shows the results of the RAD7 and AquaKIT method which were also taken from Takakaze et al. [16] (see Fig. 2 in [16]). The value of x_2 in Fig. 2c was changed to 83 Bq L^{-1} based on our recalculation, although it was initially noted as 84 Bq L^{-1} by Takakaze et al. [16].

Regarding the second criterion of the AlphaGUARD and AquaKIT, when the value of x_1 in Fig. 2a met the WHO guideline value (100 Bq L^{-1}), y in Fig. 2a was 92 Bq L^{-1}. The value of x_2 in Fig. 2a was 87 Bq L^{-1}. All degassing methods in Table 1 met the second criterion of the screening method because their the y and x_2 values were > 50 Bq L^{-1}.

The effectiveness of all degassing systems as a screening method was confirmed by comparing them with the LSC method as a reference, and the results are shown in Table 1. The screening values of the AlphaGUARD and AquaKIT and the RAD7 and AquaKIT were closer to the WHO guideline value (100 Bq L^{-1}) than that of the RAD7 and RAD H_2O. Furthermore, for the RAD7 and RAD H_2O, the requirement to leak prevention was a disadvantage. The LOD of the AlphaGUARD and AquaKIT were smaller than that of the RAD7 and AquaKIT. Therefore, when screening for radon concentration in water using the degassing method, it is recommended to use the AlphaGUARD and AquaKIT.

Conclusions

Radon concentration in water is typically measured using the LSC method; however, this method uses a harmful organic solvent as a liquid scintillator and is difficult to use in situ. Therefore, the degassing method is a viable alternative because it allows the measurable range to be expanded. Water samples with a radon concentration of > 28 Bq L^{-1} could be quantitatively measured using the AlphaGUARD and AquaKIT. By attaching a desiccant to the AlphaGUARD and AquaKIT, the damage to the AlphaGUARD caused by high humidity was reduced in this study. Further, the other two studied degassing systems were effective. Based on the above, all degassing systems in Table 1 were effective as screening devices because they satisfied two criteria.: first, the LOD were < 25 Bq L^{-1}, and second, the the y and x_2 values in Fig. 2a were > 50 Bq L^{-1} (50% of the WHO's guideline value). In this study, the LOQs were obtained from actual values, and the LOD was determined as 1/3 of the LOQ. The screening values of the AlphaGUARD and AquaKIT and the RAD7 and AquaKIT were closer to the WHO guideline value (100 Bq L^{-1}) than that of the RAD7 and RAD H_2O. Furthermore, the requirement for the RAD7 and RAD H_2O to leak prevention was a disadvantage. The detection limits of the AlphaGUARD and AquaKIT were smaller than the RAD7 and AquaKIT. Therefore, when screening for radon concentration in water using the degassing method, it is recommended to use AlphaGUARD and AquaKIT with a desiccant.

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