温泉科学（J. Hot Spring Sci.），64，402-408（2015）

短　　報

Measuring Radon in High Humidity Air Using Anhydrous Calcium Sulfate and an Activated Charcoal Detector

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(Received Nov. 17, 2014, Accepted Feb. 27, 2015)

硫酸カルシウムと活性炭型検出器を用いた高湿度環境下における空気中ラドンの測定

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要　　旨

温泉法および鉱泉分析法指針では，地下水中ラドン濃度が74 Bq/kg以上で温泉，111 Bq/kg以上で療養泉に該当すると規定されている．ラドン（^{222}Rn）は希ガスの天然放射性核種であり，容易に空気中に揮散することから，放射能泉の利用による被ばく線量評価のためには，簡便で正確な空気中ラドン濃度の測定手法の確立が求められている．これまでに筆者らは，活性炭型検出器と液体シンチレーションカウンタを用いた空気中ラドンの簡易測定法を報告してきたが，同検出器はラドン捕集部に活性炭を使用しているため，放射能泉利用施設の浴室内など，特に高湿度環境における測定の際，環境中の水蒸気が活性炭の多孔質部に吸着し，感度低下を引き起こすことが分析上の課題とされてきた．

本研究では，硫酸カルシウムを主成分とする乾燥カラムを活性炭型検出器に装着することにより，除湿処理を伴う空気中ラドンの分析の検討を試みた．相対湿度30%，60%，80%の各ラドン標準場で，空気中ラドン濃度約1,000 Bq/m^{3}の曝露を行った検出器を液体シンチレーションカウンタによる測定に供した．その結果，本測定条件下での変換係数が2.42±0.14（湿度

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80% 温度 20℃）と算出された．乾燥カラム装着による若干の感度低下は認められるものの，測定値の定量性は担保されていることから，本手法が高湿度かつラドン高濃度環境下における簡易的・汎用的な空気中ラドンの測定手法としての有効性を示唆しているものと考えられる．

キーワード：ラドン，高湿度環境，液体シンチレーションカウンタ，活性炭型検出器，放射能泉

Abstract

According to the Japanese Hot Springs Law and the Guidelines for Analysis of Kosen (fluid-type hot springs), spring water containing more than 74 Bq/kg of radon is regarded as a hot spring and one with a radon level more than 111 Bq/kg is regarded as a medical spring, also called a radioactive spring. Radon (^{222}Rn) is a radioactive element derived from the earth and a chemically inert rare gas. Therefore, to evaluate the exposure dose due to radioactive spring usage, it is important to establish an easy and accurate method to measure radon concentration in air. We have previously reported on a relatively convenient handling and highly versatile measurement method of radon concentration in air that uses both an activated charcoal detector and a liquid scintillator. The radon trapping point of the detector is made of activated charcoal. When activated charcoal detector is set up in environment with high humidity such as the bathing rooms of radioactive spring facilities, the porous component of the activated charcoal adsorbs water vapor in the air, resulting in change of detector sensitivity and issues with this measurement method.

In this study, we installed an acrylic desiccant column containing anhydrous calcium sulfate on the activated charcoal detector and performed dehumidified examinations of radon concentration in air. In a radon chamber, the radon concentration in air was set to about 1,000 Bq/m^3 and the relative humidity was set to 30% (low), 60% (normal), and 80% (high). Immediately after the exposure, we added a toluene solution of DPO (2,5-diphenyloxazole) + POPOP (1,4-bis(5-phenyl-2-oxazolyl)benzene) as a liquid scintillator, and used it to measure radon concentration with a liquid scintillation counter. The conversion coefficient under these measurement conditions was 2.42 ± 0.14 (relative humidity : 60% ; air temperature : 20℃). Although detector sensitivity was slightly lowered by installing the acrylic desiccant column, the examinations reveal that this measurement method is valid for quantitative analysis. Therefore, our measurement method allows for convenient handling, high versatility, and efficient measurement of radon concentration in air under high radon concentration and humidity.

Key words : radon, high humidity environment, liquid scintillation counter, activated charcoal detector, radioactive spring

1. Introduction

The ledger record of Mie Prefecture lists about 250 hot springs, including about 10 radioactive springs. Radon (^{222}Rn) is a main feature of radioactive springs. Rn-222 is a radioactive element formed by decay of ^{226}Ra in uranium series in the earth's crust and it is a chemically inert rare gas. Based on the Japanese Hot Springs Law (Government of Japan, 1948) and the Guidelines for Analysis of Kosen (fluid-type hot springs) (revised) (Ministry of the Environment, Nature Conservation Bureau of Japan, 2014), a spring is considered a "hot spring" if 1 kg of the spring water contains at least 74 Bq (20×10^{-10} Ci, 5.5 Mache) of radon. Similarly, if 1 kg of spring water contains at least 111 Bq (30×10^{-10} Ci, 8.25 Mache) of radon, the spring is considered a "medical hot spring" with "radioactive hot spring" properties.

Radon rapidly diffuses into air, so it is necessary to measure radon in the air at radioactive spring facilities to estimate the exposure dose (Mori *et al.*, 2013a ; 2014). We have previously reported on a relatively convenient handling and highly versatile measurement method of radon concentration in air that uses an activated charcoal detector and a liquid scintillator (Mori *et al.*, 2013b). The radon trapping point of the detector is made of activated charcoal. When samples are collected in high humidity environments, such as the bathing rooms of radioactive spring facilities, the porous component of the activated charcoal adsorbed water vapor in the air, decreases the detector sensitivity and causes problems with this measurement method (Iimoto *et al.*, 2005).

The present study focuses on this issue and investigates a suitable analytical method for measuring the concentration of radon in high humidity air, with detector comprising a desiccant made of anhydrous calcium sulfate, an activated charcoal detector, and a liquid scintillation counter.

2. Methods

We used a PICO-RAD radon detector (AccuStar Labs, USA) (hereafter referred to as "the detector") to collect radon in air. The detector adsorbs radon onto activated charcoal, providing convenient handling and high versatility. The air measured in a radon chamber under each humidity level was dehumidified with an anhydrous calcium sulfate desiccant (Drierite, 8 mesh ; W.A. Hammond Drierite Company, Ltd., USA) to avoid the decrease in detector sensitivity caused by water vapor adsorbed onto activated charcoal (Fig. 1). The desiccant itself adsorbs almost no radon from the air (Tajika *et al.*, 2014).

The radon chamber at the National Institute of Radiological Sciences (NIRS) allows for the adjustment of airborne radon concentrations and humidity settings. We built three acrylic columns, with lengths of 73 mm (A), 85 mm (B), and 110 mm (C), to determine the optimal desiccant column length. We filled each column with calcium sulfate, and placed them in the radon chamber. We also prepared a detector with a desiccant column (No. 1), a detector with no desiccant column in a resealable polyethylene bag with thickness 0.04 mm (No. 2), and a detector with no desiccant column or polyethylene bag (No. 3).

The detectors equipped with desiccant columns were exposed to the radon chamber at NIRS for 48 h. The radon concentration in the air was set to about 1,000 Bq/m^3, the temperature was 20℃, and the relative humidity was set to 30% (low), 60% (normal),

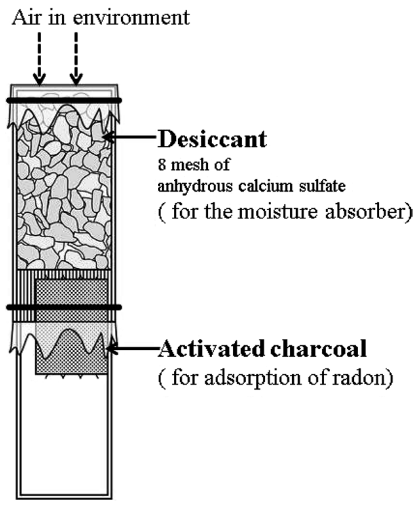

Fig. 1　Schematic drawing and cross-sectional views of the PICO-RAD activated charcoal radon detector (after Iimoto *et al.*, 2005), equipping an acrylic column of desiccant (anhydrous calcium sulfate). The lengths of the column were set as A=73 mm, B=85 mm, and C=110 mm to determine the most appropriate desiccant column length.

Table 1　Analytical methods used in this study for measuring radon in air. The measurement conditions follow our previous study (Mori *et al.*, 2013b)

Item	Method
Field fixation	Toluene fixation
Measurement device	ALOKA LSC LB-5 (Hitachi-Aloka Medical Co., Ltd.)
Detector	Activated charcoal detector PICO-RAD (AccuStar Labs)
Scintillator	DPO + POPOP toluene solution DPO (DOJINDO 2,5-diphenyloxazole, $C_{15}H_{15}NO$) POPOP (DOJINDO 1,4-bis(5-phenyl-2-oxazolyl)benzene $C_{24}H_{16}N_2O_2$) DPO+POPOP toluene solution: DPO (20 g) and POPOP (0.5 g) were dissolved in 1,000 mL of toluene to prepare the scintillator; after adsorption of the detector, 15 mL of the liquid scintillator was added to the detector as soon as possible.
Analysis time	60 min
Temperature at extraction	15 °C
Calculation method	Integral bias method
Window width	TRIPPLE (20–2,000 keV, 40–2,000 keV, 60–2,000 keV)
Dehumidification	No. 1: Installed acrylic desiccant column (Lengths: A:73 mm, B:85 mm, and C:110 mm) Desiccant: 8-mesh anhydrous calcium sulfate (W.A. Hammond Drierite Company, Ltd.) No. 2: In resealable polyethylene bag Thickness 0.04 mm No. 3: No desiccant column or polyethylene bag (control)

and 80% (high). A toluene solution of 2,5-diphenyloxazole (DPO) and 1,4-bis(5-phenyl-2-oxazolyl) benzene (POPOP) was used as a liquid scintillator. The liquid scintillation counter (LSC ; ALOKA LSC LB-5, Hitachi Aloka Medical, Ltd., Japan) was also used. The measurement conditions and reagents (Table 1) follow our previous study (Mori *et al.*, 2013b).

From the results of the LSC measurements, net counts per second (*netcps*) were converted into radon concentration according to Eq. (1).

$$Rn(Bq/m^3)=netcps\times\frac{1}{0.7264}\times\exp\left(\frac{0.693\times(t_4-t_2)}{3.825}\right)\times\frac{1}{1-\exp\left(\frac{-(t_2-t_1)}{18/24}\right)}\times\frac{1}{1-\exp\left(\frac{-(t_4-t_3)}{2/24}\right)}\times1\times37\times A \cdots(1)$$

netcps : net counts per second

t_1 : starting time of exposure in the radon chamber

t_2 : ending time of exposure in the radon chamber

t_3 : adding time of the liquid scintillator

t_4 : measurement time using the liquid scintillation counter

A : conversion coefficient

Detailed specifications for Eq. (1) are given by Passo and Floeckher (1991), Shefsky (1998), and Mori *et al.* (2013b). Radon concentrations in the chamber were measured with the AlphaGUARD (PQ2000Pro, Genitron Instruments, GmbH) at the NIRS, which was accurately calibrated in the

Physikalisch Technische Bundesanstalt, Germany (on March 2013), and was assumed to give true values. This study aims to determine the conversion coefficient A under the measurement conditions using the desiccant column.

3. Results and Discussion

3-1. Difference in detector sensitivity by column length

Table 2 shows the values measured by the detector for the three column lengths. This study focuses on differences in measured values for each column length and amount of desiccant in the column.

The result under measurement condition A for the shortest column was 1,027 Bq/m^3 (a reference value; radon concentration was calculated by conversion coefficient $A = 1.55$ (Mori *et al.*, 2013b)) and the result under measurement condition C for the longest acrylic column was 790 Bq/m^3. The longer column thus lowered sensitivity, by a factor of about 80%. The weight of the desiccant in measurement condition A was 4.031 g, and that under measurement condition C was sevenfold higher, at 29.564 g. In the next examination we therefore focused on measurement condition C, which had the longest column length, because despite the lower sensitivity, it showed higher performance for dehumidification. We believe that the appropriate length of the desiccant column depends on the humidity of the environment.

3-2. Difference in detector sensitivity by dehumidification method

We adjusted the humidity in the radon chamber, and exposed the detectors equipped with a desiccant column or polyethylene bag. Table 3 shows the conversion coefficients that were derived from the measurement results for each relative humidity.

The conversion coefficient (A) was from 2.36 to 2.48 under measurement condition No. 1, in which the desiccant column was installed in the activated charcoal detector. The conversion coefficient (A) was from 1.07 to 1.14 in control experiment No. 3, in which no desiccant column was installed in the activated charcoal detector. Compared with experiment No. 3, the desiccant column in No. 1 decreased the detector sensitivity somewhat. The coefficient of variation (CV) was 7.12 at 30% relative humidity, 2.46 at 60% relative humidity, and 5.78 at 80% relative humidity. The small variation in these data suggests that this measurement method is valid for quantitative analysis.

Table 2　Differences in sensitivity by acrylic column length and amount of desiccant

Measurement condition	Length of acrylic column (mm)	Weight of desiccant (g)	Amount of moisture after exposure (g)	Radon concentration (reference value) (Bq/m^3)
A	73	4.031	0.431	1,027
B	85	5.474	0.527	836
C	110	29.564	0.888	790

※ Exposure time 48h; air temperature in radon chamber 20℃; relative humidity 60%; n = 1.
※ Radon concentrations by AlphaGUARD are 1,075±170 Bq/m^3. Exposure date is 3-5/Aug/2013.
※ Radon concentration is calculated by conversion coefficient A=1.55 (Mori et al., 2013b). Radon concentrations in this table are only reference values.

Table 3　Conversion coefficients (*A*) under each condition

No.	Relative humidity in radon chamber	80%	60%	30%
1	Activated charcoal detector + Acrylic desiccant column	2.42 ± 0.14	2.36 ± 0.29	2.48 ± 0.26
2	Activated charcoal detector + Polyethylene bag	25.3 ± 2.29	26.9 ± 1.64	30.8 ± 1.87
3	Activated charcoal detector (control)	1.12 ± 0.04	1.07 ± 0.03	1.14 ± 0.02

※ Values are expressed as mean ± standard deviation.
※ No. 1, n = 9-10; No. 2, n = 3-5; No. 3, n = 5.
※ Radon concentrations (Bq/m^3) by AlphaGUARD are 1,027±140 (80%), 1,027±127 (60%), and 1,021±132 (30%), respectively.
※ Exposure dates are 21-23/Oct/2013 (80%), 26-28/Oct/2013 (60%), 28-30/Oct/2013 (30%), respectively.

In contrast, the conversion coefficient (*A*) was very large (from 25.3 to 30.8) under measurement condition No. 2, because the polyethylene bag enclosed water vapor but little radon in the air. This is presumably because most radon cannot penetrate the polyethylene bag, and thus cannot reach the activated charcoal.

The air temperature in the radon chamber was set to about 20℃, which was assumed to be room temperature. However, specific environments, such as saunas in hot spring facilities can be at much higher temperatures. Previous studies indicate a temperature-dependent change of airborne radon measurements with an activated charcoal detector (Shefsky *et al.*, 1993). We intend to investigate the temperature-dependent change in airborne radon measurements with an activated charcoal detector continuously. We will also validate a more practical measurement method.

4. Conclusion

The results of this study can be summarized as follows.

- We measured the sensitivity decrease of an activated charcoal detector caused by acrylic columns of various lengths containing various amounts of anhydrous calcium desiccant. Although installing the desiccant column lowered the detector sensitivity somewhat, our examination reveals that this measurement method is valid for quantitative analysis.
- Assuming reference values from the accurately calibrated AlphaGUARD at NIRS to be true values, a conversion coefficient of 2.42 was found under the measurement conditions, using an activated charcoal detector with an 11.5 mm acrylic desiccant column under 80% relative humidity.
- The conversion coefficient was very large when the detectors were put in a polyethylene bag. This is probably because most radon in air cannot penetrate the bag, and thus the radon cannot reach the activated charcoal.
- In future work, we will investigate the temperature-dependent change of airborne radon measurements with the activated charcoal detector continuously. We will also validate the more practical measurement method.

Acknowledgments

The authors gratefully acknowledge a research grant from Japan Health & Research Institute. In addition, the authors gratefully acknowledge anonymous reviewers, whose valuable and helpful comments improved our manuscript.

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（A part of this study was presented at the 67th Annual Meeting of the Japanese Society of Hot Spring Sciences on September 5, 2014）