

Preliminary Study on Determination of Radium-226 in Soil by Radon Emanation and Gamma Spectrometry Methods

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1. Introduction

Determination of radium isotopes in environmental samples is important from health physics and environmental protection standpoint because radium has high toxicity and has similar physical and biological characteristic as other earth alkali metals such as Ca, Sr, and Ba. Therefore, it is easily accumulated into the bones and emitting radiation during its decay. Consumption of food and water with increased concentration of Ra isotopes leads to accumulation of those isotopes in bones (70-80%) and uniformly in the muscle tissue of human beings, and enhancing the total annual effective radiation dose contribution [1]. One important decay product of radium is ²²²Rn, it is an inert gas with 3.82 days of half-life which make it possible to diffuse from soil and accumulate in the air. It will undergo radioactive transformation producing solid particle that can be attached in dust and inhaled by human. Radium and radon concentration will be in equilibrium after 6 of half-life of radon.

The radium content in soil, its physical and chemical properties are varied in wide range so that an accurate and precise analytical procedure is highly needed. Therefore, many measurement techniques have been, and continues to be, developed up to now. Some of those methods are alpha spectrometry, gamma spectrometry, liquid scintillation spectrometry and mass spectrometry. Gamma spectrometry is nondestructive and versatile method that can be applied in direct or indirect mode, however it has rather poor efficiency because a decay of ²²⁶Ra is followed by the emission of 186 keV (γ radiation) with probability of at least 3.5%. This method need longer time when indirect method is implemented. Liquid scintillation counting provides high efficiency and easy sample preparation procedure, however it suffers from low resolution and interference from other isotopes present in the counting vial. Alpha spectrometry shortens the analysis time and can determine ²²⁶Ra, ²²⁴Ra and ²²³Ra nuclides directly and simultaneously, however the isolation of Ra²⁺ from other alkali earth metal cations (Ca²⁺, Sr²⁺ and Ba²⁺) and preparation of a source are troublesome [2, 3].

Each of the methods has advantages and disadvantages, however, in some circumstances such as for early regulatory decision or emergency situation, direct and rapid measurement is needed. Therefore, in this study, radon emanation method was studied and compared to the well-known gamma ray spectrometry

method using HPGe detector. Radon emanation method was chosen because in several studies, this method is considered to be easier and more efficient that it can be applied directly to shorten the measurement time.

2. Materials and Methods

2.1 Sample preparation

Soil sample taken from Uijin was crushed and dried overnight at 110 °C. The soil sample for spectrometry gamma was packed into 1L plastic Marinelli beaker and sealed with parafilm to prevent radon leakage. Marinelli beaker was used because it is the most common container used in gamma spectrometry for environmental/soil sample. While for radon emanation, the soil sample was placed in an opened plate inside the chamber.

2.2 Radon emanation method

Determination of ²²⁶Ra by radon emanation method was conducted using radon chamber with dimension of 30 cm x 30 cm x 30 cm. The soil sample was placed inside the chamber and measured by DURRIDGE RAD7 continuously until radon concentration reached in equilibrium. The experimental setup of measurement system is shown in Fig. 1.

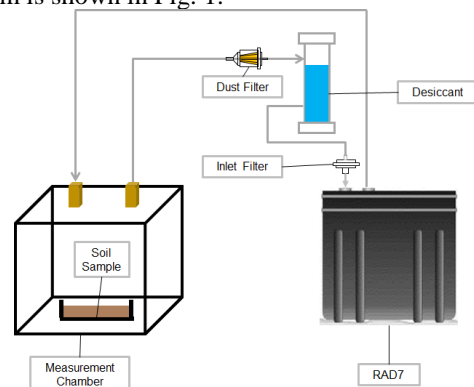


Fig. 1. Experimental setup for radon emanation method.

2.2.1 Determination of chamber leakage

The air leakage of the chamber was determined by comparing the theoretical decay with the measured decay of radon inside the chamber. The radon gas in the chamber was emitted from high natural radioactivity soil placed inside the chamber for 24 hours. Radon concentration equation for the chamber leakage determination was given in Chao's paper [4].

$$C_L(t) = \left(C_b - \frac{qC_0}{v(\lambda + \frac{q}{v})} \right) e^{-[\lambda + \frac{q}{v}]t} + \frac{qC_0}{v(\lambda + \frac{q}{v})} \quad (1)$$

where C_L is the radon concentration of the chamber with leakage, C_b is the initial radon concentration inside the chamber with leakage, q is the chamber leakage rate, V is the chamber volume, C_0 is the background radon concentration outside the chamber and λ is the theoretical decay constant of radon.

2.2.2 Determination of emanation rate and radium content

Prior to measuring the radon emanation rate, the system purging with nitrogen gas was conducted. Sample in a rectangular plate with dimension of 24 cm x 18 cm x 2.5 cm (width x length x height) was put inside the chamber and chamber was closed for sealing. Measurement of the radon concentration was performed for 10 days until saturation. Radon concentration inside the chamber is given as in Chao's paper [4]:

$$C(t) = \left(\frac{E_0 A + q C_0}{V(\lambda + D + \frac{q}{V})} \right) (1 - e^{-[\lambda + D + \frac{q}{V}]t}) \quad (2)$$

where E_0 is the initial radon emanation rate, A is the surface area of the sample and D is the back-diffusion rate.

The effective radium content (Ra_{Eff}) which is the actual amount of radium that affect radon to be emanated, can be calculated according to Abo-Elmagd's paper [5] as given in equation (3) and (4) as follows:

$$E_m = \frac{E_0 A}{m} \quad (3)$$

$$Ra_{Eff} = \frac{E_m}{\lambda + D + \frac{q}{V}} \quad (4)$$

where E_m is the mass exhalation rate and m is the mass of the sample.

2.3. Gamma spectrometry

Gamma ray measurement in direct and indirect methods was performed using the GEM 15P4 coaxial HPGe detector from ORTEC with 70-mm diameter endcap. It is equipped with inspector gamma spectrometry system with 16384 channels MCA. Detector resolution is 0.82 keV for the 122 keV peak and relative efficiency is 15% for the 1.33 MeV Co-60 peak. All gamma-ray spectra were collected during 86,400 s for 30 loops inside the 5 cm thick wall lead brick shield and covered with the 2 mm lead sheet outside measurement chamber.

For direct method, the gamma spectra were collected immediately after the Marinelli beaker was sealed until 28 days. The spectra were taken for each of 86,400 s. The ^{226}Ra activity concentration was determined taking into account its 186.2 keV photons, considering some interfering peaks. While for indirect (equilibrium) method, photon emissions from radon daughters in radioactive equilibrium of ^{214}Pb (295.2 keV) and ^{214}Bi (609.3 keV) were used to determine the radium activity concentration. The sample was measured after 28 days of sealing to obtain radioactive equilibrium.

Collected spectra were then analyzed using Aptec software. Absolute photon detection efficiency for the gamma spectrometry system was determined using the

volume source of CRM (Certified Reference Material) in agar medium of 1L Marinelli beaker with activities certified by KRISS (Korea Research Institute of Standards and Science). The standard consists of ^{241}Am , ^{109}Cd , ^{57}Co , ^{139}Ce , ^{51}Cr , ^{113}Sn , ^{85}Sr , ^{137}Cs , ^{60}Co , and ^{88}Y and has nominal density of 1.001 g/cm³.

3. Results and Discussion

3.1 Radon emanation method

The radon concentration was measured by RAD7 equipped with a drying unit. As the drying unit controlled the humidity inside the chamber, the relative humidity of chamber atmosphere was steady. Also, for the constant temperature, the laboratory atmosphere was controlled by air conditioner. Background radon concentration outside the chamber was measured by Radon Eye, the indoor radon monitor. All of these parameters are listed in the Table I.

Table I: Parameters of the measuring system for radon emanation method

Parameters	Values
Mean temperature (°C)	23.1
Mean relative humidity (%)	2
Background radon conc. (Bq/m ³)	10.1
Surface area of the sample (m ²)	0.0432
Volume of the sample (L)	1
Mass of the sample (kg)	1.317

3.1.1 Leakage rate

The result of the air leakage measurement which was conducted about 120 hours is shown in Fig. 2. Measured radon concentration in the chamber was fitted with the equation (1). The fitted equation is:

$$C = 2915.75 \times e^{-\frac{t}{74.5}} - 15.98 \quad (5)$$

$$R^2 = 0.99$$

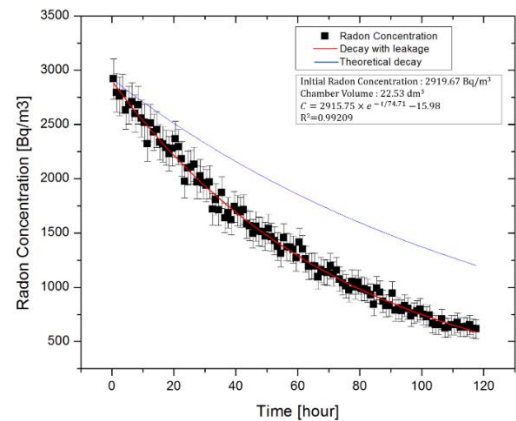


Fig. 2. Measurement of the air leakage of the chamber.

The chamber leakage was determined by simple calculation using fitted equation and the well-known radon physical decay constant of 0.0076 (h⁻¹). The calculated air leakage rate was 0.131 L/hr.

3.1.2 Emanation rate and radium content

After purging the system with nitrogen gas, Uljin soil sample in the plate was placed inside the chamber and measured about 240 hours to be saturated. Result of the measurement is shown in Fig. 3. Some data of 240-hour measurement were missing because of the system problem, but there was no significant effect on the data fitting. Because the temperature during measurement was controlled, the change of atmosphere temperature was not significant and the radon concentration was not affected by the temperature changes. The measured radon concentration was then fitted with the equation (2) which resulted:

$$C = 97.40 \times (1 - e^{-0.0231 \cdot t}) \quad (6)$$

$$R^2 = 0.81$$

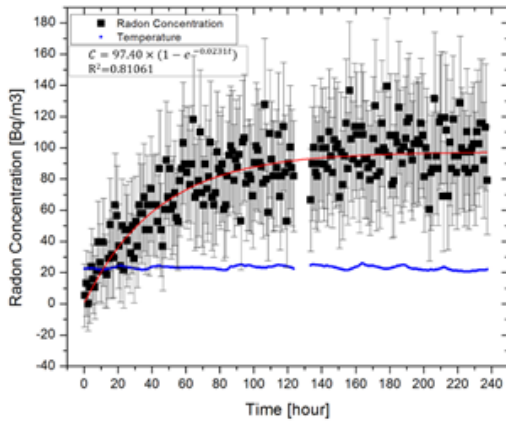


Fig. 3. Radon-222 concentration and radon chamber temperature measured by RAD7.

Beside the leakage rate, the back-diffusion rate as shown in equation (2) was determined as 0.0094 h^{-1} , which was calculated by subtracting the physical decay constant and obtained leakage rate from the total λ of 0.0231 in the fitted equation. In order to obtain the effective radium content, the initial emanation rate was determined as $1.06 \text{ Bq}/(\text{m}^2 \cdot \text{h})$. The effective radium content was calculated using equation (3) and (4), and the result was equal to $1.51 \text{ Bq}/\text{kg}$.

Determination of radium concentration in the soil by radon emanation method must consider the emanation fraction which is the fraction of radon atoms generated that escape the solid phase in which they are formed and become free to migrate through the bulk medium [6]. The radon emanation fraction depends on many factors such as the porosity and grain size of the sample, humidity, and temperature, which were not dealt in this research. In other way, calculation for the emanation fraction was done following equation in the IAEA publication [6]:

$$EF = \frac{VC_{eq}}{mA_{Ra}} \quad (7)$$

where EF is the emanation fraction, C_{eq} is the radon concentration in equilibrium and A_{Ra} is measured radium concentration by direct method as given in 3.2.1 section. Emanation fraction was calculated as 0.0328 or 3.28% and calculated radium concentration considering this emanation fraction was $46.0 \text{ Bq}/\text{kg}$ which is the effective radium content divided by the emanation fraction. The

result is comparable with the measured radium concentration by direct method.

3.2 Gamma spectrometry

3.2.1 Direct measurement

The radium concentration resulted in direct gamma ray spectrometry from photon energy peak of 186.2 keV γ -ray of ^{226}Ra with 3.555 (19) % yield was $50.8 \pm 4.9 \text{ Bq}/\text{kg}$, as shown in Fig. 4.

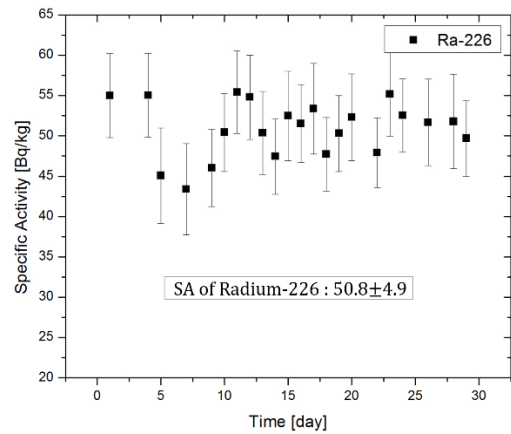


Fig. 4. Radium-226 concentration measured by HPGe.

Interference correction from other possible peak such as the 185.7 keV γ -ray of ^{235}U with 57.0 (3) % yield and the 186.1 keV γ -ray of ^{230}Th with 0.0088 (7) % yield were not performed, because this deconvolution needed other lower peaks of ^{235}U and ^{230}Th which were not found. This is due to the low intrinsic peak efficiency of p-type coaxial HPGe at low incident photon energy. This is one shortcoming of p-type HPGe gamma spectrometry, that Morera-Gomez et al [7] recommended using coaxial n-type HPGe for ^{226}Ra determination, beside the reason to minimize the true coincidence summing effect if no correction is performed. In other study by Baumgartner et al [8], deviation to the ^{226}Ra due to spectral interferences and radon leakage can contribute up to 104.3 % for tuff material. Therefore, without other peaks interference correction, the concentration resulted in p-type HPGe direct measurement can be higher than the real concentration, and other measurement for uranium and thorium concentration may be needed for further deconvolution for radium peak.

3.2.2 Indirect measurement (equilibrium)

Indirect gamma ray measurement was conducted by measuring the activity concentration of radon progeny at least 3 weeks after sealing to reach secular equilibrium between Radium and Radon. ^{214}Pb with energy of 295.2 keV and ^{214}Bi with energy of 609.3 keV were measured because these peaks have no or insignificant interference from other energy peaks [8]. The measurement result is given in Fig. 5 which shows that radioactive equilibriums were not achieved for both nuclides

The resulted concentrations were $24.4 \pm 1.1 \text{ Bq}/\text{kg}$ for ^{214}Bi and $24.2 \pm 1.0 \text{ Bq}/\text{kg}$ for ^{214}Pb . These values are

much less than the radium concentration. The inconsistency between those results was possibly caused by ^{222}Rn leakage from the Marinelli beaker, as has been studied previously by Lee [9] that plastic Marinelli beaker has significant leakage compared to aluminum can. This condition caused ^{222}Rn could not reach its equilibrium. Many other studies [8,10] have emphasized the significant effect of radon leakage from container so it must be carefully considered for indirect method.

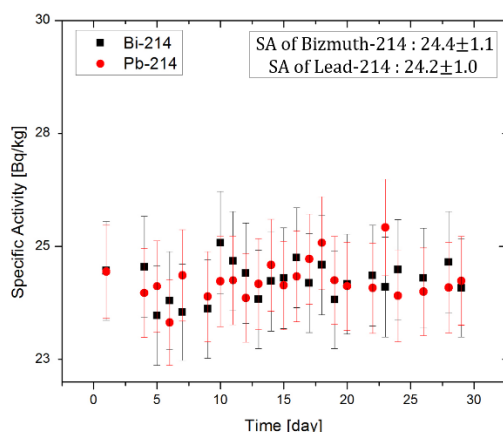


Fig. 5. Bismuth-214 and Lead-214 concentration measured by HPGe.

3. Conclusions

Determination of the ^{226}Ra has been conducted in this research using three methods which were radon emanation method, direct method and indirect method of gamma spectrometry. The results can be concluded as follows:

1. The three methods show discrepancy each other. The indirect gamma spectrometry method has the lowest value because of the possible sample container leakage that caused the secular equilibrium of radon and its progeny could not be reached. For better result, the sample container leakage must be determined beforehand.
2. Radon emanation method and direct gamma spectrometry method have close results. However, the direct method with p-type HPGe can result higher activity concentration, due to interference peaks from other nuclide energies. This interference must be corrected, which can be done by other measurement methods. On the other hand, radon emanation method needs emanation fraction parameter which depends on many factors such as grain size and porosity of the soil and environment temperature and humidity. This parameter can also be obtained using the radium concentration from direct gamma spectrometry result.
3. For more rapid measurement in determination of radium concentration, the combination of direct and radon emanation method can be implemented.

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