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A comparison of determination methods for uranium radioactivity in environmental soil samples using a gamma spectrometer

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Abstract

Comparisons of statistical analysis results between five methods using gamma spectrometry and a control group for measuring the radioactivity of uranium were performed to suggest the optimal method. In the statistical tests including linear regression, and Pearson's correlation all gamma spectrometry methods correlated with the control group method though they had each disadvantage. The Student's *t*-test results for a novel method 5 including a ^{230}Th contribution, were 0.986 (^{235}U) and 1.821 (^{238}U), respectively. It had the advantage of being more accurate when evaluating the activity of ^{235}U and ^{238}U simultaneously. The novel method 5 can thus be recommended over others.

Keywords Uranium determination · Soil sample · Gamma spectrometry · Alpha spectrometry

Introduction

Accurate measurement of uranium radioactivity series in samples is important for estimating individual or public doses based on environmental radiation [1, 2]. According to a report by the United Nations Scientific Committee on the Effects of Atomic Radiation, approximately 50% of the worldwide average annual effective dose (2.4 mSv y^{-1}) is from radon inhalation, and 21% is from terrestrial gamma rays such as ^{238}U, ^{232}Th decay series, and ^{40}K [3]. These radionuclides mainly exist in soil, and they can be used for the characterization of samples and to distinguish the origin of samples [4]. In dose assessment studies, accurately measuring the uranium and thorium activities in the soil is essential because it is known that the uranium and thorium contribution to the dose is relatively high [5, 6]. The radioactivity of these nuclides in the soil can be measured with several methods, such as mass spectrometry [7–11], alpha-ray spectrometry, and gamma-ray spectrometry [9, 12].

One of the methods for determining uranium activity, considered in this study, is gamma spectrometry, which primarily measures and analyzes the peak counts originating from gamma-ray emissions in the samples. For instance, the high purity germanium (HPGe) detector is widely used to measure the uranium activity of a sample in monitoring environmental radiation because of its good energy resolutions and minimized pretretments [13, 14].

The gamma-ray measurement methods to analyze the radioactivity of uranium in the soil can be broadly classified into three types, assuming secular equilibrium of radionuclides. The first is to use a single energy peak emitted from a radionuclide (uranium progeny) in a sample. For instance, radionuclides and emission gamma-ray energy used to determine the ^{238}U activity are ^{234}Th (63.3 keV), ^{214}Pb (351.9 keV), ^{214}Bi (609 keV), and ^{234m}Pa (1001 keV) [14–17]. The second type for evaluating the activity of ^{235}U and ^{238}U is to use correction factors for a186 keV peak, which are based on the natural abundances of uranium isotopes [18, 19]. In the third type, multiple gamma-rays emitted from the ^{238}U daughters, such as 144 and 186 keV, are used to determine the radionuclide activity. For instance, the identified peaks in the spectra can be a combination of peaks emitted by several radionuclides, e.g., the 186 keV peak is the combination peak of ^{226}Ra and ^{235}U in the soil

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[19–22]. These methods, however, have some limitations and problems such as emission intensities of the gamma-ray, the low detection efficiency of a detector, analysis uncertainty, and a coincident summing effect. For example, the emission intensity of the 1001 keV gamma-ray of $^{234\ mPa}$ is as low as 0.8435%, thus determining the uranium activity using the 1001 keV should be very carefully performed [23].

The method for determining uranium activity for a control group is the alpha spectrometry that assess ^{235}U, ^{238}U, and radionuclides of the uranium decay series [7, 24, 25]. Although this method requires complex chemical processes including incineration, acid dissolution, and electrochemical deposition [26, 27], the alpha spectrometry is known to have high accuracy with low background noise.

In this study, A novel method, which reflects the ^{230}Th contributions in 144 and 186 keV peaks, is proposed to determine the precise radioactivity of the ^{235}U and ^{238}U. Analysis results of the five methods, which included the novel method were compared with alpha spectrometer results for 26 soil samples. In addition, this study discusses the validity of the methods for evaluating the radioactivity of the ^{235}U and ^{238}U for regular survey samples of environmental radiation monitoring.

Experimental

In this study, 26 soil samples were obtained from 0 to 5 cm below the ground surface in Gyeongju city, Republic of Korea, between April 2016 and April 2021, as shown in Fig. 1. After the soil samples were dried and pulverized, rocky and biological materials of large size were removed using a 2-mm mesh sieve.

After incineration (450 °C and 48 h) for alpha spectrometry, a few portions of the dry samples were chemically pretreated including a tracer (^{232}U). Dissolution using mixed acid (HF, HNO_3, and $HClO_4$, 1:4:1, respectively), and separation of iron and uranium using a UTEVA resin were performed [26–28]. The treated samples were deposited electrochemically on a plate for measurements with an alpha spectrometer (Alpha duo, ORTEC, USA) for 100,000 s [7]. The detection efficiency of the alpha spectrometer was corrected using an alpha-emitting ^{232}U tracer (5263 and 5320 keV). The minimum detectable activity (MDA) of ^{235}U and ^{238}U with the alpha spectrometer was determined to be about 0.10 and 0.3 Bq kg^{-1}, respectively. The results from alpha spectrometry were applied as a control group for a statistical comparison with gamma spectrometry results in this study.

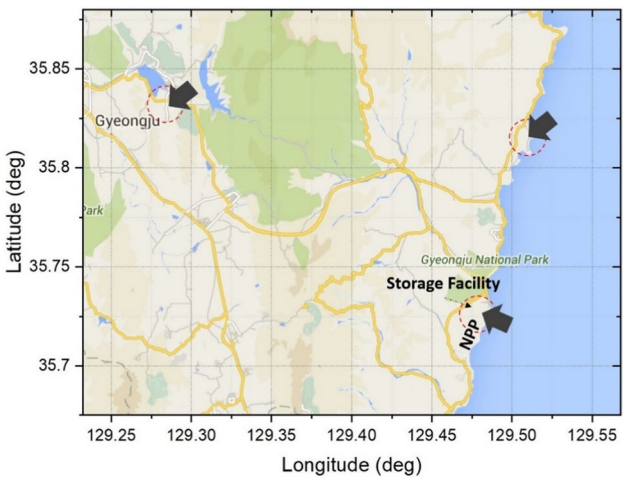

Fig. 1 Soil sampling locations in Gyeongju city, Republic of Korea

Soil samples for measurements using a gamma spectrometer were placed in a 450 mL Marinelli beaker with a silicone cover. The soil samples were measured for nearly one day (live time: 86,000 s), and nine p-type HPGe detectors in a radiation research laboratory were randomly used during the radiation monitoring. The measurement results were analyzed using GENIE 2000 or an Aptec Multichannel Analyzer. A nuclide library file (eml300.lib) was used for nuclide identification. Detection efficiency of these HPGe detectors was determined using a certificated reference material of the Korea Research Institute of Standards and Scienc, including ^{214}Am (59.54 keV), ^{109}Cs (88.03 keV), ^{57}Cd (122.06 keV, 135.47 keV), ^{139}Ce (165.86 keV), ^{51}Cr (320.08 keV), ^{113}Sn (391.70 keV), ^{85}Sr (514 keV), ^{137}Cs (661.7 keV), ^{60}Co (1173.23 keV, 1332.49 keV), and ^{88}Y (898.04 keV, 1836.05 keV). The detection efficiency was corrected for self-absorption related to the density [29–31].

The measurements of the real soil samples were performed without waiting for radon secular equilibrium in the Marinelli beaker; however, the uranium activities in the soil samples were determined under the assumption of secular equilibrium, including radon gas. The uncertainty of the measurement results could thus be increased becuase of the nonequilibrium influence of chemical reactions and biological interactions of materials in the soil, which was taken into consideration [16]. The MDA of the gamma spectrometry was assessed referring to the Currie method and a recommended method of ISO-11929. [32, 33].

The first type of activity evaluation was a single peak analysis that used a single gamma-ray line emitted from a radionuclide, in some cases with corrections from other radionuclide contributions. The second activity evaluation type used correction factors based on an abundance of natural uranium (^{235}U and ^{238}U) [18, 19]. The third activity evaluation type was a multiple peak analysis method, which evaluates radioactivity considering two or more energy peaks simultaneously, such as the 144 and 186 keV peaks [20, 21]. Table 1 shows summaries of the radioactivity determination methods and the main energy peak used at assessment.

Table 1 Summary of activity determination methods [34–39]

Decay series	Nuclide	Half life	Gamma lines close to a 144 keV peak		Gamma lines close to a 186 keV peak	
			Energy (keV)	I_g (%)	Energy (keV)	I_g (%)
^{235}U	^{235}U	7.0×10^{8} y	143.76	10.96	185.7	57.2
	^{223}Ra	11.435 d	144.27	3.36	n/a	n/a
^{238}U	^{230}Th	75,380 y	143.87	0.049	186.05	0.0088
	^{226}Ra	1600 y	n/a	n/a	186.21	3.64
^{232}Th	^{228}Ac	6.15 h	145.84	0.158	184.54	0.07

Table 2 lists the radionuclides contributing to the peaks at 144 and 186 keV.

Single peak analysis method

The single peak analysis method used the most prominent energy peak of the radionuclide to determine the radioactivity. In this study, two methods using different energy (method 1 (63.6 keV) and method 2 (352 keV)) were applied only to determiate the ^{238}U activity, because a prominent peak worth consideration cannot be found for the ^{235}U radionuclide.

In method 1, ^{238}U is determined by the activity of ^{234}Th (63.3 keV, 3.765%) [34]. Its main emission peak subtracts the contribution of ^{232}Th (63.8 keV, 0.263%) [34], which is evaluated from ^{228}Ac (911 keV, 25.8%) [37]. As ^{234}Th is the first progeny of ^{238}U, method 1 could be used for evaluating the ^{238}U activity, when assuming secular equilibrium [14, 40]. An average of the MDAs of method 1 using the Currie method was 16.17 ± 12.02 Bq kg^{-1}.

In method 2, the ^{238}U activity is determined via the activity of ^{214}Pb (352 keV, 35.6%) [36], which is one of the progenies of ^{222}Rn, assuming radioactive equilibrium in a perfectly sealed container, unlike the actual situation. With the probable leakage of radon gas, it was expected that the measurements with this method would be lower than the real value [16]. Nevertheless, we carried out the activity evaluation of method 2 for a comparison. The measured activities with methods 1 and 2 can be calculated using Eq. (1).

$$A = \frac{C_{Net}}{T \times m \times I_r \times \varepsilon} \tag{1}$$

where A denotes an activity concentration (Bq kg^{-1}) of a radionuclide; C_{Net} is a net count of an analysis peak (the net count when all necessary subtractions have already been done); T is measurement time (s); m is a sample mass (kg); e is full energy peak detection efficiency, and I_g denotes an emission probability of the specific gamma-ray. The MDA

Table 2 Radionuclides contributing to peaks at 144 and 186 keV

Method	Gamma peaks used for ^{238}U activity		Gamma peaks used for ^{238}U activity		Note (Energies are in keV)	Type
	Energy (keV)	Contributing Nuclides	Energy (keV)	Contributing Nuclides		
Method 1	63.3	^{234}Th	n/a	n/a	63.8 peak (^{232}Th) portion subtracted using ^{228}Ac	Type 1: Single peak analysis
Method 2	352	^{214}Pb	n/a	n/a	Equilibrium easily broken, since ^{214}Pb is 9th progeny of ^{238}U and second progeny of ^{222}Rn	
Method 3	186	^{226}Ra	186	^{235}U	f_{186}^{238} : 0.583, f_{144}^{235} : 0.417 (Assuming equilibrium and from abundance data)	Type 2: Correction factor method
Method 4	186	^{235}U ^{226}Ra	144	^{235}U ^{223}Ra	(1) ^{228}Ac contributions subtracted (2) ^{235}U activity determined for a 144 peak (3) ^{226}Ra activity determined from a 186 keV	Type 3: Multiple peaks analysis
Method 5	186	^{235}U ^{230Th} ^{226}Ra	144	^{235}U ^{230Th} ^{223}Ra	Contributions of ^{230}Th are included in method 4, in the resulting, 144 and 186 keV are calculated simultaneously	

average of method 2 using the background of the 352 keV ROI was 0.63 ± 0.17 Bq kg^{-1}.

Correction factor method

The correction factor method (method 3) evaluates the activities of ^{235}U and ^{238}U. This method evaluates the ^{226}Ra activity from the 186 keV peak net count and a correction factor (0.583 ± 0.01) based on the uranium natural abundance. Similarly, the ^{235}U activity measurements are obtained by applying another correction factor (0.417 ± 0.01) [18, 19]. Equation (2), a slight modification to Eq. (1), is used to evaluate the activities of ^{235}U or ^{238}U.

$$A = \frac{C_{186} \times f^{nuc.}}{T \times m \times I_r \times \varepsilon} \tag{2}$$

where C_{186} is a net count of 186 keV peak, $f^{nuc.}$ is a correction factor of nuclides; i.e., 0.583 for ^{238}U and 0.417 for ^{235}U. However, it should be noted that the uranium abundance that is a basic assumption of method 3 may vary by region, as indicated in the study by Di Lella [41–43]. The MDA average of ^{235}U and ^{238}U of method 3 using the background of the 186 keV were 0.81 ± 0.24 Bq kg^{-1} and 3.36 ± 0.96 Bq kg^{-1}, respectivtly.

Multiple peaks analysis method

The multiple peaks analysis method uses two or more gamma peaks emitted from several nuclides at the same time. In this study, to provide accurate radioactivity, the 144 keV and 186 keV peaks were corrected ^{228}Ac (145.85 keV, 184.54 keV) contributions. Moreover, the ^{228}Ac contribution to 144 keV and 186 keV peaks can be easily evaluated from a 911 keV energy peak.

Method 4 was previously published by other researchers; it uses a relation formula of radionuclides, which emits gamma rays near 186 keV and 144 keV. The formula was derived from the relation of ^{226}Ra (186.21 keV), ^{223}Ra (144.23 keV, 323.87 keV), and ^{235}U (143.76 keV, 185.7 keV), assuming secular equilibrium [20, 21].

Method 5 is a suggestion method to evaluate the activity of ^{235}U and ^{238}U using a relation formula, similar to method 4, however, method 5 includes a correction for the activity of ^{230}Th (143.87 keV, 186.05 keV). ^{230}Th is the fifth progeny of ^{238}U, and the emission gamma rays of this radioisotope could influence the radioactivity evaluation of ^{235}U and ^{238}U, considering the ratio of ^{235}U and ^{238}U. Becuase ^{235}U (143.76 keV), ^{230}Th (143.87 keV), and ^{223}Ra (144.23 keV) gamma lines are very close, they usually form one single peak at 144 keV. The region of interest (ROI) of the 144 keV peak was roughly selected from 142 to 147 keV to reduce the analysis process uncertainty because it can be identified as a peak including ^{228}Ac (145.85 keV), as shown in Fig. 2. We observed a broadened ROI for 11 of 26 cases. Similarly, the ^{228}Ac (184.54 keV), ^{235}U (185.7 keV), ^{230}Th (186.05 keV), and ^{226}Ra (186.21 keV) peaks were combined to form the 186 keV peak [37].

The united count can be expressed as the count relation formula, including each radionuclide. Counting equations of 144 and 186 keV in broadened ROI cases are shown as follows:

$$C_{144} = C_{144}^{235} + C_{144}^{223} + C_{144}^{230} + C_{144}^{228} \tag{3}$$

$$C_{186} = C_{186}^{235} + C_{186}^{226} + C_{186}^{230} + C_{186}^{228} \tag{4}$$

where C_a is a net count of a broad ROI. A superscript and a subscript of C_a^b are the mass number of a nuclide and gamma radiation energy (keV) emitted from the nuclide, respectively. For instance, 223, 226, 228, 230 and 235 denote ^{223}Ra, ^{226}Ra, ^{228}Ac, ^{230}Th, and ^{235}U, respectively. The formulas corrected for the ^{228}Ac contribution in the peak ROI are as follows:

$$C_{144}^{*} = C_{144} - C_{144}^{228} = C_{144} - A_{144}^{228} I_{144}^{228} T m \varepsilon_{144} \tag{5}$$

$$C_{186}^{*} = C_{186} - C_{186}^{228} = C_{186} - A_{186}^{228} I_{186}^{228} T m \varepsilon_{186} \tag{6}$$

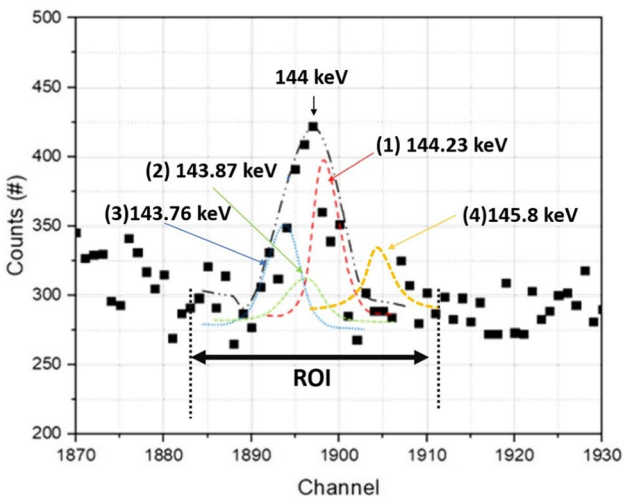

Fig. 2 Gamma lines contributing to the144 keV peak: (1) ^{223}Ra, (2) ^{230}Th, (3) ^{235}U, and (4).^{228}Ac

where C*denotes a net count of the ROI after subtracting the ^{228}Ac counts; A^b is the radioactivity (Bq kg^{-1}) of'b' nuclide in the soil sample. If the uranium series are in secular equilibrium (A^{235} equals A^{223}, A^{226} equals A^{230}), the radioactivity-count relation formulas become the followings:

$$\frac{C^*_{144}}{T \times m \times \varepsilon_{144}} = A^{235} I^{235}_{144} + A^{223} I^{223}_{144} + A^{230} I^{230}_{144} = A^{235}(I^{235}_{144} + I^{223}_{144}) + A^{226} I^{230}_{144} \quad (7)$$

$$\frac{C^*_{186}}{T \times m \times \varepsilon_{186}} = A^{235} I^{235}_{186} + A^{226} I^{226}_{186} + A^{230} I^{230}_{186} = A^{235} I^{235}_{186} + A^{226}(I^{226}_{186} + I^{230}_{186}) \quad (8)$$

where ε_{144} and ε_{186} denote the detection efficiency for the 144 and 186 keV energy peaks, respectively; and I^b_a is the gamma-ray intensity of the radionuclides [34–38]. A system of linear Eq. (7) and Eq. (8) in which the radionuclide activity are variables is rearranged for the count. Equation (9) for the ^{235}U activity is obtained from Eq. (7), and this equation can be put into Eq. (8) and rearranged to get Eq. (10) with one variable, A^{226};

$$A^{235} = \frac{\frac{C^*_{144}}{Tm\varepsilon_{144}} - A^{226} I^{230}_{144}}{I^{235}_{144} + I^{223}_{144}} \quad (9)$$

$$\frac{C^*_{186}}{Tm\varepsilon_{186}} = \frac{\frac{C^*_{144}}{Tm\varepsilon_{144}} - A^{226} I^{230}_{144}}{I^{235}_{144} + I^{223}_{144}} I^{235}_{186} + A^{226}(I^{226}_{186} + I^{230}_{186}) \quad (10)$$

Final formulas regarding the ^{235}U activity and the ^{226}Ra (^{238}U) activity with radionuclide gamma-ray emission rate thus are summarized in Eq. (11) and Eq. (12), as below [34–38];

$$A^{235} = \frac{\frac{C^*_{144}}{Tm\varepsilon_{144}} - \frac{C^*_{186}}{Tm\varepsilon_{186}} \times \frac{I^{230}_{144}}{I^{230}_{186} + I^{226}_{186}}}{I^{235}_{144} + I^{223}_{144} - \frac{I^{235}_{186} I^{230}_{144}}{I^{230}_{186} + I^{226}_{186}}} = \frac{\frac{C^*_{144}}{Tm\varepsilon_{144}} - \frac{C^*_{186}}{Tm\varepsilon_{186}} \times 0.0136}{0.1345} \quad (11)$$

$$A^{226} = \frac{\frac{C^*_{186}}{Tm\varepsilon_{186}} - \frac{C^*_{144}}{Tm\varepsilon_{144}} \times \frac{I^{235}_{186}}{I^{235}_{144} + I^{223}_{144}}}{I^{230}_{186} + I^{226}_{186} - \frac{I^{235}_{186} \times I^{230}_{144}}{I^{235}_{144} + I^{223}_{144}}} = \frac{\frac{C^*_{186}}{Tm\varepsilon_{186}} - \frac{C^*_{144}}{Tm\varepsilon_{144}} \times 4.0207}{0.03403} \quad (12)$$

Before the ^{230}Th correction, the denominator correction value (0.03403) of Eq. (12) was 0.0359, and the corrected terms of Eq. (11) were 0 (numerator) and 0.1423 (denominator). It has been assumed that the detection efficiency of a unified peak is the same because the energy of the emission gamma-rays is close, and the uncertainty of the calibrated efficiency had been approximately 4%. In this study, the detection efficiency of the central energy of ROI was used. For example, the efficiency of 144 and 186 keV were 0.049952 and 0.026549, respectively, in the roughly searched peaks. The MDA averages of ^{235}U and ^{238}U of methods 4 and 5 using the background of the 144 and 186 keV were 1.24 ± 0.31 Bq kg^{-1} and 1.31 ± 0.33 Bq kg^{-1}, 20.25 ± 5.00 Bq kg^{-1} and 21.80 ± 5.44 Bq kg^{-1}, respectively.

The correlation, linearity, and statistical similarity were compared to select a suitable gamma-ray analysis method based on the analysis cases. First, as the correlation, a Pearson's correlation coefficient was calculated between those of each method and the alpha spectrometry results. If the Pearson's correlation coefficient is close to 1, the comparison subjects are considered correlated. Second, as for the linearity, a simple linear regression with a weighting factor from the data's uncertainty, which is the inverse of a square value of the radioactivity uncertainty, was performed by the Origin pro 2021 program as the linearity check or a linear model fitting. Finally, as for the statistical similarity, a paired t-test (Student's *t*-test) was performed to confirm the statistical similarity between each gamma spectrometry method and the alpha spectrometry (control group) [44]. In the Student's *t*-test, the null hypothesis (H_0) is that the comparison subjects are the same, and the alternative hypothesis (H_1) is they are not the same, generally [44]. If the t-value is higher than a critical value, it supports a statistical difference. In other words, if the t-value of an analysis variable is smaller than other, the variable could be considered to be relatively closer to the control group than to the others. In this study, the control group for statistical comparisons is the alpha spectrometer results, the experimental group results are those from the gamma-ray analysis methods.

Results and discussion

In this study, the uncertainty of these averages was shown as a 95% confidence interval with the standard uncertainty of each average, including the uncertainty of each measurement value, and the error term for each dataset was estimated with a general statistical method (e.g., uncertainty propagation).

In the comparison of simple arithmetic statistics, the average of ^{238}U radioactivity evaluated with the alpha spectrometry results was 30.29 ± 2.79 Bq kg^{-1}. The averages of ^{238}U radioactivity for the five gamma spectrometry methods

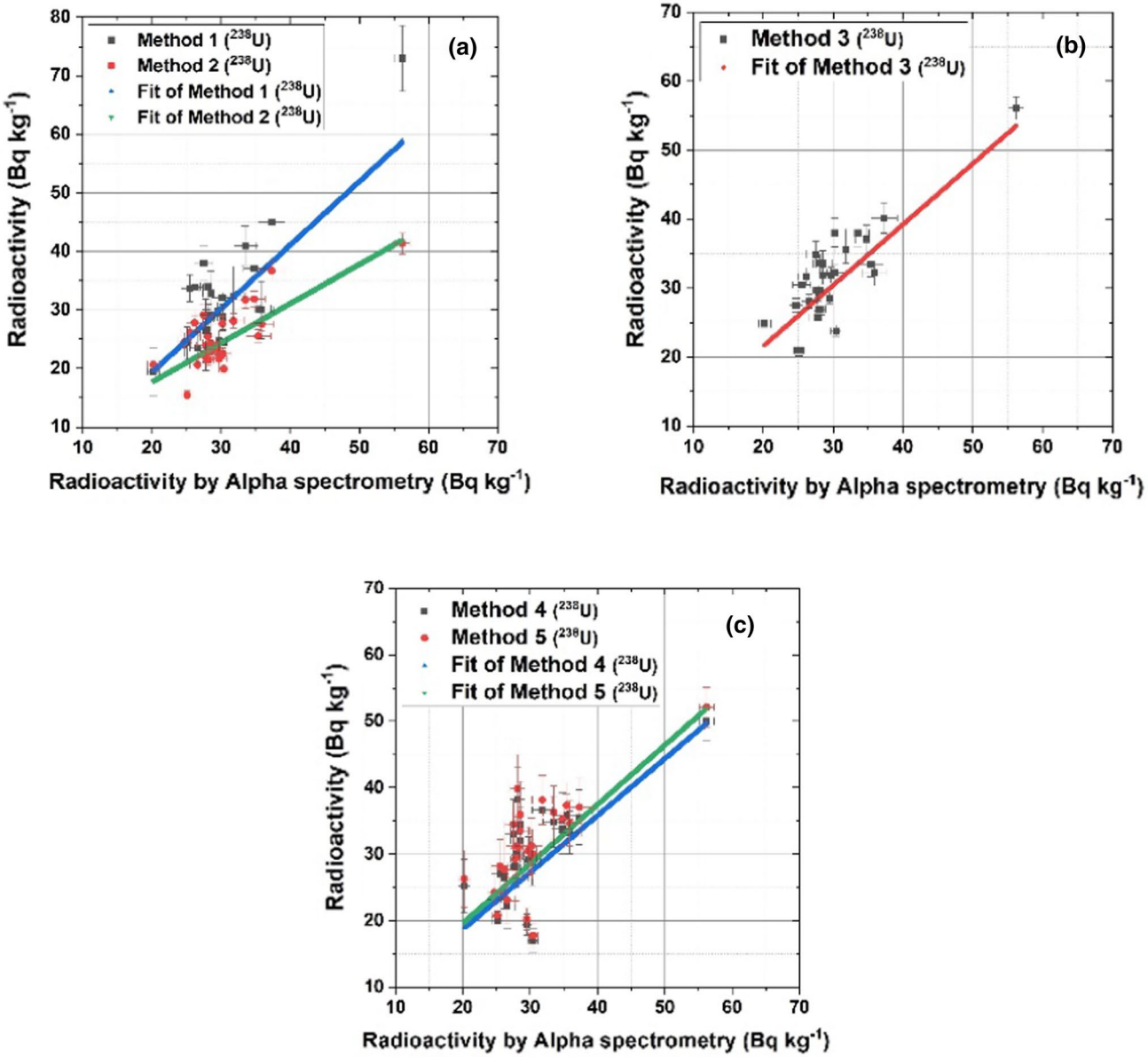

Fig. 3 ^{238}U radioactivity comparison between alpha and gamma spectrometry results: **a** methods 1 and 2, **b** method 3, and **c** methods (4) and (5)

ranged from 25.56 ± 2.13 Bq kg^{-1} to 32.16 ± 2.63 Bq kg^{-1}. The average of ^{235}U radioactivity evaluated with the alpha spectrometer was 1.39 ± 0.14 Bq kg^{-1}. The averages of ^{235}U radioactivity for the three evaluation methods ranged from 1.46 ± 0.31 Bq kg^{-1} to 1.58 ± 0.16 Bq kg^{-1}. The mean of the ^{228}Ac activity for the peak count correction was evaluated as 33.08 ± 4.30 Bq kg^{-1}. The contribution average of the ^{228}Ac on the broadened ROI were calculated as $23.3\% \pm 4.2\%$ in the 144 keV peak and $1.1\% \pm 0.1\%$ in the 186 keV peak.

^{238}U radioactivity evaluation results

The results of the evaluation of ^{238}U radioactivity are shown in Fig. 3. The ^{238}U activity average of method 1 was 31.81 ± 4.19 Bq kg^{-1}, which was consistent with the average of the alpha spectrometry results as expected. The standard deviation (SD) of the ^{238}U radioactivity was 10.28 Bq kg^{-1}. The contribution of the 63.8 keV peak (^{232}Th) into the 63.3 keV peak was determined to be $8 \pm 3\%$. Therefore, considering the ^{232}Th activity is better to evaluate the ^{234}Th activity more accurately. The Pearson's correlation coefficient of method 1 was 0.66; and the Student's *t*-test result was 1.359. A slope, the y-intercept, and the determinant

coefficient of the linear regression were 1.09 ± 0.23 and -2 ± 7 Bq kg^{-1}, and 0.48, respectively.

In method 2, assuming radioactive equilibrium in a leak-tight container, the radioactivity average of ^{238}U was evaluated as 25.56 ± 2.21 Bq kg^{-1}, which is only 84.39% of the alpha spectrometer results. The SD of method 2 was 5.47 Bq kg^{-1}. As expected, the reason for the lower activity results in this study could to attribute to a non-airtight container and a lack of waiting time to reach secular equilibrium. The Pearson's coefficient was 0.70. However, the slope was 0.7 ± 0.1, the intercept was 4 ± 4 Bq kg^{-1}, and R^2 of the simple linear regression was 0.48. The paired *t*-test value was 5.84. In method 2, because of the time problem and the expected radon gas leakage from the sample container, the radioactivity of the evaluation was lower by 15.61%, and method 2 was thus considered invalid. However, if the container is ensured to be airtight and the time is adequate, the results should be better than in this study, as reported in another study [45].

The ^{238}U activity average with method 3 was 32.16 ± 2.73 Bq kg^{-1}. The SD of method 3 was calculated to be 6.75 Bq kg^{-1}. Although the Pearson's correlation coefficient of method 3 was evaluated to be 0.77, the R^2 of the linear regression result of this method was 0.59, the slope of the fitting was 0.9 ± 0.2, and the intercept was 4 ± 4 Bq kg^{-1}. The *t*-value of the paired *t*-test was 2.636.

The average values of ^{238}U radioactivity as evaluated by method 4 and method 5 were 29.99 ± 2.89 Bq kg^{-1} and 31.27 ± 3.01 Bq kg^{-1}, respectively. The SDs of these were 6.98 Bq kg^{-1} and 7.27 Bq kg^{-1}. Although the ^{230}Th contribution to the 186 keV peak count was included in method 5, the ^{238}U evaluation results of method 5 were roughly 4% higher than those of method 4. This is because the ^{230}Th activity contribution caused the 144 keV peak count or the ^{235}U activity to decrease. The Pearson coefficients were 0.68 in both methods 4 and 5. The R^2 values of the linear regression were 0.46 in method 4 and 0.47 in method 5, the slopes were 0.9 ± 0.2, and the intercepts were 2 ± 6 Bq kg^{-1}.

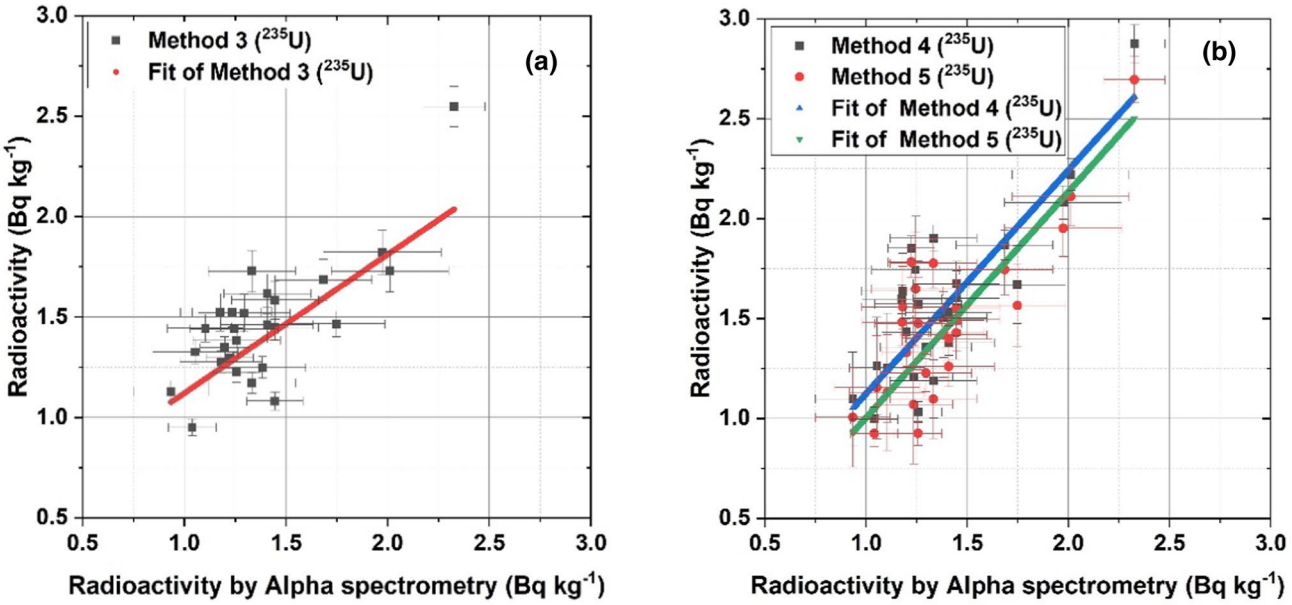

Fig. 4 ^{235}U radioactivity comparison between alpha and gamma spectrometry results: **a** method 3, and **b** methods (4) and (5)

Table 3 Correlation comparison of gamma-ray analysis methods

	^{238}U					^{235}U				
	Intercept (Bq kg^{-1})	Slope	R^2	Pearson	*t-value	Intercept (Bq kg^{-1})	Slope	R^2	Pearson	*t-value
Method 1	-2.33 ± 6.76	1.09 ± 0.23	0.48	0.66	1.359	–	–	–	–	
Method 2	4.24 ± 4.1	0.67 ± 0.14	0.48	0.70	5.840	–	–	–	–	
Method 3	3.95 ± 4.30	0.88 ± 0.15	0.59	0.77	2.636	0.43 ± 0.20	0.69 ± 0.15	0.47	0.69	1.742
Method 4	1.66 ± 5.67	0.86 ± 0.19	0.46	0.68	0.307	0.01 ± 0.24	1.12 ± 0.17	0.64	0.80	4.262
Method 5	1.72 ± 5.90	0.90 ± 0.19	0.47	0.68	0.968	0.13 ± 0.25	1.13 ± 0.18	0.61	0.79	1.821

*Significance level: 5%, $t_{25,0.025}$: 2.055

The multiple peaks analysis results were correlated to those from the alpha spectrometry and linearity was observed. The paired *t*-test results were 0.307 and 0.968. Based on the results of this analysis, both methods 4 and 5 provided acceptable t-test results when evaluating the radioactivity of ^{238}U.

^{235}U radioactivity evaluation results

The results of the evaluation of the ^{235}U activity are shown in Fig. 4. The analysis results are presented in Table 3. The ^{235}U radioactivity average of method 3 was 1.46 ± 0.30 Bq kg^{-1}, and the SD was 0.31 Bq kg^{-1}. The Pearson's correlation coefficient was evaluated to be 0.69. The R^2 value of the linear regression was 0.47, the slope of the fitting was 0.7 ± 0.2, and the intercept was 0.4 ± 0.2 Bq kg^{-1}. The paired *t*-test result was 1.742.

The average ^{235}U activity values of method 4 and method 5 were 1.58 ± 0.16 Bq kg^{-1} and 1.47 ± 0.18 Bq kg^{-1}, respectively, and SDs were 0.41 Bq kg^{-1} and 0.40 Bq kg^{-1}, respectively. The ^{235}U activity average difference resulting from the ^{230}Th radionuclide correction was roughly 7%. In the 144 keV energy peak count, the meager gamma-ray intensity of the Th was offset to be effective, because the high contribution of the ^{230}Th activity and a low emission rate of the ^{235}U. The Pearson's correlation coefficients of method 4 and method 5 were 0.80 and 0.79, respectively. The R^2 values of the linear regression results were 0.64 and 0.61; the slopes were 1.1 ± 0.2; the intercepts were 0.0 ± 0.2 Bq kg^{-1} and 0.1 ± 0.3 Bq kg^{-1}, respectively. The paired *t*-test values were 4.262 and 1.821. Based on the results of this analysis, method 5 was better than method 4 with evaluating the radioactivity of ^{235}U.

Comparisons

Table 3 shows a summary of statistical analysis results of this study. The Pearson's correlation coefficients between gamma spectrometry methods and alpha spectrometry were greater than 0.66. Excluding methods 2 and 3 that lacked linearity of the slope, methods 4 and 5 resulted in the best value, 0.68. The determination coefficients of linear regression analyses were 0.46 to 0.59 in the ^{238}U cases and 0.47 to 0.64 in the ^{235}U cases. The slopes of methods 4 and 5 were close to unity. In the Student's *t*-test between gamma spectrometry methods and the control group, the t-values were assessed from 0.307 to 5.840 on both ^{238}U and ^{235}U. In the ^{238}U activity, the t-values for methods 2 and 3 were higher than the critical value of a 95% level of confidence (2.055), and in the ^{235}U activity, the t-value of method 4 was higher. Based on these comparison results, it could be regarded that the gamma-ray spectrometry method results were all correlated with the alpha spectrometry results. Considering the statistical results and the linear regression, method 5, which was novel in this study, thus showed advantages of being more accurate when evaluating ^{235}U and ^{238}U simultaneously.

There are some problems with method 1, in that radioactivity assessment using 63.3 keV is difficult because around the low energy peak the detection efficiency of a p-type HPGe detector is generally low and correction factors like a density correction are needed [40]. In this study the activities from method 2 are obtained without waiting for radon secular equilibrium. It is expected that the measured values of ^{238}U is reduced for the radon gas leakage and broken equilibrium. Nevertheless, if the soil container is airtight and the waiting time is long enough for equilibrium, the results can be better than those obtained in this study, as reported in previous research [46]. Method 3 has a drawback in that the abundance ratio of natural uranium may show regional variations especially for enrichment-related regions [11]. The weakness of methods 4 and 5 is that the MDAs were higher than with other methods but, the MDAs of methods 4 and 5 would improve by 18% (^{235}U) and 16% (^{238}U) when an ROI range at a 144 keV peak was reduced by excluding ^{228}Ac.

Conclusions

In this study, to confirm validity of the novel and traditional uranium activity evaluation methods, the authors presented analysis results and statistical comparison results of five gamma spectrometry methods for measuring the activity of ^{238}U and ^{235}U in environmental soil samples. While each method had weaknesses, e.g., an uncertainty problem, broken secular equilibrium by gas leakage, the natural abundance differences of uranium, and the high MDA, all gamma spectrometry results in this study were correlated with the control group method. In addition, based on the statistical evidence, method 5, which included a ^{230}Th contribution into consideration, possessed the advantage of being more accurate when evaluating the activity of ^{235}U and ^{238}U simultaneously, as shown in Table 3. Method 5 can thus be recommended as a method for evaluating the activity ^{235}U and ^{238}U. It is expected that the results of this study would be useful in selecting a uranium analysis method with gamma spectrometry for general environmental radioactivity monitoring.

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