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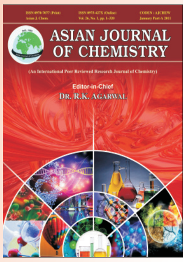

Direct Measurement of ^{226}Ra from γ-Ray Spectroscopy Using an Interference Correction†

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There are several methods used to determine the concentration of ^{235}U, ^{238}U and ^{226}Ra in natural occurring radioactive materials samples through a radiochemical analysis using an alpha spectrometer, a mass spectrometer and a liquid scintillation counter. However, a γ-ray spectrometer still has an effect on the assessment of radioactive concentrations for these nuclides and their progenies. In this study, a direct measurement with the interference correction and an indirect measurement, which means the identification of ^{226}Ra indicators such as ^{214}Pb and ^{214}Bi after the secular equilibrium in the natural occurring radioactive material sample, were introduced and compared for analyzing ^{235}U and ^{226}Ra. Their results were also compared with those from the inductively coupled plasma mass spectrometer (ICP-MS) for the same samples and the optimum method for direct measurement of ^{226}Ra was then selected as considering its accuracy and uncertainty. Finally, the results of ^{226}Ra were used to evaluate the radioactive disequilibrium in raw materials and by-products.

Keywords: Natural occurring radioactive material, ^{226}Ra, γ-Spectrometer, Interference correction, Disequilibrium.

INTRODUCTION

The "Act on safety control of radioactive rays around living environment" was established to protect the public from natural radionuclides in raw materials and by-products in Korea in 2011. The safety control of radiations emanating from them has been imposed to reduce unnecessary exposure around the living environment. In general, ^{226}Ra in the uranium series is one of the important nuclides to estimate the natural radioactivity level of raw materials and by-products because it is a decay product of ^{238}U and is present at various concentrations in nature. Furthermore, its progenies have a large portion of the effective dose to the human body.

Therefore, the method development and technical feasibility for radioactive determination of raw materials should be verified and validated with respect to accuracy and time and cost constraints. There are several methods used to determine the concentration of ^{235}U, ^{238}U and ^{226}Ra in the natural occurring radioactive material samples through a radiochemical analysis using an α-spectrometer, a mass spectrometer and liquid scintillation counter. However, a γ-ray spectrometer still has an effect on the assessment of radioactive concentration for these nuclides and their progenies owing to its rapidity of analysis, simplicity of a sample preparation and availability for a large quantity of samples compared with a radiochemical analysis.

In this study, direct measurement with an interference correction technique[1] and indirect measurement using ^{226}Ra indicators such as ^{214}Pb or ^{214}Bi[2] were introduced for analyzing the concentration of ^{226}Ra in natural occurring radioactive material samples using a HPGe detector. The optimum method for the direct measurement, which is a rapid analysis method compared with the indirect measurement because of not necessity of a secular equilibrium between ^{226}Ra and its progenies was selected by comparing the results between two measurements. The results of ^{226}Ra for selected direct measurement were also compared with those of ^{238}U from the ICP-MS for the same samples. As a result, their comparison was a crucial result to analyze the radioactive equilibrium or disequilibrium state for ^{238}U and ^{226}Ra.

EXPERIMENTAL

Sample preparations and measurements: Ten samples were prepared to represent raw materials such as vermiculite, perlite, bentonite, bauxite, ceramic, Zr sand and clay and by-products such as coal ash. After removing the moisture content in materials, as shown in Fig. 1, they were sealed in Al cans to secure the confinement of radon gases, which are progenies from the uranium series in it. The direct measurement of ^{226}Ra was then made by analyzing a peak area of 186.2 keV

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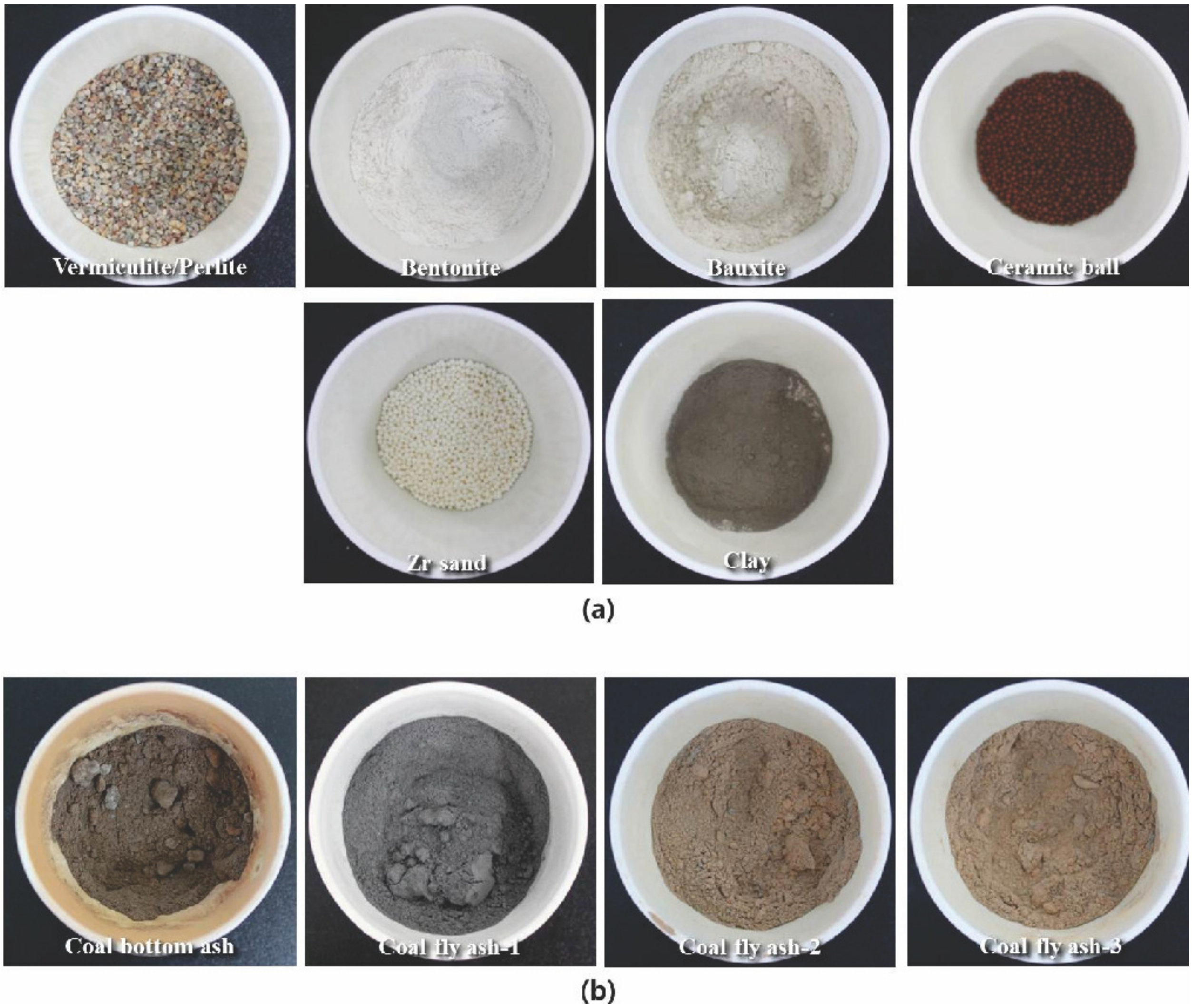

Fig. 1. Naturally occurring radioactive materials: (a) raw materials and (b) by-products

with the help of the interference correction. The indirect measurement of ^{226}Ra which means the quantification of ^{226}Ra indicators such as ^{214}Bi or ^{214}Pb in the sample was also conducted, after attaining the secular equilibrium in decay series as holding samples in sealed cans during 7 half-lives of ^{220}Rn of about 1 month.

In addition, the direct measurement of ^{238}U using the ICP-MS[3] was applied to ten samples to compare ^{238}U with ^{226}Ra from the γ-spectrometry. Samples after the γ-measurement were digested from $LiBO_2$ fusion at 1000 ºC and dissolved into 3 M HNO_3. Through Fe co-precipitation at pH 7, final sample solutions were prepared for the ICP-MS measurement.

Interference corrections for 186.2 keV of ^{226}Ra: A full energy absorption peak for 186.2 keV of ^{226}Ra is heavily interfered by γ-ray with 185.7 keV of ^{235}U. A single peak around 186 keV is therefore detected in the energy spectrum owing to limitation on the energy resolution of the γ-spectrometer. The interference correction is then to subtract a contribution of ^{235}U from a single peak, since the radioactivity of ^{235}U can be quantified from other γ-energies of it as well as from the radioactivity of ^{234}Th on the assumption that ^{238}U and ^{234}Th are in equilibrium and in the natural isotopic ratio between ^{238}U and ^{235}U.

As shown in eqn. (1), a net peak area for 185.7 keV of ^{235}U can be calculated from the information on reference peaks, which are generally selected to 143.8 keV or 205.3 keV of ^{235}U or 63.3 keV of ^{234}Th. In the case of using 63.3 keV of ^{234}Th, its reference peak should be corrected by the natural isotopic ratio and the decay constant, as shown in eqn. (2).

$$N_{185.7} = N_{ref}\frac{(\gamma\varepsilon)_{185.7}}{(\gamma\varepsilon)_{ref}} \tag{1}$$

$$N'_{ref} = N_{63.3}\times\frac{(\theta\lambda)_{235}}{(\theta\lambda)_{238}} \tag{2}$$

where, $N_{185.7}$ and N_{ref} are the net peak areas at 63.3 keV, 185.7 keV and energy of a reference peak, $(\gamma\varepsilon)_{185.7}$ and $(\gamma\varepsilon)_{ref}$ are the γ-emission rate and the peak efficiency at 187.5 keV and energy of a reference peak, respectively, $N_{63.3}$ and N'_{ref} are net peak area and its corrected area by the natural isotopic ratio and the decay constant and $(\theta\lambda)_{235}$ and $(\theta\lambda)_{238}$ are the natural isotopic ratio and the decay constant of ^{235}U and ^{238}U.

RESULTS AND DISCUSSION

Indirect measurement of ^{226}Ra: After the secular equilibrium between ^{226}Ra and ^{220}Rn was attained into an Al can,

^{226}Ra indictors such as ^{214}Bi and ^{214}Pb were quantified from the γ-spectrometer. Since these indicators generally emit many kinds of γ-rays through the cascade decay, the coincidence summing correction has to be applied to their analysis results. In this study, correction factors (COI) of it were determined to be 0.862 and 0.934 for ^{214}Bi and ^{214}Pb, respectively, at the geometry of the n-type HPGe detector with 45 % of a relative efficiency and an Al can with a 100 mL volume.

The activity (A) of ^{226}Ra was then obtained from one of ^{214}Bi or ^{214}Pb, as shown in Fig. 2, as expressing the activity ratio between two indicators for the x-axis and their activities for the y-axis. Almost the same analysis results between them were maintained with the help of COIs. This means an underestimation of ^{226}Ra would be made in the indirect measurement using ^{226}Ra indicators, in the case that COIs are not applied to the γ-spectrometer.

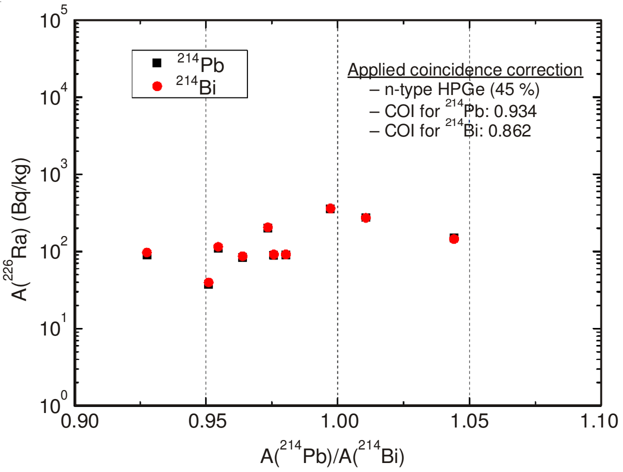

Fig. 2. Analysis results of ^{226}Ra from the indirect measurement

Direct measurement of ^{226}Ra: The interference correction using γ-ray peaks of ^{235}U and ^{234}Th, as shown in (1) and (2), was applied to the assessment of the net peak area for 186.2 keV of ^{226}Ra. Since the net peak area for 185.7 keV of ^{235}U can be calculated from other γ-rays of ^{235}U and ^{234}Th, the subtracted results of the contribution of ^{235}U from a single peak at around 186 keV belongs to the net peak area of ^{226}Ra. First, the reference peaks from ^{235}U were selected to be 205.3 keV (Method 1), which is the only spectrally undisturbed peak and 143.8 keV (Method 2), which is the second high intensity for the γ-ray emission. In the case of Method 2, a γ-peak of 143.8 keV is also spectrally interfered by two other γ-rays, which are from ^{230}Th in the uranium series and ^{223}Ra in the actinium series. A second-order correction is therefore required to calculate the net peak area of a γ-peak of 143.8 keV.

The activity of ^{235}U and ^{226}Ra was calculated from the net peak areas for them and represented in Fig. 3 by comparing with indirect measurements in the same samples. In the graphs, the x-axis means the activity of ^{226}Ra from the indirect measurement and the y-axis means one of ^{235}U and ^{226}Ra from the direct measurement in the same samples. The dotted line in the graphs means the same activity of ^{226}Ra between indirect and direct measurements. Therefore, the linearity between a dotted line and a fitting result of ^{226}Ra from the direct measurement is related to the validation of the measurement method of ^{226}Ra with an interference correction.

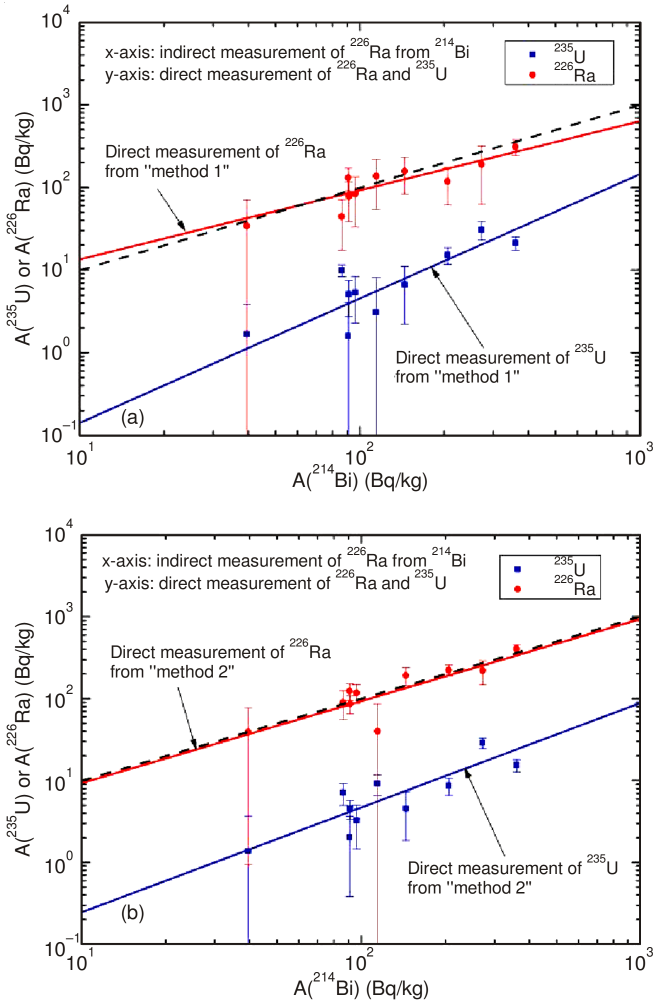

Fig. 3. Analysis results of ^{226}Ra from the direct measurement: (a) Method 1 and (b) Method 2. The dotted line means the same activity of ^{226}Ra between indirect measurements from ^{214}Bi and direct measurements

As shown in Fig. 3, there were extremely high uncertainties in low concentrations of both ^{235}U and ^{226}Ra in the two methods owing to the relative low emission rate of γ-rays used as reference peaks. A good linearity was shown in Method 2, but a complicated second-order correction at 185.7 and 143.8 keV of ^{235}U and still high uncertainty in low concentration made the use of Method 2 unpractical. On the other side, Method 3 using 63.3 keV of ^{234}Th as a reference peak showed that very low uncertainties were maintained because of an almost maximum counting efficiency at 63.3 keV for an *n*-type HPGe detector and a good linearity between direct and indirect measurement was also attained, as shown in Fig. 4(a).

The lower limit of quantification (LLOQ) for the measu-rement was selected when the calculated activity (m) was the same with three-times the uncertainty (3σ) in the analysis results, as shown in (3). To evaluate the LLOQ of ^{226}Ra in Method 3, values for m-3σ of ^{226}Ra were calculated and displayed in graph form according to their activities (m) of ^{226}Ra, as shown in Fig. 4(b). From a linear regression, the LLOQ of ^{226}Ra in Method 3 was determined to be about 27.0 Bq/kg by selecting it when the value of m-3σ reached zero.

$$\text{LLOQ} : m - 3\sigma = 0 \quad (3)$$

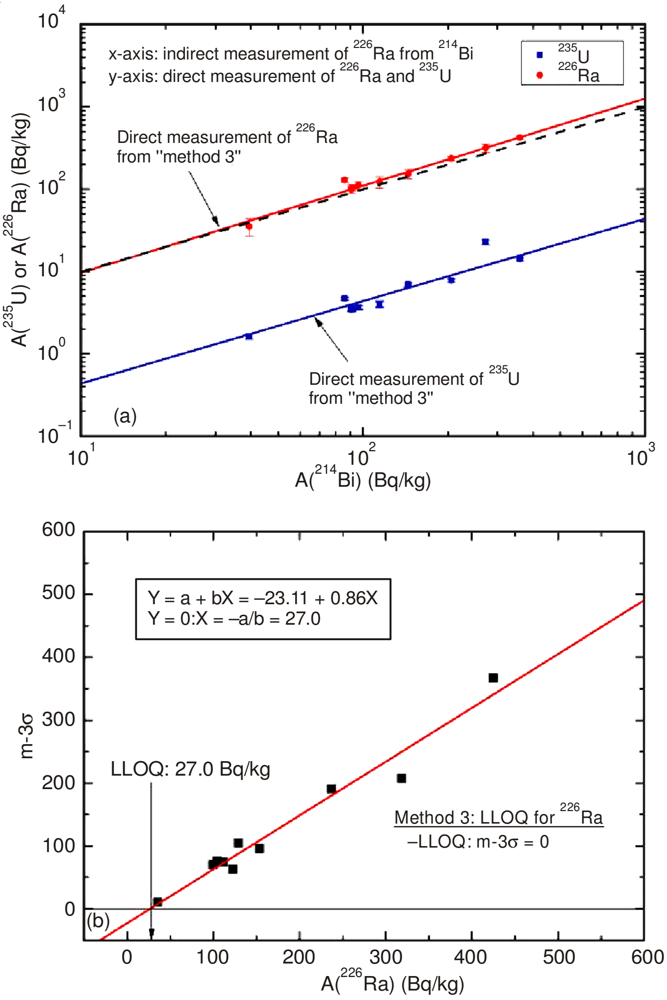

Fig. 4. Analysis results of ^{226}Ra from the direct measurement: (a) Method 3 and (b) LLOQ of ^{226}Ra in Method 3

Disequilibrium in the uranium decay series: In general, the radioactive concentration can be significantly different in the uranium decay series owing to various geochemical proce-sses in the environment such as leaching and erosion[4]. In particular, ^{226}Ra can be selectively removed from the decay chain owing to a different solubility with ^{238}U. Since it is therefore possible to have radioactive disequilibrium in raw materials and by-products, estimating the activity of ^{238}U from the analyzed results on ^{226}Ra can induce serious error. Fig. 5 shows the radioactive ratios between ^{238}U and ^{226}Ra in the same samples. The radioactive equilibrium was well maintained in the by-products such as coal ash; on the other hand, there were samples with a definite disequilibrium state between ^{238}U and ^{226}Ra in processed raw materials such as a ceramic ball and Zr sand. It was interpreted that ^{226}Ra had been removed at the chemical process of relevant raw materials.

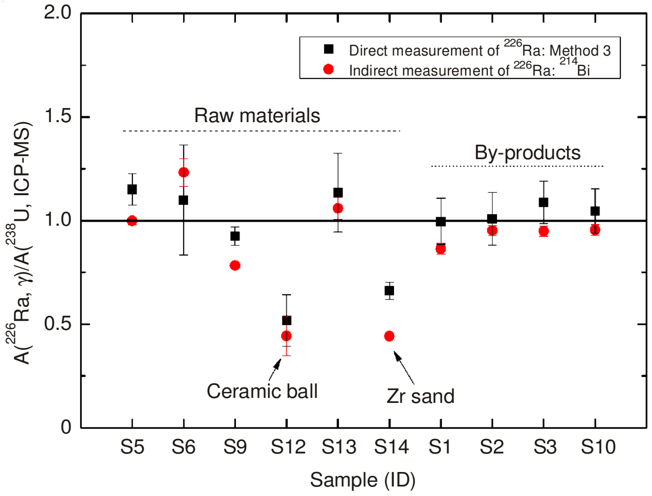

Fig. 5. Activity ratio between ^{238}U from ICP-MS and ^{226}Ra from γ-spectrometer

Conclusion

The direct measurement methods for ^{226}Ra using the interference correction at the γ-spectrometer were reviewed and the most suitable method was selected by considering the accuracy and uncertainty. The interference correction using a γ-peak from 63.3 keV of ^{234}Th as a reference peak was shown to be a good linearity between direct and indirect measurement and very low uncertainties. This made it have the lowest LLOQ of 27.0 Bq/kg at the direct measurement of ^{226}Ra. From the application of the direct measurement to a comparison of analysis results for ^{226}Ra using an ICP-MS, it was possible to recognize the definite disequilibrium state between ^{238}U and ^{226}Ra in processed raw materials such as a ceramic ball and Zr sand.

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