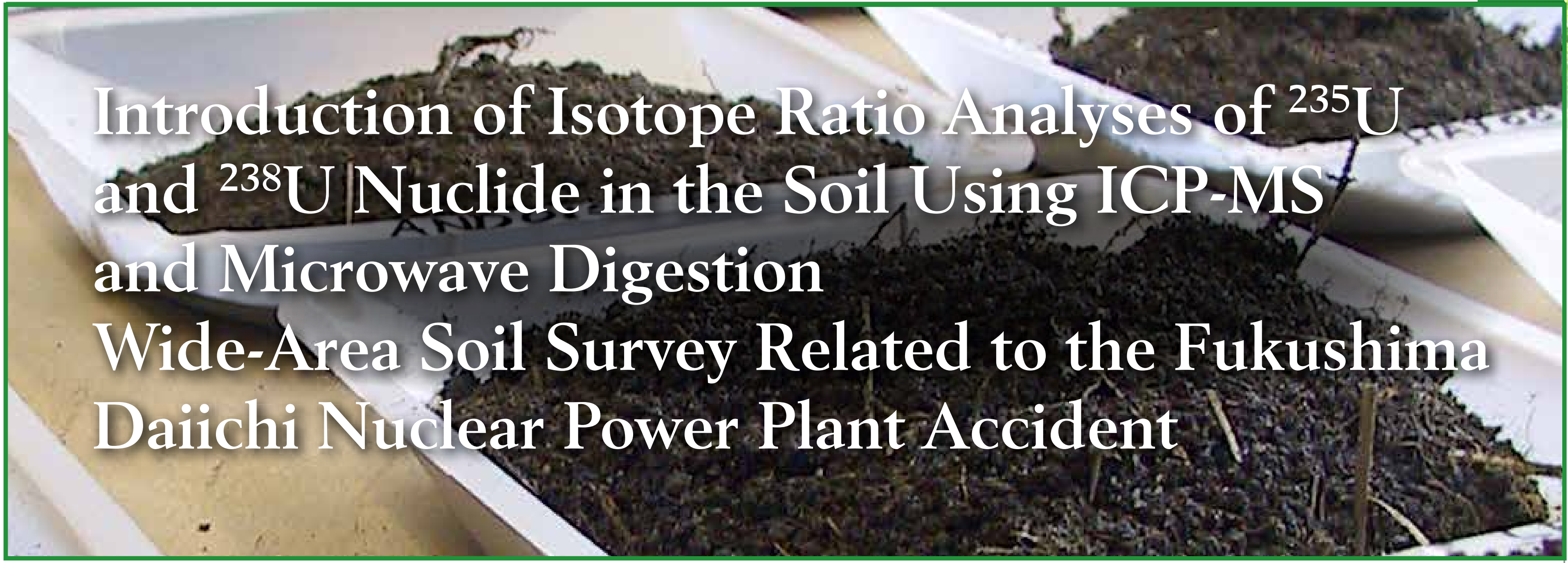

Introduction of Isotope Ratio Analyses of ^{235}U and ^{238}U Nuclide in the Soil Using ICP-MS and Microwave Digestion

Wide-Area Soil Survey Related to the Fukushima Daiichi Nuclear Power Plant Accident

This paper provides an overview of a wide-area soil study[1] related to the Fukushima Daiichi Nuclear Power Plant based on isotope ratio analysis of ^{235}U and ^{238}U in the soil using ICP-MS (Y. Takagai, *Bunseki Kagaku,* 60, pp. 947–958 (2011)). In order to perform precise isotope ratio analysis using ICP-MS, we successfully established isotope ratio of uranium as index of the isotope ratio obtained from the actual test samples. This was done by using uranium in a geochemical reference material instead of a uranium reference sample. Furthermore, we used the ICP-MS cell pass voltage to calibrate and/or correct mass bias when performing mass spectrometry. The result was that we were able to measure the isotope ratio of uranium with an accuracy of 0.37% without using a radioactive standard source. We were also able to determine both ^{235}U and ^{238}U, with a lower detection limit of 0.010 µg/kg for each. During nuclear disasters and other emergencies, this technique should be more effective than traditional ICP-MS and α-particle spectroscopy for rapidly ascertaining conditions of wider area. We also monitored locations ranging between 5 and 80 km in distance from Tokyo Electric Power's Fukushima Daiichi Nuclear Power Plant (115 locations within Fukushima Prefecture). Our results showed that although there were differences in the amount of uranium found at different sampling sites, the isotope ratio was nearly the same as uranium's natural abundance.

> *"In this study, we obtained the isotope ratio by comparing the peak strength ratio of the natural uranium contained in the geochemical reference material without the use of a generic metal standard solution, in order to measure the isotope ratio of uranium using ICP-MS."*

Yoshitaka Takagai®[1],
Makoto Furukawa[2]
[1]Cluster of Science and Technology,
Fukushima University,
1 Kanayagawa, Fukushima
960-1296 Japan
[2] PerkinElmer Japan Co., Ltd.,
134 Godo-cho,
Hodogaya-ku, Yokohama
240-0005 Japan

1. Introduction

During the accident at Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant, which occurred in conjunction with the Great East Japan Earthquake (in March 2011), a large swathe of eastern Japan became contaminated with radioactive substances, causing a serious problem. Because the dispersal of radioactive substances was related to weather conditions and covered a range extending beyond not just the vicinity of the accident but into other prefectures as well, rapid multipoint monitoring became indispensable. Levels of ^{134}Cs, ^{137}Cs, ^{131}I, and other γ-nuclides in soil samples can be directly measured using Ge semiconductor detectors and NaI detectors, making it possible to provide monitoring data at relatively early stage. However, the analysis of ^{235}U and other α-nuclides requires either α-ray spectrometer on chemically processed and isolated samples or high-frequency inductively coupled plasma mass spectrometry (ICP-MS) on soil that has been dissolved. Because both methods require time for pre-processing, they are slower to provide data on ^{235}U originating from nuclear fuel than the method for γ-nuclides does. ICP-MS is very good for simultaneous determination of several metallic elements at part-per-thousand (ppt) levels as well as polyspecimen continuous analysis, but when measuring radioactive metallic elements, the standard solutions are required respectively. This standard solution (which, in this case, must have a higher proportion of radioactive uranium than the natural abundance of uranium) is subject to regulations on the handling of radioactive elements at general analysis laboratories that do not work with radiation, which is a hindrance to the analysis needed to satisfy the public's strong demand for monitoring. A quick method of measuring that will enable general analysis laboratories to analyse polyspecimen samples under emergency conditions is therefore needed.

Additionally, locally distinct levels (distributions) of uranium pose a problem for analysing uranium during nuclear disasters. Natural soil geologically contains natural uranium at levels ranging from ppb to ppm, and those levels vary greatly by location[2]. Uranium level measurements based solely on spatial radiation dose rate and generic soil dissolution methods are not capable of determining whether or not a nuclear disaster has caused the radiation fallout. These issues also necessitate a rapid measurement technique for use in emergencies.

In this study, we developed a method of quickly distinguishing the status of ^{235}U fallouts that originated as nuclear fuel by using ICP-MS to perform isotope ratio analysis of the radioactive isotopes ^{235}U and ^{238}U. We offer a means of analysis that will enable efficient multipoint monitoring during nuclear disasters and other emergencies, and which can be performed at generic laboratories without the use of a ^{235}U standard solution.

2. Experimentation

2.2 Reagents

For ICP-MS, we used an ELAN DRC II manufactured by PerkinElmer. To confirm the isotope ratio (peak strength) and mass precision in the mass spectrum of uranium (^{235}U and ^{238}U), we used geochemical reference material JG-1a (granodiorite from Sawairi, Gunma, averaging 4.80 µm in diameter) produced by the National Institute of Advanced Industrial Science and Technology.

2.3 Isotope ratio analysis of ^{235}U and ^{238}U using ICP-MS

Geochemical reference material JG-1a was dissolved in acid using a microwave digestion device, and we utilised this solution (hereinafter referred to as the "geochemical reference solution") as a standard solution for determining the isotopes of ^{235}U and ^{238}U. Our target ions for mass spectrometry were m/z = 235.044 (^{235}U) and 238.05 (^{238}U). This method requires that the cell pass voltage be determined each time, rather than not using a uranium standard solution. The cell pass voltage was determined by measuring the geochemical reference solution and finding a cell pass voltage that corresponded to a natural abundance of 0.7252. By determining the cell pass voltage, our target mass number under these experiment conditions was to have an average isotope ratio of 0.7237 for n = 10, measured to a precision of relative standard deviation (RSD) 0.37%.

3. Results

3.4 Proof of the accuracy of uranium isotope ratio analysis utilising geochemical reference solution JG-1a.

In this study, we obtained the isotope ratio by comparing the peak strength ratio of the natural uranium contained in the geochemical reference material without the use of a generic metal standard solution, in order to measure the isotope ratio of uranium using ICP-MS. In specific terms, by controlling the cell pass voltage in this method, we were able to calculate the isotope ratio of uranium in unknown samples by inputting the isotope ratio of natural uranium in the already-known geochemical reference material (^{235}U / ^{238}U x 100 = 0.7252) during ICP-MS. With quadrupole ICP-MS, the measurement sensitivity will vary if the mass number differs, even with the same element, because the amount of analysis material that passes through the cells and quadrupoles differs according to the mass number (Fig. 1, upper diagram). In most cases, a correction is made for this mass bias, which means the results have to be calculated by applying a sensitivity correction coefficient to the measured intensity level. In contrast to this, we attempted, with our method, to take measurements using the natural abundance by adjusting the ICP-MS cell pass voltage in accordance to these sensitivity differences, without performing any sensitivity corrections on the actual measurement values (Fig. 1, lower diagram). The effect of cell pass voltage on isotope ratio measurements is shown in Fig. 2. The application of a negative voltage to the cells caused the amount of ^{235}U and ^{238}U ions passing through the cells to vary, resulting in variation in the isotope ratio. Using this method, we measured the geochemical reference solution, obtained the voltage values that corresponded to an isotope ratio of 0.7252, and set the cell pass voltages to those values. This relationship between cell pass voltage and isotope ratio was measured prior to the experiment in order for those adjustments to be made.

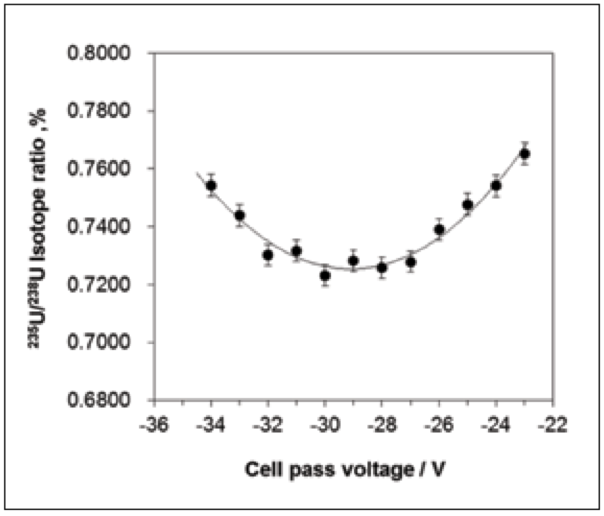

Fig. 2 Relationship between cell pass voltage and ^{235}U/^{238}U isotope ratio.

At the same time, however, if the uranium concentration level is low because of the mass spectrometric intensity of ^{235}U is more than two digits lower than that of ^{238}U at natural abundance, then the mass spectrometric intensity of ^{235}U will vary widely, and for that reason, wide variation in the measured isotope ratio values can also be expected. Variation (in RSD) in the measured isotope ratio values obtained from the mass spectrometric intensity of ^{235}U is shown in Fig. 3. From this power approximation curve, it can be understood that the RSD of the measured isotope ratio value will be 3.0% or less whenever the mass spectrometric intensity of ^{235}U is 150 cps or higher. 150 cps is equivalent to a measured intensity of 60σ or higher over 10 blank measurements, and this strength is sufficient for doing measurements. In this study, we obtained the isotope ratio by making our effective detection strength for ^{235}U to have a detection strength of at least 150 cps.

3.5 Results of uranium concentration determination

As mentioned in 2.5 Experimentation, this method enables not only isotope ratio measurement, but determination as well. The lower quantitative value limit for ^{235}U and ^{238}U using this method was 0.033 μg/kg for both isotopes. We obtained the lower quantitative value limit from the 10σ pre-dilution value obtained from the standard deviation of ten blank solution measurements. The minimum detection limit (3σ) was 0.010 μg/kg for both ^{235}U and ^{238}U. The quantitative values obtained using this method are limited to uranium that can be dissolved in mixed acids.

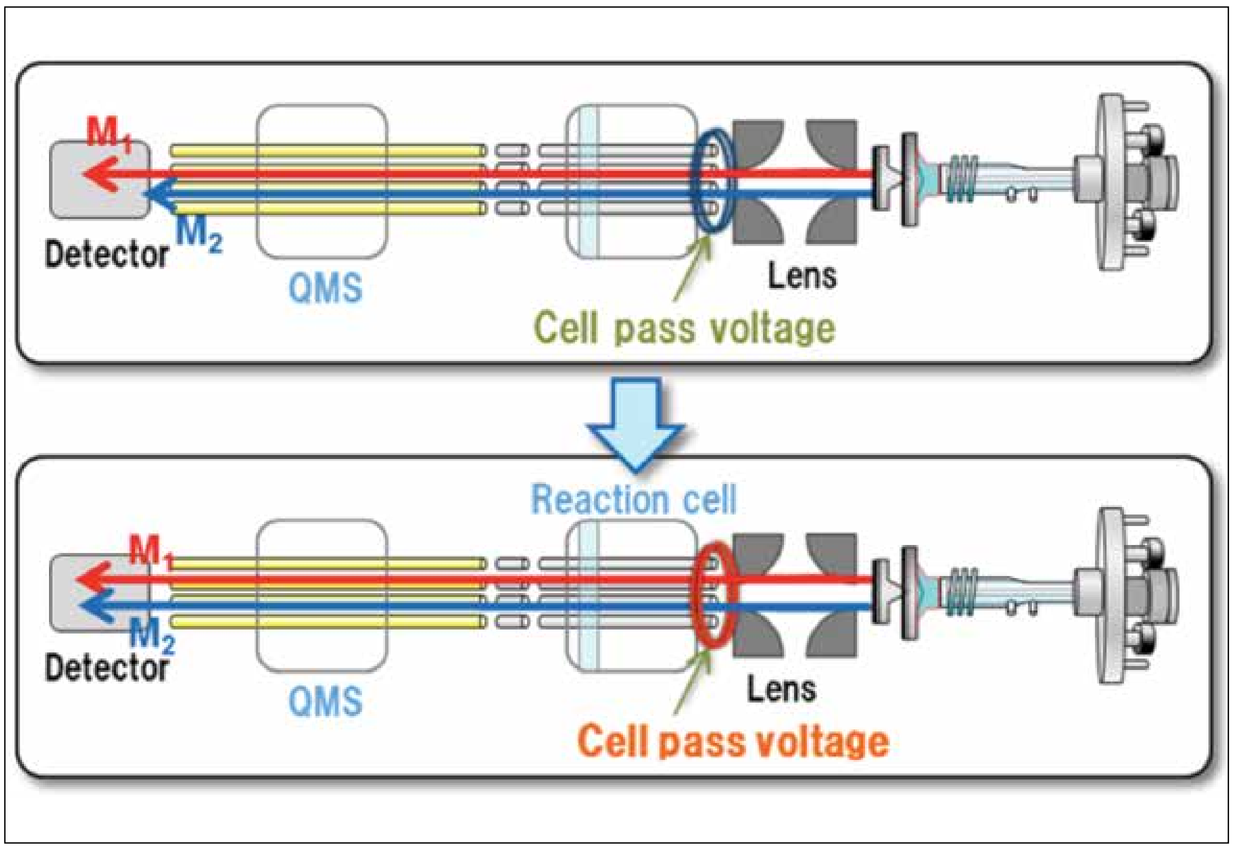

Fig. 1 Mass bias controlling based on configuration of cell pass voltage.

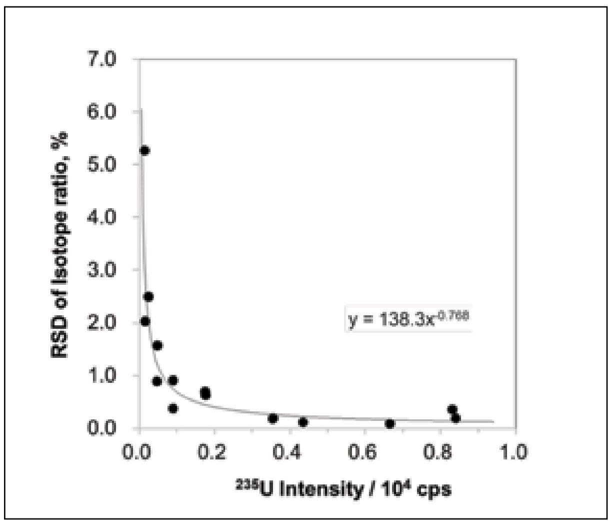

Fig. 3 Relationship between accuracy of uranium isotope ratio and the ICP mass spectrometric intensity of ^{235}U.

3.6 Wide-area soil studies in Fukushima Prefecture

We took soil samples from 115 locations in Fukushima Prefecture where relative radiation levels were high and conducted uranium isotope ratio analyses. The locations from which we took our samples ranged between 7 and 80 km in distance from Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant. The results were given over three pages total, in English in Table 1 of the original paper[1], along with a map, and I would like the reader to refer to those results. They indicate the date each sample was taken, the latitude and longitude of each sample location, the level of radiation in the air, uranium isotope levels and accuracy, quantitative uranium values and radiation conditions, and the soil properties of each sample. The concentration of ^{238}U in the soil is seen to vary between 0.10 and 3.42 mg/kg by location throughout Fukushima Prefecture, and these values do not deviate from the uranium concentration distribution in soil throughout Japan[2]. Despite the variance in overall uranium levels by sample site, we observed isotope ratios that were nearly identical to the natural abundance. We did not observe any correlation with the fallouts of radioactive iodine (^{131}I) or cesium (^{134}Cs and ^{137}Cs) during the initial stage of the nuclear power plant accident. We did not clearly observe uranium fallout from the nuclear accident in the soil sampled for this study. These soil samples showed no correlation with distance from Fukushima Daiichi, but because we did not analyse any soil taken within 5 km of Fukushima Daiichi Power Plant, we cannot be certain as to whether or not there were any fallouts. Furthermore, we observed no connection between air radiation levels and the concentration of radioactive uranium fallouts.

4. Conclusion

In this paper, we have summarised a method for analysing uranium isotope ratios in the soil during emergencies like the nuclear disaster described in *Bunseki Kagaku*[1]. We have reported on new method for isotope ratio analysis of uranium using ICP-MS with the natural uranium contained within geochemical reference as an index, and without using a uranium reference solution, which must be handled and managed as a nuclear material.

References

1. Y. Takagai, M. Furukawa, Y. Nagahashi, T. Takase, O. Shikino, and Y. Kameo, *Bunseki Kagaku*, 60, pp. 947–958 (2011).
2. Geological Survey of Japan, Ed., "Geochemical Map of Japan (2004)", National Institute of Advanced Industrial Science and Technology.