

Determination of uranium concentrations and its activity ratios in coal and fly ash from Philippine coal-fired thermal power plants using ICP-MS and TIMS

By S. K. Sahoo^{1,*}, V. K. Parami², L. L. Quirit³, H. Yonehara¹, T. Ishikawa¹ and S. Tokonami¹

¹ Research Centre for Radiation Protection, National Institute of Radiological Sciences, 4-9-1 Anagawa, Inage, Chiba 263-8555, Japan

² Philippine Nuclear Research Institute, Diliman, Quezon City 1101, Philippines

³ Institute of Chemistry, University of the Philippines, Diliman, Quezon City 1101, Philippines

(Received December 1, 2009; accepted in revised form November 12, 2010)

*TENORM / Uranium / Activity ratio /
Gamma spectroscopy / ICP-MS / TIMS*

Summary. The specific activity of ²³⁸U as a technologically enhanced naturally occurring radioactive material (TENORM) in feed coal, bottom and fly ash samples from four major coal-fired thermal power plants in the Philippines have been measured using high-resolution gamma-ray spectroscopy system equipped with a high-purity germanium (HPGe) detector. The uranium concentration has been determined from same samples using inductively coupled plasma mass spectrometry (ICP-MS). There was a good correlation between the measured uranium using both methods and has been estimated to be 0.98. Uranium from coal, bottom and fly ash samples were chemically separated and activity ratio (²³⁴U/²³⁸U) and ²³⁵U/²³⁸U ratio was measured using a thermal ionization mass spectrometer (TIMS). The highest concentration of uranium was found in fly ash and lowest was for feed coal. Uranium isotopic composition plays an important role in studying its biogeochemical behavior and is a good tracer on the sources of uranium in the environment.

1. Introduction

Increased interest in measuring naturally occurring radionuclide concentrations in coal and fly ash is due to the awareness of health hazards and of these materials contributing to environmental pollution [1]. The worldwide production of coal ash is approaching 1 Gt annually and the amount of ash containing NORM and other mobile toxic elements that has to be dealt with is continuously increasing. Combustion by-products of coal-fired power plants are distributed in the environment as atmospheric discharges. Bottom and fly ash is disposed in landfill or settling ponds and sea, they are also used for the manufacture of building, road and dam construction materials. These contain long-lived radionuclides such as ²³⁸U and ²³²Th. In the Philippines, the determination of TENORM levels in fly ash becomes imperative as the country has more than ten coal-fired thermal power plants currently in operation and more plants are to be constructed in the future.

Uranium is one of the heaviest naturally occurring radioactive elements. Depending on the geological condition, its worldwide median concentration in soil is 35 Bq/kg or 2.8 mg/kg [2]. Its radiotoxicity and chemical toxicity have been well documented [3]. Uranium comprises three natural occurring isotopes *e.g.* ²³⁴U, ²³⁵U and ²³⁸U with the isotopic abundances being approximately of 0.0055%, 0.7200% and 99.2745%, respectively [4]. The principal isotopes of primordial origin are ²³⁸U and ²³⁵U, with ²³⁴U present approximately in radioactive equilibrium with ²³⁸U [5], ²³⁶U occurs in nature at ultra trace concentrations. ²³⁵U and ²³⁸U ratios may have small variations depending on the geographic origin of the sample, due to natural isotopic fractionation, nuclear reactions or anthropogenic contamination. Under normal circumstances, enriched ²³⁵U indicates a source of nuclear weapon test or nuclear reactor accidents whereas depleted ²³⁵U is a result of uranium enrichment in the manufacture of enriched uranium used as a fuel in nuclear reactors and nuclear weapons [6, 7]. Another source of radioactivity in the environment is the release of technologically enhanced naturally occurring radioactive material (TENORM) by coal, fly ash, oil, natural gas, mineral, ore refining, production of phosphate fertilizers and disposal of uranium mill tailings. As opposed to above mentioned instances there is no change in the isotopic composition of ²³⁵U/²³⁸U. However, ²³⁴U/²³⁸U isotopic composition (activity ratio) variation has been noticed in water, soil, sediment and uranium ore sample [8–10]. Therefore, uranium isotopic composition plays an important role in studying its biogeochemical behavior and is a good tracer on the source of uranium in the environment.

Although α -spectrometry is the common choice for the measurement of activity ratios, in recent days, mass spectrometry using inductively coupled plasma as an ion source (ICP-MS) is now accepted as a versatile analytical technique for elemental and isotopic analysis [11–13]. Thermal ionization mass spectrometry (TIMS) has been accepted as a “benchmark” technique for isotopic analysis [14, 15]. Recently, high precision uranium isotopic measurements are in rapid process using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [9, 16, 17] and thermal ionisation mass spectrometry (TIMS) equipped with energy filters [18, 19].

* Author for correspondence (E-mail: sahoon@nirs.go.jp).

Extraction chromatography with UTEVA resin has been utilized for the preconcentration and separation of U [20, 21].

The concentration of uranium in coal, bottom and fly ash samples from Philippine coal-fired thermal power plants has been determined using ICP-MS whereas $^{234}\text{U}/^{238}\text{U}$ activity ratio and $^{235}\text{U}/^{238}\text{U}$ ratio have been measured using thermal ionization mass spectrometry. The resulting data can be used as bases for regulatory control, radiological impact assessment, and classification of coal ash for construction purposes.

2. Experimental procedure

2.1 Study area

The coal-fired thermal power plants A, B, C and D where feed coal and ash samples were obtained are all located in Luzon Island, Philippine. Plants A and B are located in the southern part of Luzon whereas C and D plants are located in northern part of Luzon (Fig. 1). Each plant's operating capacity, start of operation, origin of coal used during the sampling period, size of ash ponds, and height of stacks are given in Table 1.

2.2 Sample collection and preparation

About 2–3 kg of feed coal (FC), bottom ash (BA) and fly ash (FA) samples were collected from four Philippine thermal

Table 1. Description of four Philippines coal-fired thermal plants.

Plant name	Production (MW)	Starting year	Coal origin	Ash pond area (m ²)	Stack height (m)
A-1	300.00	1984	Indonesia		120
A-2	350.00	1995		640 000	150
B-1	367.50	1996	Indonesia		220
B-2	367.50	1996		222 570	
C-1	300.00	1998	China		150
C-2	350.00	1998		816 800	
D-1	609.00	1999	China		240
D-2	609.00	1999		1 400 000	

power plants. The FA samples from plant B were collected from the 1st and 2nd stages (near to the stack) of the electro static precipitator (ESP) whereas the FA sampling points of the other plants ESP stages were not indicated. All samples were oven dried at 80 °C until weight was constant, pulverized using a mortar and pestle (except for the fly ash samples), and homogenized using a 500 µm mesh size sieve.

2.3 Instruments

A high-purity germanium detector (ORTEC GEM-100210) γ -spectroscopy coupled with a multi-channel analyzer (ORTEC-7700-010) and gamma studio software (Seiko EG&G, 2000) was used for the measurement of specific activity of radionuclides.

A Hewlett Packard ICP-MS HP-4500 (Yokogawa Analytical Instruments, Tokyo, Japan) was used for the measurement of U which yielded detection limits of 0.01–0.003 µg/L (0.12–0.037 mBq/kg). The ICP-MS detection limit was calculated as three times the standard deviation of the calibration blank measurements (1 : 1 v/v HNO₃: Milli Q water, $n = 10$). The relative error of ICP-MS results for the reference sample (lake sediment JLK-1) for ^{238}U was 0.56%. The parameters for data acquisition and optimization conditions are reported elsewhere [22].

A VG Sector 54-30 thermal ionization mass spectrometer (VG Isotopes Ltd., UK), equipped with nine Faraday cup collectors and Daly ion detection system positioned behind axial Faraday and wide aperture retardation potential (WARP) energy filter, was used for the isotopic measurement of uranium.

2.4 Reagents and standards

High purity water was obtained with a Millipore Milli-Q water purification system. High purity HCl, HNO₃, HF and HClO₄ were purchased from Tamapure chemical industries (Kawasaki, Japan). The strong anion exchange resin Dowex 1X-8 (200–400 mesh, Cl⁻ form) was purchased from Bio-Rad Labs (Richmond, CA). It was soaked in 6 M HNO₃ and subsequently washed with distilled water. Commercial extraction chromatographic resin, UTEVA was purchased from Eichrom Industries (Darien, IL) and was conditioned with 8 M HNO₃.

2.5 Chemical procedures

Feed coal (FC), bottom ash (BA) and fly ash (FA) samples were digested with HNO₃, HF and HClO₄ in PTFE pressure



Fig. 1. Map showing sampling stations in Luzon island.

decomposition vessels. A microwave unit (MLS 1200 mega, Italy) was used for heating the sample. The samples were evaporated to dryness on a hot plate after digestion. Finally, the residues were dissolved in 8 M HNO₃ to yield the sample solution for chemical separation.

We have used a combination of anion exchange and extraction chromatography with a little modification of earlier methods [20, 21]. First column was prepared using pre-cleaned anion exchange resins (Dowex 1X-8, 200–400 mesh, Cl⁻ form) and packed into 2 cm internal diameter Pyrex columns up to a height of 6 cm and the second 1.0 × 0.5 cm internal diameter column containing Eichrom UTEVA resin. Both columns were conditioned by passing 15 ml of 8 M HNO₃. The sample was transferred to anion exchange column and the eluent was subsequently passed onto the UTEVA column. Both columns were washed with 10 ml of 8 M HNO₃ followed by 20 ml of 3 M HNO₃. U was eluted from UTEVA column using 5 ml of 0.02 M HCl. Concentration of eluent was adjusted to 9 M HCl. The resulting solution was loaded onto an anion exchange column preconditioned with 9 M HCl and washed with 10 ml of 9 M HCl. Finally, U was eluted with 10 ml of 0.02 M HCl and the eluent was evaporated to dryness in a Teflon beaker. Recovery of U from the samples were about 80 ~ 90%.

2.6 Gamma spectroscopy

About 100 g of split homogenized dried samples were stored in airtight U-8 standard cylindrical containers (diameter = 48 mm; height = 58 mm) for 30 d to attain secular equilibrium of ²²⁶Ra and its progeny. The detector efficiency was determined using a 100 g multi-nuclide standard source supplied by Japan Radioisotope Association with quoted gamma energies ranging from 60 to 1333 keV an overall uncertainty of less than 5%. The activity concentration of ²²⁶Ra was measured using the HPGe γ -spectrometer described above. Details of this technique have been given elsewhere [23]. The results were compared with a natural soil standard IAEA-375 (International Atomic Energy Agency, natural soil standard) to check the reproducibility of method. The ²²⁶Ra concentrations were determined by measuring the activities of its decay products ²¹⁴Pb (295 and 352 keV) and ²¹⁴Bi (609 and 1120 keV).

2.7 Mass spectrometry

A triple filament assembly was used for the thermal ionization of uranium isotopes. The filament material was 5 pass zone refined rhenium ribbon (H. Cross, 99.999%) with 0.003 cm thickness and 0.07 cm width. The isolated U fraction was loaded onto a separable outer filament and heated with a 0.9 A current to leave a dry residue. Mass spectrometry analytical scheme in detail has been described elsewhere [15].

3. Results and discussion

The results of three replicate analyses of the uranium concentrations (Bq kg⁻¹) in FC, BA and FA samples from the four coal-fired thermal power plants were measured by γ -spectroscopy and ICP-MS are summarized in Table 2. The

Table 2. Comparison between γ -spectroscopy and ICP-MS methods for the measurement of uranium concentration (Bq kg⁻¹).

Sample	Plant	γ -spectroscopy ²²⁶ Ra	ICP-MS ²³⁸ U
FC	A	11.7 ± 1.4	2.6 ± 0.1
BA	A	29.9 ± 2.2	30.2 ± 1.2
ESP 1 st	A	53.4 ± 3.4	59.8 ± 2.4
ESP 2 nd	A	56.3 ± 3.6	69.9 ± 4.2
FC	B	1.8 ± 1.3	2.9 ± 0.1
BA	B	51.6 ± 3.6	57.9 ± 3.5
FA	B	50.8 ± 3.4	268.0 ± 10.7
FC	C	6.7 ± 1.2	5.8 ± 0.1
BA	C	106.7 ± 6.7	55.6 ± 1.7
FA	C	109.6 ± 6.8	83.2 ± 2.1
FC	D	10.1 ± 1.5	13.7 ± 0.8
BA	D	83.3 ± 5.3	100.2 ± 4.1
FA	D	131.13 ± 8.1	132.4 ± 10.6

highest activity concentration of ²²⁶Ra was observed in FC samples of plant A while for plant B was the lowest in FC irrespective of same origin *i.e.* from Indonesia. In case of BA samples, Plant C had the highest concentration of ²²⁶Ra. Plant D had the highest concentration of ²²⁶Ra in FA samples. Concentrations of ²³⁸U were found to be high in China FC samples operated in plants C and D in comparison to Indonesia FC used in plants A and B. There were different trends for BA and FA samples. Plant D had the highest ²³⁸U concentration whereas plant B had the highest activity concentration of ²³⁸U in FA sample. The concentration of ²³⁸U was comparable in BA and FA samples from plants A and C.

The correlation of ²²⁶Ra with ²³⁸U for samples analyzed using ICP-MS and HPGe γ -spectroscopy is shown in Fig. 2. A good correlation ($R^2 = 0.98$) was obtained between the two analytical techniques excluding three aberrant data points. The slopes for the HPGe γ -spectroscopy vs. ICP-MS data had values near unity (around 0.90) and intercept near zero which indicates an approximate one to one correspondence between the two techniques. The data points for FA sample (Plant B) were more aberrant in the correlation plots in comparison with FA and BA samples (Plant C) to a lesser degree in the ²³⁸U series. Plant C's BA and FA samples have higher concentration of ²²⁶Ra than ²³⁸U. The degree of partitioning of the radionuclide between bottom ash and fly ash during the combustion process is influenced by the condition of plants furnace and the physical and chemical form of the

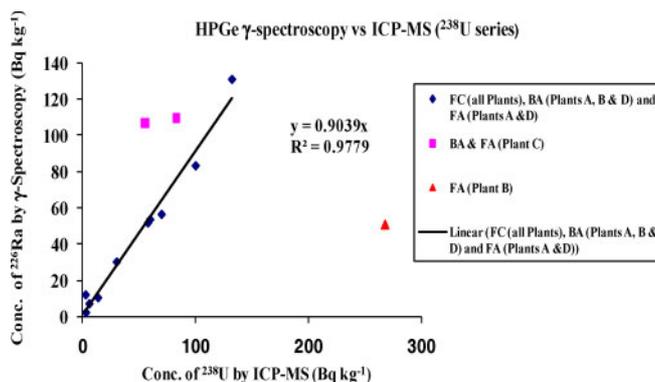


Fig. 2. Correlation between the ICP-MS and γ -spectroscopy measurement.

Table 3. Measurement of $^{234}\text{U}/^{238}\text{U}$ isotope ratio and activity ratio.

Sample	$^{234}\text{U}/^{238}\text{U}$	Activity ratio
Zircon (Sulinjarvi)	0.0000547	0.9998
Zircon (Perak)	0.00005469	0.9997

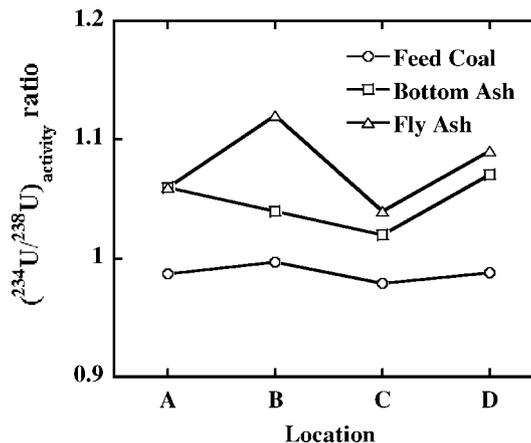
For activity ratio calculation, $\lambda_{238} = 1.551 \times 10^{-10}$ and $\lambda_{234} = 2.835 \times 10^{-6}$ has been used [9].

feed coal. The results indicate that the HPGe γ -spectroscopy analytical technique can generally be used for activity concentration determination of radionuclides. However, this is an indirect method and is based on the assumption that secular equilibrium exists between ^{238}U and its decay products. In order to accurately measure TENORM concentrations, various available techniques have to be utilized depending on the physical and chemical form of radionuclide of interest. Since ICP-MS method measures mass concentrations, it is more accurate.

In coal samples, secular equilibrium exists between ^{238}U and its decay products, especially when the coal is undisturbed for very long period of time. But this may not be true for relatively “young coal” *e.g.*, lignites and sub-bituminous. Definitely, secular equilibrium may not exist in combusted coal or in ashes. Therefore, activity ratio measurement may be helpful to understand its origin if there is a large variation in the concentration.

To check accuracy of the isotopic composition of uranium by TIMS method, NBS standards, NBS U010 with known isotopic compositions were analysed. The isotope ratio, $^{235}\text{U}/^{238}\text{U}$ was corrected for non-linearity of Daly-ion detector by 0.15% per 10^{-13} A. The results of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ isotope ratios were 0.0000546 ± 0.0000002 and 0.0101424 ± 0.000005 against certified value of 0.0000546 and 0.010140 respectively. Thus, the measurements of the isotopic ratio in the standards demonstrate that isotopic fractionation, if occurring in the system, is less than the uncertainty in the measurement. A precision of better than 0.20% at the 95% uncertainty level ($n = 60$) on $^{235}\text{U}/^{238}\text{U}$ has been obtained. Zircon samples were analysed for comparison of $^{234}\text{U}/^{238}\text{U}$ isotope ratio to detect the accuracy of activity ratio, results are given in Table 3.

The results of three replicate analyses of uranium isotope ratios in coal, bottom and fly ash samples from coal-fired thermal plants are summarized in Table 4 with the objective of detecting any variability in the presence and potential source of anthropogenic uranium. The $^{235}\text{U}/^{238}\text{U}$ isotope ra-

**Fig. 3.** Activity ratio of feed coal, bottom and fly ash samples.

tios fall in the range of 0.007245 to 0.007259 which are expected for natural uranium and close to the well known “normal terrestrial” ratio of 0.00725. From replicate runs of each sample, one can confirm that such deviations from natural ratios were readily reproducible at statistical levels predicted by standard measurements.

$^{234}\text{U}/^{238}\text{U}$ isotope ratio has been expressed as activity ratio, it varies from the lowest *i.e.* 0.979 ~ 1.12, showing an increase in the natural abundance of ^{234}U in the samples. The original $^{235}\text{U}/^{238}\text{U}$ ratio was established in the *r*-process (rapid neutron capture) of nucleosynthesis in a stellar, presolar environment and has then decreased due to alpha decay since that time, leading to the present terrestrial ratio [19]. Although mass spectrometric measurements are calculated on the abundance ratio, the obtained abundance ratios are re-calculated to the radioactivity ratio taking into account the decay constant. Thus, it becomes very easy to discuss the accomplishment of radioactive secular equilibrium when $(^{234}\text{U}/^{238}\text{U})_{\text{activity}} = \text{unity}$. It can be seen in Fig. 3, some uranium samples appear not to be in radioactive equilibrium. Kigoshi [24] proved that ^{234}Th is ejected into the aqueous phase from the surface of zircon into the coexisting aqueous phase as an effect of recoil energy. As a result, the ^{234}U content in water phase of nature is often too high in comparison with its content in solid silicate phase. It is very likely that the pore water of fly ash contained slight excess of ^{234}U . To the contrary, if weathering proceeds to excess, it is probable that the radioactivity ratio in question becomes lower than unity. In case of feed coal samples, all values are less than unity. However, activity ratios were higher in case of fly ash samples followed by bottom ash samples.

Table 4. Isotopic composition of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ in coal and ash samples.

Location	FC		BA		FA	
	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
A	0.987 ± 0.03	0.007248 ± 11	1.06 ± 0.02	0.007246 ± 13	1.06 ± 0.02	0.007257 ± 12
B	0.997 ± 0.01	0.007254 ± 13	1.04 ± 0.03	0.007247 ± 14	1.12 ± 0.02	0.007245 ± 13
C	0.979 ± 0.02	0.007247 ± 14	1.02 ± 0.05	0.007248 ± 15	1.04 ± 0.03	0.007252 ± 12
D	0.988 ± 0.03	0.007251 ± 13	1.07 ± 0.04	0.007249 ± 16	1.09 ± 0.04	0.007259 ± 15

$^{234}\text{U}/^{238}\text{U}$ isotope ratio stands for activity ratio and errors are given as 2σ std dev and $^{235}\text{U}/^{238}\text{U}$ ratio analytical uncertainties refer to the least digit of significant figures.

4. Conclusions

We have measured $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios in coal and fly ash samples to better than 0.2% at two standard deviation (sd). This method should be applicable to a wide range of environmental and geological problems which are limited by sample size or for which higher precision is required. Results obtained here for uranium activity ratios are preliminary in nature. However, systematic studies are necessary to ascertain the behavior of activity in surrounding area soil samples to study soil water interaction.

Acknowledgment. One of us (SKS) is highly grateful to Professor A. Masuda, University of Tokyo for zircon sample and helpful discussions. V. K. Parami was awarded a fellowship grant under Nuclear Researchers Exchange Program, Ministry of Education, Science and Technology of Japan (NSRA/MEXT) to visit NIRS, Chiba, Japan in co-operation with the Philippine Nuclear Research Institute. The authors express their sincere thanks for the assistance to Mr. S. Canete and Mr. H. Arae.

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