Microchemical Journal 95 (2010) 181–185

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Accurate determination of naturally occurring radionuclides in Philippine coal-fired thermal power plants using inductively coupled plasma mass spectrometry and γ-spectroscopy

Vangeline K. Parami [a], Sarata Kumar Sahoo [b,*], Hidenori Yonehara [b], Shino Takeda [b], Leni L. Quirit [c]

[a] Philippine Nuclear Research Institute, Diliman, Quezon City 1101, Philippines
[b] Research Centre for Radiation Protection, National Institute of Radiological Sciences, 4-9-1 Anagawa, Inage, Chiba 263-8555, Japan
[c] Institute of Chemistry, University of the Philippines, Diliman, Quezon City 1101, Philippines

ARTICLE INFO

Article history:
Received 6 November 2009
Received in revised form 17 November 2009
Accepted 17 November 2009
Available online 26 November 2009

Keywords:
NORM
Activity concentration
Coal
Fly ash
ICP-MS
γ-spectroscopy

ABSTRACT

There is an increased interest in measuring naturally occurring radioactive materials (NORM) like coal, fly ash considering health hazards caused by naturally occurring radionuclides. This paper presents activity concentration (AC) of ^{226}Ra, ^{228}Ra, ^{232}Th, ^{238}U and ^{40}K in feed coal, bottom and fly ash samples from Philippines coal-fired thermal power plants using inductively coupled plasma mass spectrometry (ICP-MS) and high-purity germanium gamma spectroscopy (HPGe γ-spectroscopy). Coal, bottom and fly ash samples were digested using a microwave oven with a mixture of HNO_3, $HClO_4$ and HF. Uranium (^{238}U) and thorium (^{232}Th) ACs were also analyzed from samples using ICP-MS. A good correlation was found for the measurement of U and Th using both techniques ($R^2 = 0.97$ and 0.94 respectively). ICP-MS measurements showed the highest AC of ^{232}Th and ^{238}U in fly ash and lowest for feed coal samples. With HPGe γ-spectroscopy measurements, highest AC (in Bq kg^{-1}) of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K, were noticed in fly ash followed by bottom ash and feed coal. ICP-MS method is rapid for the measurement of uranium and thorium in comparison to γ-spectroscopy as secular equilibrium is not required. Activity concentrations of bottom and fly ash samples were found to be within the reported values worldwide and below the International Atomic Energy Agency recommended values for regulatory control.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Technologically enhanced naturally occurring radioactive material (TENORM) in industrial by-products, residues, and wastes has received global attention and concern due to the very large amounts produced annually. Coal and fly ash are technologically important material resulting from coal fired thermal power plants. Coal like most fossil fuels contains ^{238}U, the most important parent element of the natural uranium decay series. Large quantities of fly ash are produced by coal-fired thermal plants and they may contain enhanced levels of radionuclides along with other toxic elements [1]. Increased interest in measuring these 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. The worldwide production of coal ash is approaching 1 Gt annually and this amount of ashes contain NORM and other mobile toxic elements that have to be dealt with is continuously increasing [2,3].

Combustion by-products of coal-fired power plants are distributed in the environment as atmospheric discharges and bottom and fly ashes are disposed in landfill or settling ponds and sea, also they are used for the manufacture of building, road and dam construction materials. These contain long-lived radionuclides such as ^{238}U and ^{232}Th, their decay products, and ^{40}K. Coal-fired power plants were also identified as contributing to the elevated levels of atmospheric radon [4]. Comparison studies have been done for coal and nuclear power plants in terms of radioactivity levels, radioactive atmospheric discharges, and radiological impacts [5–11]. Measurements of TENORM in soils near coal-fired power plants were also done [12–15]. There are a few reports on TENORM surveys on the national, regional and international levels [16–18] and TENORM is regulated in some of countries [19]. In some countries, building materials are classified according to TENORM levels in order to protect the public from additional radiation exposure [20–23].

In the Philippines, the determination of TENORM levels in fly ashes 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.

Inductively coupled plasma mass spectrometry (ICP-MS) has the potential to be an ideal tool for precise, accurate, and rapid determination of Th and U. There have been extended efforts in environmental analytical chemistry to optimise multi-element ICP-MS technique [24–27]. The extremely low detection limits, high resolution,

* Corresponding author. Tel.: +81 43 206 3096; fax: +81 43 251 4853.
E-mail address: sahoo@nirs.go.jp (S.K. Sahoo).

0026-265X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2009.11.008

short measurement time and capability for isotopic analysis make it superior to any other techniques such as neutron activation analysis (NAA), alpha spectrometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES). This paper reports determination of ^{238}U, ^{226}Ra, ^{232}Th, ^{228}Ra, ^{228}Th and ^{40}K in split samples of feed coal (FC), bottom ash (BA) and fly ash (FA) using ICP-MS and low background HPGe γ-spectroscopy. The resulting data can be used as bases for regulatory control, radiological impact assessment, and classification of coal ashes for construction purposes.

2. Material and methods

2.1. Sampling sites

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, Philippines (Fig. 1). Plants A and B are located in the northern part of Luzon whereas C and D plants are located in the southern part of Luzon. Table 1 provides information about each plant's operating capacity, start of operation, origin of coal used during the sampling period, size of ash ponds, and height of stacks.

2.2. Sample collection and preparation

About 2–3 kg of feed coal, bottom ash, fly ash, and ash pond samples were collected from four Philippine Power Plants. All samples were oven dried at 60 °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.

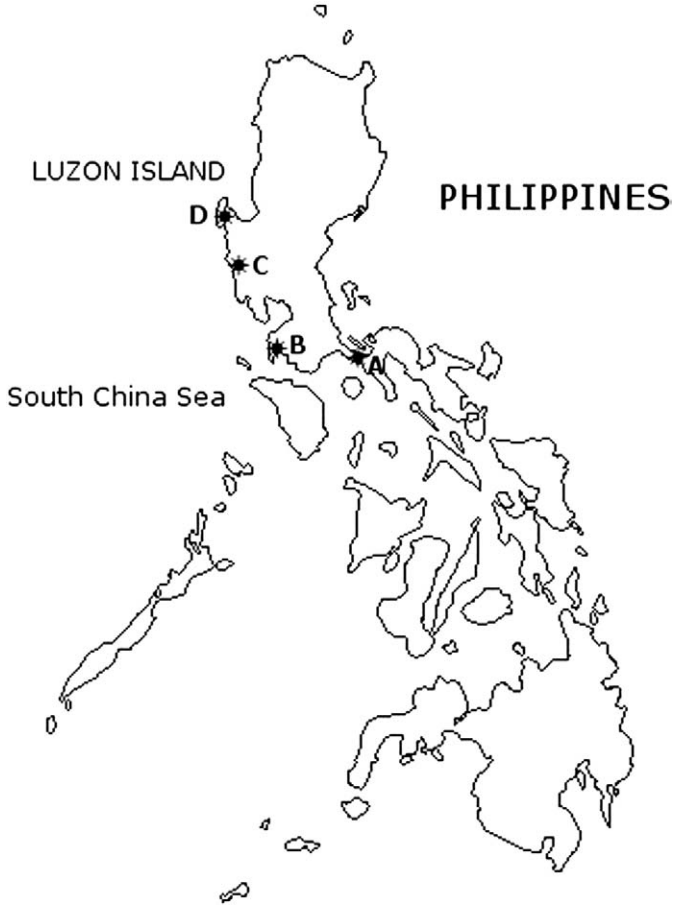

Fig. 1. Location of coal-fired thermal power plants in Luzon island of Philippines.

Table 1
Description of four coal-fired 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		
B-2	367.50	1996		222,570	220
C-1	300.00	1998	China		
C-2	350.00	1998		816,800	150
D-l	609.00	1999	China		
D-2	609.00	1999		1,400,000	240

2.3. Gamma spectroscopic determination

About 100 g of homogenized dried samples were stored in airtight U-8 standard cylindrical containers (diameter = 48 mm; height = 58 mm) for 30 days to attain radioactive equilibrium of ^{226}Ra and ^{228}Th and their progeny. The activity concentration of ^{226}Ra, ^{228}Th and ^{40}K were measured using 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). Details of this technique have been given elsewhere [23].

The ^{226}Ra concentrations were determined by measuring the activities of its decay products ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 and 1120 keV). The activity of ^{40}K was determined by the 1461 keV gamma-rays, the ^{232}Th by the 911 keV gamma-rays of ^{228}Ac and the 2614 keV gamma-rays of ^{208}Tl [28].

2.4. Measurement of ^{238}U and ^{232}Th using ICP-MS

ICP-MS used was a Hewlett Packard-4500 (Yokogawa Analytical Corporation, Japan) for the determination of ^{238}U and ^{232}Th in certified soil samples which yielded detection limits of 0.01–0.003 μg/L. The parameters for data acquisition and optimization conditions are reported elsewhere [24]. Under these analytical conditions, the oxide formation level of Ce was found to be 0.4–2.0% (CeO^+/Ce^+). An internal standard, Rh, was used to assess any changes in analytical signals during measurement. Standard solutions were prepared from SPEX multi-element Plasma standards (SPEX Industries, Inc.,) and used to derive calibration curves. Standard reference materials were used to validate the analytical procedure. Sediment reference sample, JLK-1 was used for soil analysis. The precision calculated using three independent runs were better than 5% RSD with a comparable accuracy. The relative errors of ICP-MS results for the reference sample (lake sediment JLK-1) for ^{232}Th and ^{238}U were 0.52% and 0.56%, respectively.

Coal, bottom and fly ash sample digestion was performed in a closed vessel (PTFE vessels) microwave unit (MLS 1200 mega, Italy) with a combination of high purity acids HNO_3, $HClO_4$, and HF. After digestion, samples were evaporated to dryness on a hot plate and the residue was dissolved in 5% HNO_3 to yield a sample solution for ICP-MS determination.

3. Results and discussion

3.1. Results of AC in FC, BA and FA samples

Table 2 presents the ACs (Bq/kg) of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K in FC, BA, and FA samples measured by HPGe γ-spectroscopy. Among FC samples, the highest AC of ^{226}Ra, ^{228}Ra and ^{40}K was noticed in plant A while for plant B was the lowest irrespective of same origin i.e. from Indonesia. In case of BA samples, Plant C had the highest AC of ^{226}Ra while Plant D had the highest AC for ^{228}Ra, ^{228}Th and ^{40}K. Plant D had the highest AC of ^{226}Ra, ^{228}Ra and ^{228}Th in FA samples while Plant C had the highest AC of ^{40}K. Among the radionuclides, the AC's of ^{40}K are

Download English Version:

https://daneshyari.com/en/article/1227966

Download Persian Version:

https://daneshyari.com/article/1227966

Daneshyari.com