1.44 Particulate Matter and Neutron Activation Analysis

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Abstract

In these years, economy of East Asian region is rapidly growing, and countries in this region are facing serious environmental problems. Neutron activation analysis is known as one of high-sensitive analytical method for multi elements. And it is a useful tool for environmental research, particularly for the study on atmospheric particulate matter that consists of various constituents. Elemental concentration represents status of air, such as emission of heavy metals from industries and municipal incinerators, transportation of soil derived elements more than thousands of kilometers, and so on. These monitoring data obtained by neutron activation analysis can be a cue to evaluate environment problems. Japanese government launched National Air Surveillance Network (NASN) employing neutron activation analysis in 1974, and the data has been accumulated at about twenty sampling sites. As a result of mitigation measure of air pollution sources, concentrations of elements that have anthropogenic sources decreased particularly at the beginning of the monitoring period. However, even now, concentrations of these anthropogenic elements reflect the characteristics of each sampling site, e.g. industrial/urban, rural, and remote. Soil derived elements have a seasonal variation because of the contribution of continental dust transported by strong westerly winds prevailing in winter and spring season.

The health effects associated with trace elements in particulate matter have not been well characterized. However, there is increasing evidence that particulate air pollution, especially fine portion of particles in many different cities is associated with acute mortality. Neutron activation analysis is also expected to provide useful information to this new study field related to human exposures and health risk.

Keywords: Instrumental neutron activation analysis; Atmospheric particulate matter; National Air Surveillance Network, PM_{10}, $PM_{2.5}$, Human health, Transition metal

Introduction

Instrumental neutron activation analysis (INAA) technique was first applied to atmospheric particulate matter (PM) utilizing the neutron source of research reactor and high resolution

Ge(Li) semiconductor detector in early 1970's[1]. Advantages of INAA for the analysis of particulate matter are i)amount of particulate matter is very small, generally less than 0.1 gram in total weight, and ii)various elements are concentrated and existed in PM relatively higher concentration than other environmental samples. Therefore, INAA has been used effectively as analytical tool of PM both for the routine atmospheric monitoring network[2] and for the research projects[3]. For the evaluation of analytical results of PM, standard reference material of PM can play an important role particularly for inter-laboratory comparison[4].

Lesson from former projects

Scientists in East Asian region and Australia had collaborated and intensively discussed in the Workshops on the Utilization of Research Reactors. During its seventh Workshop 1998 at Yogyakarta/Serpong, Prof. Harasawa, Institute for Atomic Energy, Rikkyo University reported progress of the activities of the neutron activation analysis group[5]. Seven countries submitted analytical results on the standard reference material of vehicle exhaust particulate (NIES No.8). As described in Fig.1, concentration of elements on NIES No.8 obtained by inter-laboratory comparison ranged from 0.1 to 10000 ppm. More than three countries reported data on these 26 elements.

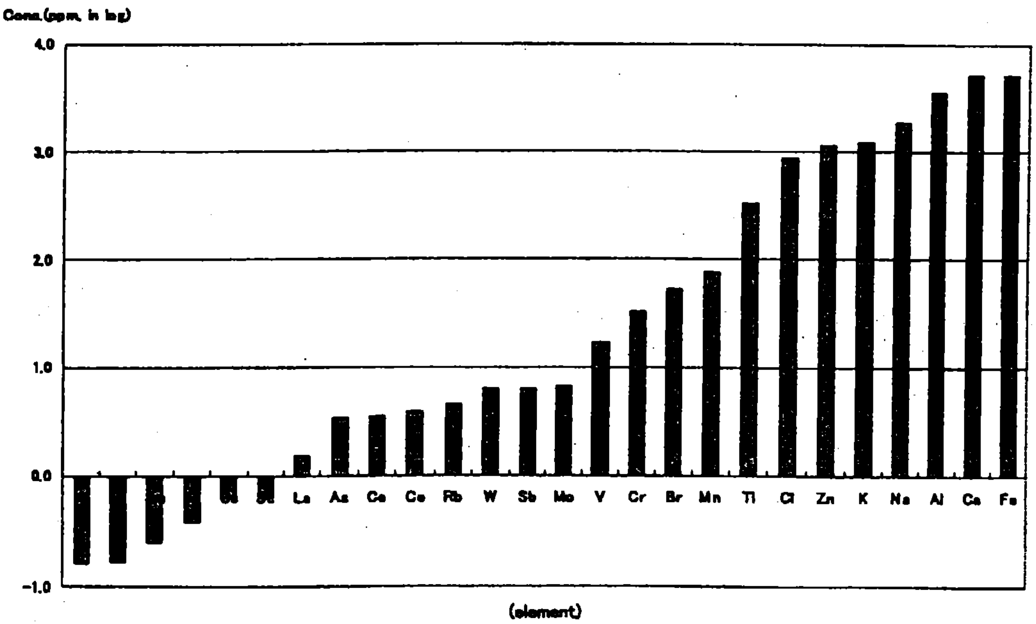

Fig.1 Elemental concentration of NIES No.8 by INAA inter-laboratory comparison

Coefficients of variance (CV) of data represent the precision of analysis for each element.

As described in Fig.2, CV values for more than half of elements are less than 20%. Additionally, bias of analytical data apart from certified value of NIES No.8 was almost satisfactory only exceptions of Eu and Cs that showed large CV values.

From these results obtained by inter-laboratory comparison, the neutron activation analysis group was recognized to have the certain technical capability to analyze PM.

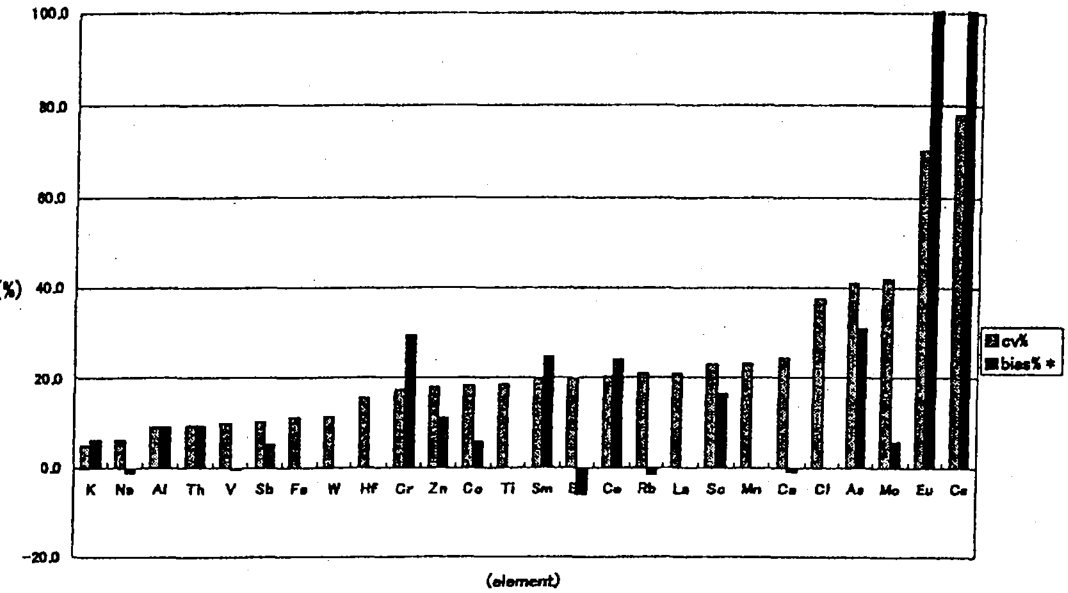

Fig.2 Precision (cv%) and bias from certified value of NIES No.8 analytical data obtained by INAA inter-laboratory comparison

* (bias% = (mean analytical data/certified value)×100−100)

After confirmation of analytical capability of laboratories, the discussion was focus on sampling procedures for PM. High-volume air sampler was selected because only this type of samplers was available in all participated countries. Brief description of sampling and analytical condition is follows:

-PM is collected on the membrane filters;

-Frequency of sampling is at least four times per year (possibly on the 15 of January, April, July and October);

-Samples should be taken at least two sites representing an urban and a rural;

-Elements to be determined are those that can provide parameter for source emission identification, i.e. Al, As, Ba, Br, C (if possible), Ca, Cl, Co, Cr, Fe, K, Mn, Na, Ni, Pb (if possible), Sc, Se, Te, Th, U, V, Zn and rare earth elements pattern.

Air concentration data obtained through this project provided useful information on the status of air pollution around the sites for individual country. However systematic evaluation of the data across the nation was not carried out.

Japanese experience on PM monitoring

The National Air Surveillance Network (NASN) was established in 1965 to measure air quality throughout Japan. In 1974, INAA was first applied to PM samples collected at the Network for the determination of trace elements. Since then, air concentration data of 16 monitoring sites has been accumulated more than 20 years. Brief description of the activities are as following.

-PM sample: PM sample was collected every month on nitrocellulose membrane filter by low-volume air sampler (flow rate of 20liter/m) for 25 days. The sampler was designed to collect particles less than 10 micrometer in diameter.

-INAA and X-ray fluorescence (XRF) method: A quarter of filter was irradiated at reactor for the measurement of short-lived nuclides, e.g. Al, Br, Ca, and another quarter of filter was irradiated for the measurement of medium-lived nuclides, e.g. As, K, Na, and long-lived nuclides, e.g. Cr, Fe, Zn. The rest of the filter was used for the determination of Cd, Ni and Pb by XRF method. In total, 31 elements in PM sample were determined.

Atmospheric concentration of PM and elements are quite varied among sites in large/industrialized cities, sites in small/rural cities, and sites located in remote area. As shown in Fig.3, element such as Cr, Fe, and Ni, which has anthropogenic emission sources in Kawasaki (typical industrialized city) was higher concentration than that of Sapporo (rural) and Nopporo (remote).

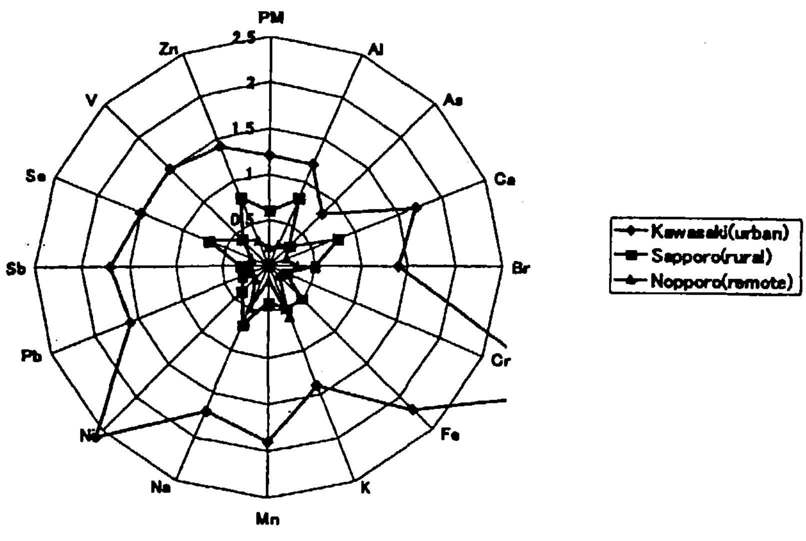

Fig.3 Relative average concentrations in several NASN sites (1996)

As shown in Fig.4, the annual average concentration of As in Kawasaki declined clearly compared to Sapporo and Nopporo. Similar trend of concentration change of elements emitted mainly from anthropogenic sources can be seen. Decrease of the concentrations was steep during the first half of the monitoring period, but more gradual during the second half of the period.

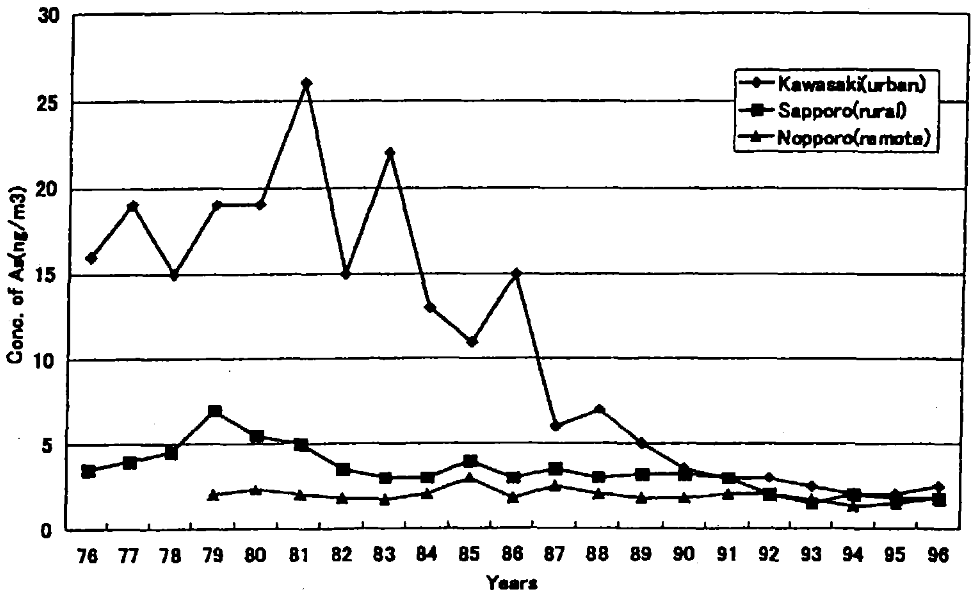

Fig.4. Annual average concentration of As in several NASN sites (1976~1996)

Importance of fine particles for human health

It is well known that during the London smog episode of December 4-8 1952, serious air pollution including over 1.0 mg/m^3 concentrations of sulfur dioxide and PM caused more than 4000 human deaths above the expected figures. Pollutants of coal combustion emitted from both industrial and domestic sources were the main cause of the tragedy. Size distribution of PM is also important parameter for human health. In general, fine particles less than 10 micrometers ($<10\mu$m) may pass through the nose and be collected in the lower respiratory tract. Therefore, ambient air quality standard for PM was first set up in 1971 by U.S. EPA as "total suspended particulate" (TSP), and then revised in 1987 to focus on protecting against human health effects associated with exposure to ambient "PM less than 10 micrometers" (PM_{10}). Based on the latest scientific information on adverse effects on human health, newly standard of "PM less than 2.5 micrometers" ($PM_{2.5}$) were promulgated in 1997 together with the modified PM_{10} standard[6]. As shown in Fig.5, "PM_{10}" include a part of coarse particles and all of fine particles, and "$PM_{2.5}$" represents simply fine particles. Major components of fine particles are heavy metals, semivolatile compounds such as ammonium nitrate, and certain organic substance including carcinogens emitted directly from combustion sources or secondary partilcles. Transition metals including iron, vanadium, nickel, manganese, zinc, and copper can promote the production of reactive oxygen species, and may be implicated in mortality effects of PM. Other important aspects of fine particles are PM associated acid and hazardous organic compounds and so on. On the other hand, most of coarse particles are originated from natural sources or mechanical emission sources.

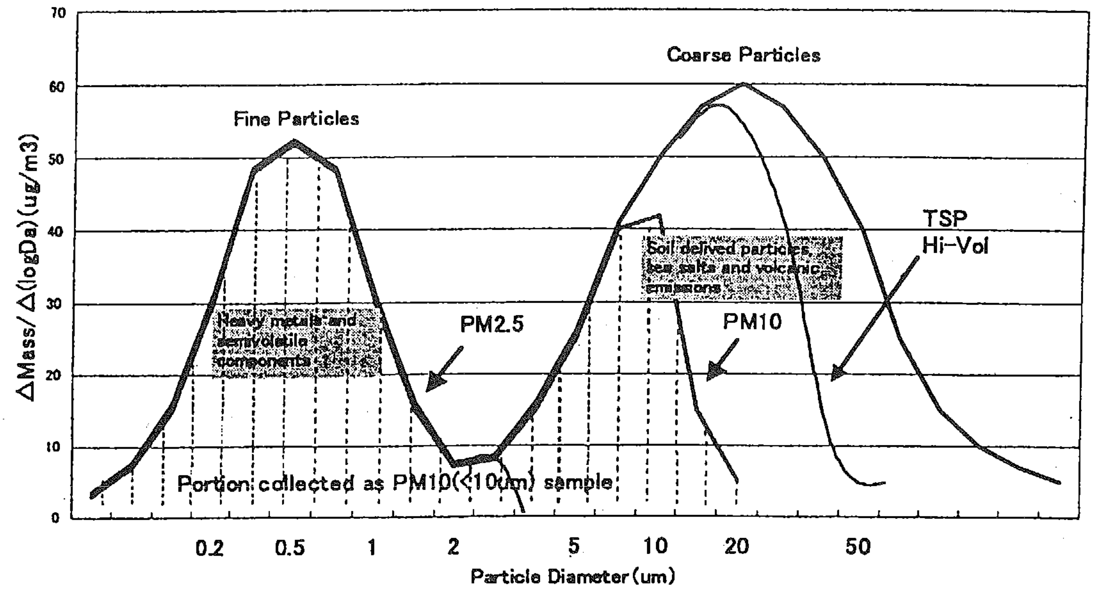

Fig.5 Idealized size distribution of PM in air and portion collected by various samplers

Conclusion

Activities of the neutron activation analysis group of the Workshop on the Utilization of Research Reactors, and Japanese PM monitoring Network employing INAA technique is introduced. Importance of size distribution of PM in terms of its components and human health is also discussed.

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