Non-destructive analysis of trace elements in the airborne particulate matter by INAA

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1. Introduction

With increasing a public recognition for an environmental contamination and a human well-being which is caused by rapid industrialization and urbanization, vehicle increment, etc., public concerns has been also increased recently. In particular, airborne particulate matter (APM) consists of various elements originated from both artificial and/or natural status. When the level of total suspended airborne particulate matter and/or the content of specific elements in PM_{10} (<10 μm aerodynamic diameter, EAD) are high relative to normal level, the short-term impact as well as long-term effects on human health are insidious and important. Therefore, the sampling and the analysis of APM ($PM_{2.5}/PM_{10}$) is the first step to evaluate the air quality and air contamination level. Up to μg/g ~ ng/g concentrations for about 30 trace elements in APM can be analyzed using instrumental neutron activation analysis (INAA). The results can be used to conduct epidemiological studies, to investigate a source identification and apportionment, to study a long-range transport and back-trajectory, trans-boundary air pollution and atmospheric processes, and to establish a more cost-effective air quality management.[1] Based on the results on elemental compositions of APM, we attempted to explain the distribution characteristics of industrial and suburban area, we also tried to evaluate the temporal distribution patterns of metals, to examine an enrichment factor verifying the emission source over monthly scale.

2. Experimental

Samples were collected from two urban regions, a industrial complex area and suburban residential area of Daejeon city located in the South Korea on selected sampling dates (working and non-working days). For the collection of APM for the fine (<2.5 μm EAD) and coarse particle (2.5-10 μm EAD) fractions, the Gent SFU sampler (low volume air sampler with fine and coarse fraction) with polycarbonate filters (φ 47 mm, 0.4 and 8 μm pore size, Nuclepore) was used according to the recommended method. The flow rate was adjusted to 18 l/min. at the beginning of sampling and collected for 24 hours twice a week from January 2000 to December 2003. In this period, 256 samples for two particle fraction were collected at two sites individually. The collected samples were pre-stored for 24 hours in a controlled atmosphere (20°C, RH 50%) and prepared in polyethylene vials after weighing in the same conditions. Electrostatic charges are controlled by ^{210}Po

radioactive source. For both fine and coarse filters, each filter was cut into three parts, half for the analysis of long half-life nuclides, a quarter for the short half-life nuclides and the rest for storage.

Collected APM samples were irradiated with thermal neutrons using the Pneumatic Transfer System (PTS, Φ_t = 2.95 x 10^{13} n/cm^2·s, R_{cd} ~ 200) at the HANARO research reactor at the Korea Atomic Energy Research Institute. The measurements were carried out using calibrated gamma-ray spectrometer (HpGe detector, GEM 35185P and 919A MCB, Gamma Vision software, EG&G ORTEC). The details of the analytical condition are given in table 1. The concentration of the elements was calculated using the new Windows PC-code, Labview software of KAERI with the nuclear data library, which was developed at this laboratory for rapid and simple data treatment with the gamma-ray spectrum obtained at preset detection conditions. The detection limits for the elements can be calculated by Currie's quantitative definition with 10% allowable uncertainty.[2] The measurement uncertainty was evaluated as a combined uncertainty including most of the sources of standard uncertainty to be considered in INAA.[3]

Table 1. Analytical condition of NAA

	Irradiation time	Decay time	Counting time	Element
Short- lived nuclide	3 min	10 min	500 sec	Al, Ca, Cu, In, Ti, V
		30 min	2000 sec	Ba, Cl, K, Mn, Na, I
Long- lived nuclide	4 hour	3~5 day	4000 sec	As, Br, La, Sb, Sm
		8~14 day	15000 sec	Ce, Co, Cr, Fe, Hg, Sc, Se, Zn

3. Results and Discussion

In order to verify the accuracy and precision for quality control of the analytical method, the standard reference materials (NIST, the National Institute of Standards and Technology, U.S.A., NIST SRM 2783, urban dust on filter media) were used firstly. The concentrations of elements were determined and compared statistically with the certified (or recommended) values. The results contain experimental mean values, standard deviations and relative errors resulting from at least five runs were showed in the Fig. 1. The relative errors of all elements except As (14.1%), Sc (10.9%) for the NIST SRM 2783

were less than 10% with a good precision. Secondary, the proficiency test which is supported by the IAEA is carried out using NIST SRM 2783, urban dust on filter media. Z-score value for all of elements is below 2 as an acceptable level except for Sm (3.5). It is quite clear that the analytical performance for most elements was acceptable and reliable. Thirdly, the assessment of measurement uncertainty is implemented for analytical procedure containing the sample preparation and the measurement system. The combined uncertainty results from sources of standard uncertainty; 1) preparation of sample and standard, 2) sample irradiation, 3) Gamma-ray measurement was estimated below 4.5%.
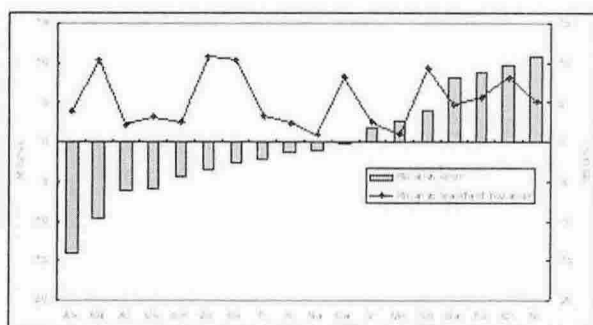

Figure 1. Analytical results of NIST SRM 2783

The concentrations of 25 elements, i.e., Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cu, Fe, Hg, I, In, K, La, Mn, Na, Sb, Sc, Se, Sm, Ti, V and Zn were determined from APM samples. The average of elemental concentration obtained from the measured values of individual sample together the C/F ratios of measured for each element in two fraction particles in the Daewha and Kaeri areas are summarized in the Table 2. The means for Co, In, and Sc with coarse and fine fraction in the two areas were less than 1 ng m^{-3} as a minor components, while that for K, Fe, Al, Ca, Na and Cl were more than several hundreds ng m^{-3} as a major components with each size fraction in the two areas. C/F ratios of elements originated from crustal origin Al, Ce, Fe, La, Na, Sc, Sm, and Ti were higher than 5.0 in the industrial area, those, however, in the Kaeri area became lower than 5.0 except La (5.7). The C/F ratios of anthropogenic originated elements, such as As, Br, Co, Cr, Cu, Hg, I, Mn, Sb, Se, V, and Zn, were lower than 3.0 in the Daewha area.

3. Conclusions

To enhance the use of the neutron activation analysis as a routine monitoring tool for air pollution studies, the concentrations of the trace elements in airborne particulate matter were measured with two particle sizes at two regions. The analytical quality control is used for environmental certified reference materials and the relative error were less than 10% except for some elements. Elemental concentrations of the coarse fraction in the industrial area were higher than those of the fine fraction, but in the case of the suburban area, the concentrations of the pollutant elements in the fine fraction were higher than the other elements.

Table 2. Annual mean concentration of elements, C/F ratio at sampling site

	Daewha (ng/m³)			Kaeri (ng/m³)		
	Coarse	Fine	C/F	Coarse	Fine	C/F
Al	1033	150	6.88	450	145	3.1
As	2.98	1.33	2.24	1.56	2.53	0.6
Ba	25.6	5.77	4.43	8.63	4.23	2.0
Br	21.7	10.3	2.11	15.1	14.8	1.0
Ca	734	146	5.03	382	83	4.6
Ce	2.32	0.40	5.72	1.01	0.36	2.8
Cl	302	67.2	4.49	132	59.6	2.2
Co	0.78	0.34	2.30	0.54	0.30	1.8
Cr	26.9	10.1	2.66	14.8	9.81	1.5
Cu	27.1	8.58	3.16	5.34	7.61	0.7
Fe	1091	158	6.91	488	147	3.3
Hg	2.32	0.88	2.65	1.40	1.14	1.2
I	1.27	1.10	1.16	0.59	1.55	0.4
In	0.34	0.06	5.67	0.02	0.05	0.4
K	916	203	4.52	449	344	1.3
La	1.75	0.13	13.1	0.86	0.15	5.7
Mn	27.3	10.5	2.61	7.72	6.73	1.1
Na	541	119	4.55	238	130	1.8
Sb	10.7	7.15	1.49	6.74	6.28	1.1
Sc	0.23	0.02	10.7	0.11	0.03	4.1
Se	1.32	0.75	1.77	0.63	1.43	0.4
Sm	2.32	0.19	12.5	1.28	0.30	4.2
Ti	80.5	15.7	5.14	36.8	14.0	2.6
V	4.46	1.70	2.62	1.20	1.46	0.8
Zn	85.2	39.7	2.14	26.9	33.4	0.8

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