

Measurement of the Elemental Composition in Airborne Particulate Matter Using Instrumental Neutron Activation Analysis

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Abstract

For the evaluation of emission sources by air sampling, airborne particulate matter for fine ($<2.5\ \mu\text{m}$ EAD : $\text{PM}_{2.5}$) and coarse particle ($2.5\text{--}10\ \mu\text{m}$ EAD : $\text{PM}_{2.5\text{--}10}$) fractions were collected using a Gent stacked filter unit low volume sampler and two types of polycarbonate filters. Air samples were collected twice monthly at two regions in and around Daejeon city in the Republic of Korea from January to December 2002. Monthly mass concentration of $\text{PM}_{2.5}$ and $\text{PM}_{2.5\text{--}10}$ were measured and the concentrations of 10 marker elements (Al, Sc, Ti ; Na, Cl ; As, V, Sb, Br, Se) were determined by an instrumental neutron activation analysis. Analytical quality control was carried out using certified reference materials. Enrichment factors were also calculated from the monitoring data to classify the anthropogenic and crustal origins.

Key Words : airborne particulate matter, instrumental neutron activation analysis, elemental composition, analytical quality control, enrichment factors

1. Introduction

Owing to its cost-effectiveness and numerous advantages, Neutron Activation Analysis (NAA) plays a leading role among nuclear analytical techniques. In particular, the utilization of NAA in the field of environmental research related to air pollution and human health has increased very rapidly [1, 2]. Airborne particulate matter (APM) is

a very useful indicator for monitoring environmental conditions. In this regard, sampling and elemental analysis of APM composed of fine particle (FPM : $<2.5\ \mu\text{m}$ EAD) and coarse particle (CPM : $2.5\text{--}10\ \mu\text{m}$ EAD) fractions are very important for considering the health impact of APM as well as estimating air quality and air pollution levels [3]. Elemental composition and the concentration of APM can be measured up to a

µg/g-ng/g level of concentration for more than 30 trace elements by Instrumental Neutron Activation Analysis (INAA).

Since 1993, as an IAEA/RCA cooperative project, ongoing air pollution studies have been carried out using airborne particulate matter and the NAA method at rural and urban regions in Korea [4-12]. The results of the air monitoring can be used to conduct epidemiological studies, investigate source identification, study long-range transport and atmospheric processes, and establish more cost-effective air quality management procedures. Air pollution sources can be identified by employing several statistical methods or a receptor modeling [13] of analytical data such as mass concentration of elemental carbon, elemental concentration, enrichment factors [14, 15], emission sources and apportionment, etc. For these studies, the collection of comprehensive analytical data is required. In addition, the selection of a sampling site, sampling methods, and an air sampler are dependent on the aims of the research and the elements to be analyzed. The present study has been carried out as an international nuclear technical cooperative project in the environmental area supported by IAEA and FNCA regional collaborative research. The obtained results will contribute to advancement and wider utilization of this nuclear analytical technique for air pollution studies.

In this study, APM with two fractions were collected at two urban sites according to a well-organized sampling method [3] for evaluation of the emission sources. 10 elements, Al, Sc, Ti (indices for soils, silicates); Na, Cl (indices for sea salts); As, V, Sb, Br, Se (indices for pollutants), in the collected sample were analyzed by INAA. These marker elements were selected in consideration of their strong association to several major sources of air particulate pollution.

2. Experimental

2.1. Sampling and Sample Preparation

Airborne particulates for fine particle (<2.5 µm EAD) and coarse particle (2.5-10 µm EAD) fractions were collected using a Gent SFU sampler (low volume air sampler) with two kinds of polycarbonate filters (Ø 47 mm, 0.4 and 8 µm pore size, Nuclepore) according to the recommended method.[3] The flow rate of the sampler was calibrated using a Gillian Gilibrator2 Calibration System (Sensidyne Inc.). Samples were collected from two regions (suburban and industrial sites of Daejeon city located in the southwestern region of Korea) as shown in Fig. 1. Longitude, latitude, and altitude of the sampling site are about E127°, N36°, and 50-70 m, respectively. The suburban sampling site within KAERI is located several kilometers from a heavy-traffic intersection of the four-lane Honam expressway and there is a small mountain at the rear of the sampling site. At the Daewha industrial complex sampling site there are many wooden and metal fabrication factories. The sampler was placed about 6 m above the ground. Meteorological conditions such as temperature, humidity, wind direction, wind velocity, and change in weather conditions obtained from the Korea Meteorological Administration (www.kma.go.kr) were recorded regularly during the collection of the samples and are shown in Fig. 2. The flow rate was adjusted to 18 l/min at the beginning of the sampling and collected for 24 hours once a week from January to December 2002. In this period, about 50 samples for two particle fractions were collected at the two sites individually. The total volume of the air sampled through the filter was calculated from a reading of the volume meter and compared with the obtained value from the average of the initial

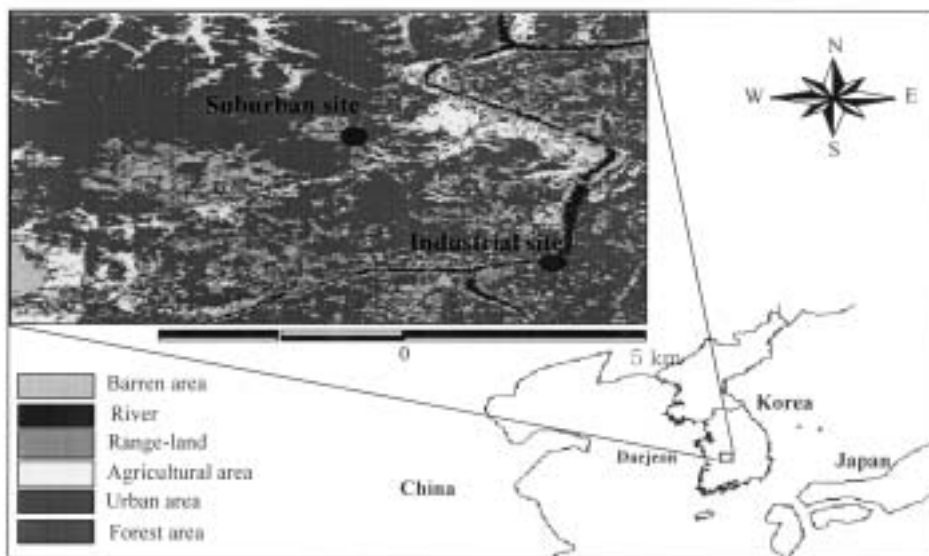


Figure. 1. Map of Two Sampling Site in Daejeon City of Korea

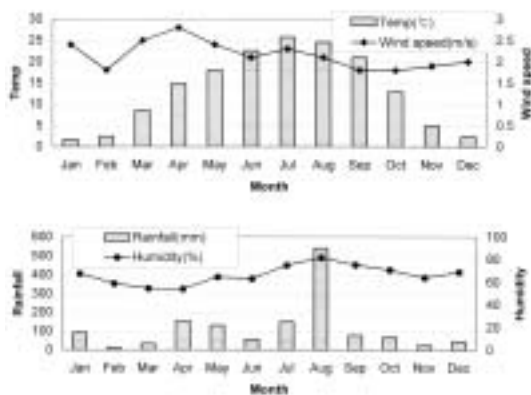


Figure. 2. Meteorological Conditions of the Sampling Region During the Sampling Period

and the final flow rate. The collected samples were pre-stored for 24 hours in a controlled atmosphere (20°C, 50% relative humidity) and prepared in polyethylene vials after weighing in the same conditions. Electrostatic charges were controlled by a ^{210}Po radioactive source. For both the fine and coarse filters, each filter was cut into three parts, half for the analysis of the medium and long half-life nuclides, a quarter for the short

half-life nuclides, and the remainder for storage.

2.2. INAA Analysis of the Sample

Collected samples were irradiated with thermal neutrons using a Pneumatic Transfer System (PTS, $\phi = 2.80 \times 10^{13} \text{ n/cm}^2 \cdot \text{s}$, $R_{cd} \sim 205$) at the HANARO research reactor at the Korea Atomic Energy Research Institute. Samples were irradiated at the same position to minimize geometric errors. For the neutron flux monitoring, activation wires (R/X activation wire, Reactor Exp. Inc., USA), Au-Al, Co, and Fe, were used. Analytical conditions were optimized after considering the preliminary results. Irradiation time (T_i), cooling time (T_d), and counting time (T_c) as typical values were as follows: 1) for short-lived nuclides: $T_i = 2 \text{ m}$, $T_d = 10\text{-}30 \text{ m}$, $T_c = 300\text{-}600 \text{ s}$; 2) for medium-lived nuclides: $T_i = 10 \text{ m}$, $T_d = 1\text{-}2 \text{ d}$, $T_c = 2000 \text{ s}$; and 3) for long-lived nuclides: $T_i = 4 \text{ h}$, $T_d = 1\text{-}2 \text{ w}$, $T_c = 4000\text{-}8000 \text{ s}$. The measurements were carried out using a high purity Ge detector with a 25% relative efficiency and 1.85 keV resolution (FWHM) at 1332 keV of ^{60}Co

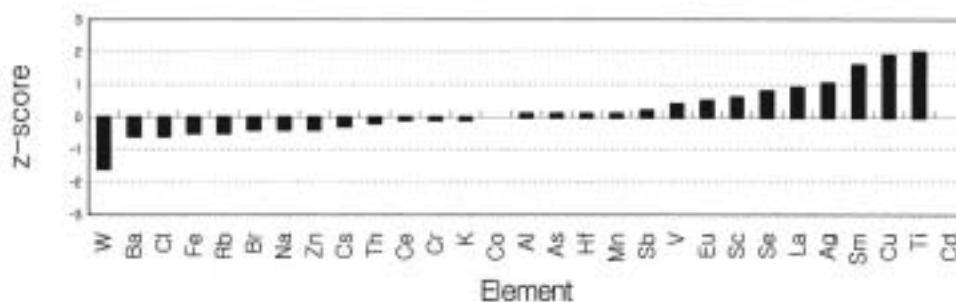


Figure. 3. Results of the Proficiency Test (NAT-7) for an Urban Dust Sample Supported by IAEA

and the peak to Compton ratio was 45:1 was coupled to a personal computer and an 8k-multichannel analyzer (919A MCB, EG&G ORTEC, USA). Energy and efficiency calibrations were performed using multi-nuclide reference sources (Isotope Products Lab., ML 7500 series, 0.118" active diameter, disc type) traceable to NIST. GammaVision software was used (EG&G ORTEC, USA) for the energy and efficiency calibrations, and acquisition of the gamma spectra and peak analysis was also employed [16].

2.3. Data Treatment

Under optimum analytical conditions including those for irradiation and counting time, the elemental concentrations in both the samples and the blank filters were measured. Concentrations of the elements were calculated using a new Windows PC-code, Labview software of KAERI with the nuclear data library [17, 18], which was developed at this laboratory for rapid and simple data treatment with a gamma-ray spectrum obtained at preset detection conditions. The detection limits for the elements can be calculated by Currie's quantitative definition with a 10% allowable uncertainty [19]. The assessment of the measurement uncertainty was evaluated as a combined uncertainty including most of the

sources of the standard uncertainty considered in the INAA [20]. The analytical data was treated statistically using Microsoft Excel.

3. Results and Discussion

3.1. Analytical Quality Control

After the optimum analytical conditions such as irradiation time, cooling time, counting time, etc.

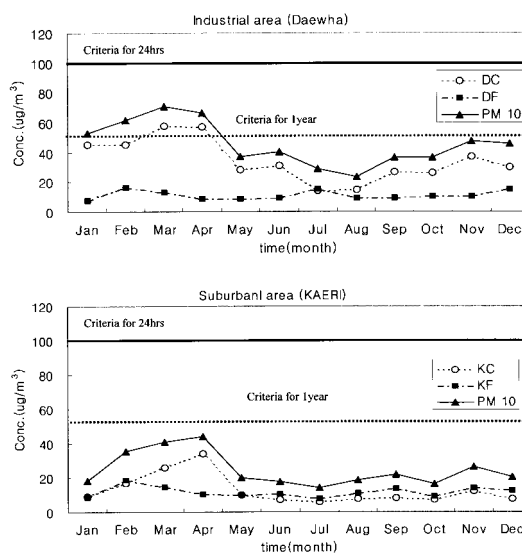


Figure 4. Variation of Mass Concentrations for the FPM and the CPM in Two Regions

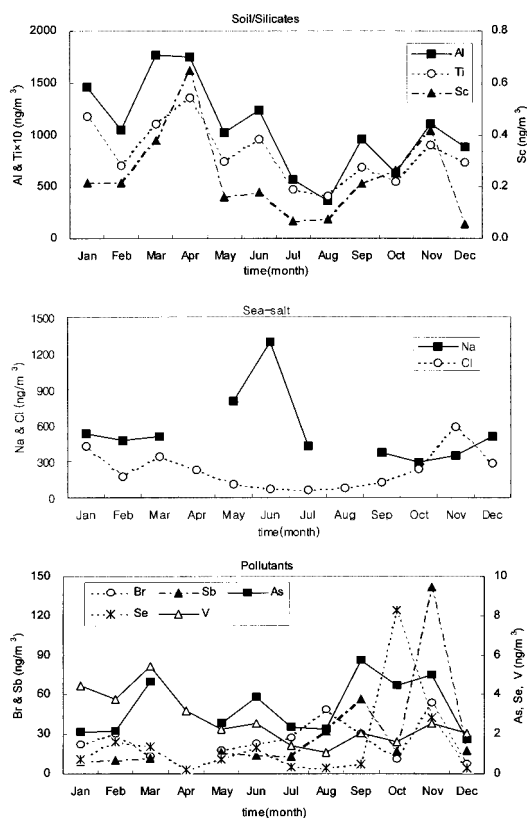


Figure 5a. The Variation of Elemental Concentration with Sampling Site during Sampling Period Coarse Fraction at the Industrial Area (Daewha)

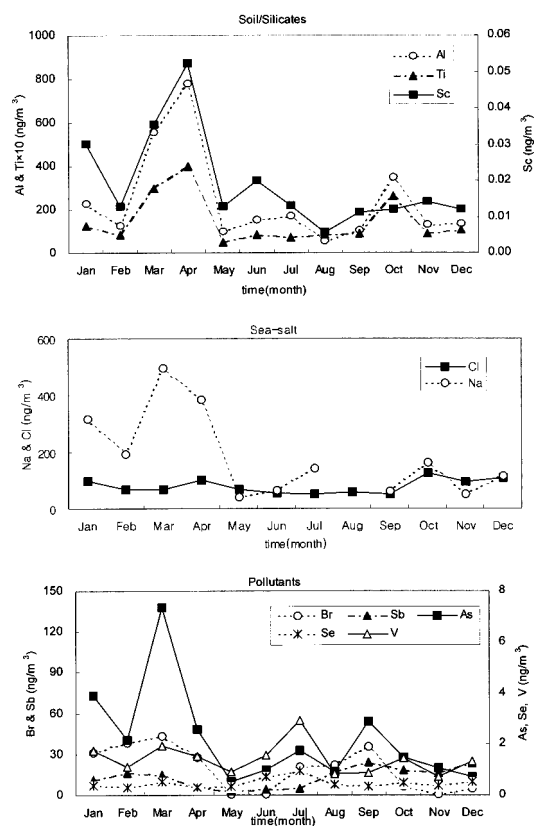


Figure 5b. The Variation of Elemental Concentration with Sampling Site During Sampling Period: Fine Fraction at the Industrial Area (Daewha)

Table 1. Analytical Results of Certified Reference Material, NIES CRM No-8, Urban Dust

Element	Nuclide (keV)	Experimental Value(mg/kg)		Certified Value(mg/kg)	Relative Error(%)
		Range	Mean \pm SD		
Al	Al-28 (1779)	3098~3365	3230 \pm 119	3300 \pm 200	-2.1
Sc	Sc-46~889	0.54~0.57	0.55 \pm 0.22	0.55	-0.4
Ti	Ti-51 (320)	281~364	318 \pm 36	-	-
Na	Na-24 (1368)	1369~1976	1958 \pm 20	1920 \pm 80	2.0
Cl	Cl-38 (1642)	862 ~1018	908 \pm 63	-	-
As	As-76 (559)	2.68~3.27	3.01 \pm 0.30	2.6 \pm 0.2	15.8
V	V-52 (1434)	14.89 ~16.12	15.50 \pm 0.46	17 \pm 2	-8.8
Sb	Sb-122 (564)	5.77~5.88	5.81 \pm 0.07	6.0 \pm 0.4	-3.2
Br	Br-82 (554)	57.7 ~60.5	58.7 \pm 1.5	56	4.8
Se	Se-75 (264)	1.59 ~1.89	1.79 \pm 0.17	1.3	37.7

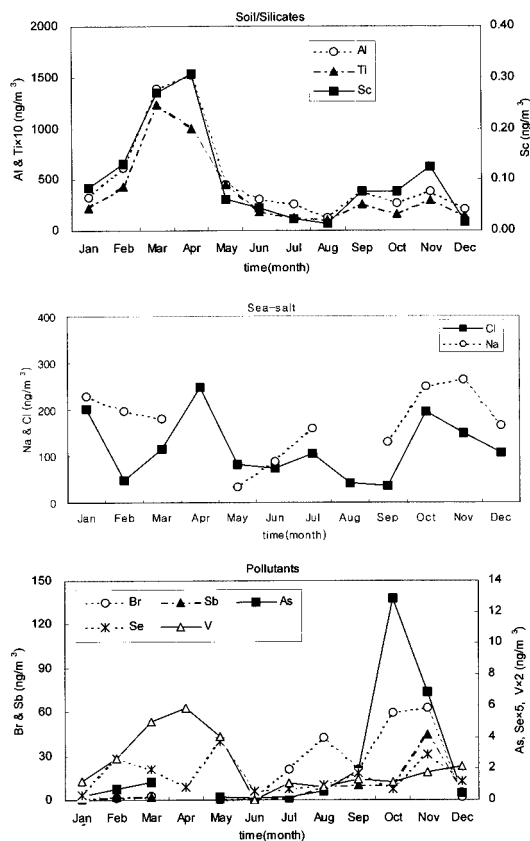


Figure 5c. The Variation of Elemental Concentration with Sampling Site During Sampling Period: Coarse Fraction at the Suburban Area (Daewha)

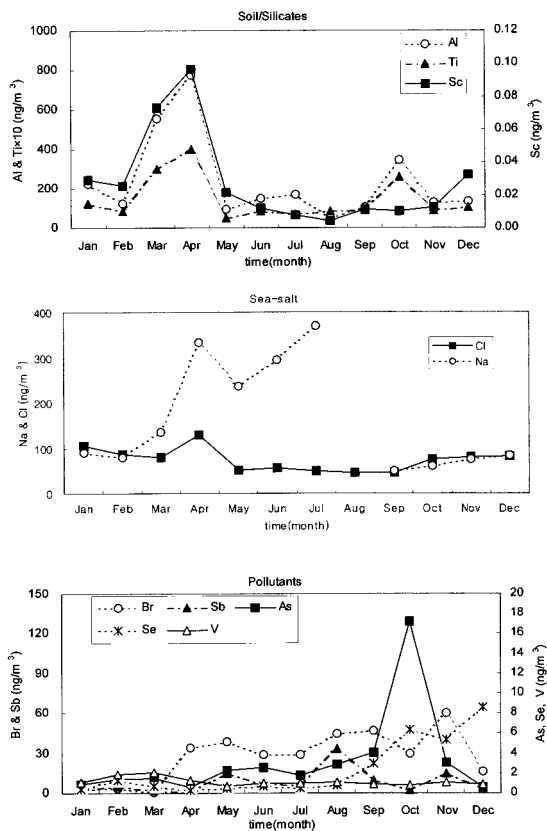


Figure 5d. The Variation of Elemental Concentration with Sampling Site During Sampling Period: Fine Fraction at the Suburban Area (KAERI)

Table 2. Summary of the Elemental Concentration Data Determined from Daejeon City During 2002

	DAEWHA (ng m ⁻³)		KAERI (ng m ⁻³)	
	Coarse (DC)	Fine (DF)	Coarse (KC)	Fine (KF)
Al	1066 ± 439.0	238 ± 218	523 ± 456	173 ± 173
Sc	0.24 ± 0.17	0.02 ± 0.01	0.10 ± 0.09	0.03 ± 0.02
Ti	81.6 ± 28.9	14.6 ± 11.0	38.7 ± 36.3	13.4 ± 12.1
Na	556 ± 295	183 ± 151	170 ± 71.8	164 ± 120
Cl	228 ± 159.7	79 ± 25.1	117 ± 68.5	74 ± 26
As	3.4 ± 1.42	2.2 ± 1.91	2.3 ± 4.01	3.2 ± 4.54
V	2.7 ± 1.29	1.4 ± 0.61	1.2 ± 0.90	1.1 ± 0.40
Sb	30.9 ± 39.2	13.3 ± 7.4	7.9 ± 12.7	8.4 ± 9.14
Br	25.7 ± 14.5	19.2 ± 16.1	19.6 ± 24.5	28.0 ± 18.8
Se	1.54 ± 2.26	0.48 ± 0.18	0.30 ± 0.21	2.36 ± 2.8
BC	-	8.3 ± 2.8	-	7.0 ± 2.48
APM	34.5 ± 14.5	11.2 ± 2.9	12.7 ± 8.7	11.8 ± 3.1

were pre-estimated according to previous procedures, certified reference materials (NIES CRM, No.8, urban dust) were used as analytical quality controls [21]. The analytical results are presented in Table 1. In addition, we participated in the proficiency test program of the IAEA (NAT-7, Air filter sample, 2001) and received reliable results for all measured elements except for Cd, as shown in Fig. 3 [10, 22]. The filter blank values of the major impurities were used for correction of the individual concentrations. The concentrations of interfering elements such as Al, Cl, Br, and Na were low relative to other filter types.

3.2. Mass Concentrations of APM

The mass concentration of a coarse fraction at the Daehwa industrial site (DC), a fine fraction at the Daehwa industrial site (DF), a coarse fraction at the KAERI site (KC), and a fine fraction at the KAERI site (KF) located in a suburban area were measured from Jan. to Dec. 2002. The monthly monitored data during the period of study is presented in Fig. 4 in accordance with the sampling site, date, and particle size. The mass concentration of the coarse fraction (DC) was in the range of 14~58 $\mu\text{g}/\text{m}^3$ (Mean : 34.5 $\mu\text{g}/\text{m}^3$) and that of the fine fraction (DF) was in the range of 8~16 $\mu\text{g}/\text{m}^3$ (Mean : 11.2 $\mu\text{g}/\text{m}^3$) in the industrial area. The mass concentration of the coarse fraction (KC) was in the range of 6~34 $\mu\text{g}/\text{m}^3$ (Mean : 12.7 $\mu\text{g}/\text{m}^3$) and that of the fine fraction (KF) was in the range of 8~19 $\mu\text{g}/\text{m}^3$ (Mean : 11.8 $\mu\text{g}/\text{m}^3$) in the suburban area. The annual average mass concentrations of the total PM_{10} in the suburban and industrial areas are 24.5 $\mu\text{g}/\text{m}^3$ and 45.7 $\mu\text{g}/\text{m}^3$, respectively, and are much lower than the value of the Korean air quality criteria (100 $\mu\text{g}/\text{m}^3$ for 24 hr). The mass concentration of the coarse samples collected from March to May is relatively higher than in the

other sampling periods. This is likely caused by the phenomena of Asian dust from continental Asia. The average concentrations of APM in the industrial site were higher than those of the suburban site. The mass concentration of CPM for the industrial site was higher than that of the suburban site and in the case of FPM, an opposite trend was observed.

3.3. Elemental Concentrations in APM

The range and annual average of the elemental concentration were obtained from the measurement values of the individual samples and the results together with the number of samples measured for each element are reported. The concentrations of 10 elements of interest, Al, As, Br, Cl, Na, Sb, Sc, Se, Ti, and V were determined and the results together with the mass concentrations of black carbon (BC) and APM are summarized in Table 2. The variation and distribution of the elemental concentration with the sampling site and the sample size during the sampling period are presented in Fig. 5. In comparison with particle size, most of the elemental concentrations of the coarse fraction in the industrial area were higher than those in the suburban area, whereas in the case of the fine fraction, the trend was reversed. Comparing the sampling sites, most of the 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 (As, Br, Sb, Se, V) in the fine fraction were higher than the other elements. Also, the variation and the level of the concentration of the pollutant elements in APM with the sampling date is larger than the other grouped element in both of the two areas, as shown in Fig. 6.

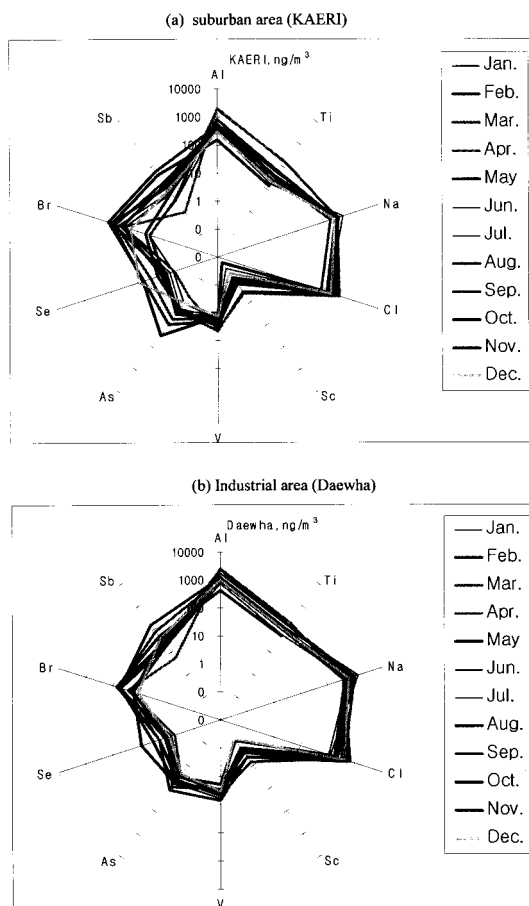


Figure 6. The Variation and the Level of the Elemental Concentration with the Sampling Date

3.4 Evaluation of Enrichment Factor

In order to determine the major emission sources, enrichment factors (EF) were calculated from the measured elemental concentrations using Mason's crustal abundances [15] for the sampling period. An enrichment factor is given by the double ratio of the element of interest in the sample (X_i) to a reference element in the sample (C_i) divided by the ratio of the same element found in a reference material (e.g. rock, soil, etc); $EF = (X_i/C_i)_{APM} / (X_i/C_i)_{REF}$. Sc is taken as the reference element because it is considered a

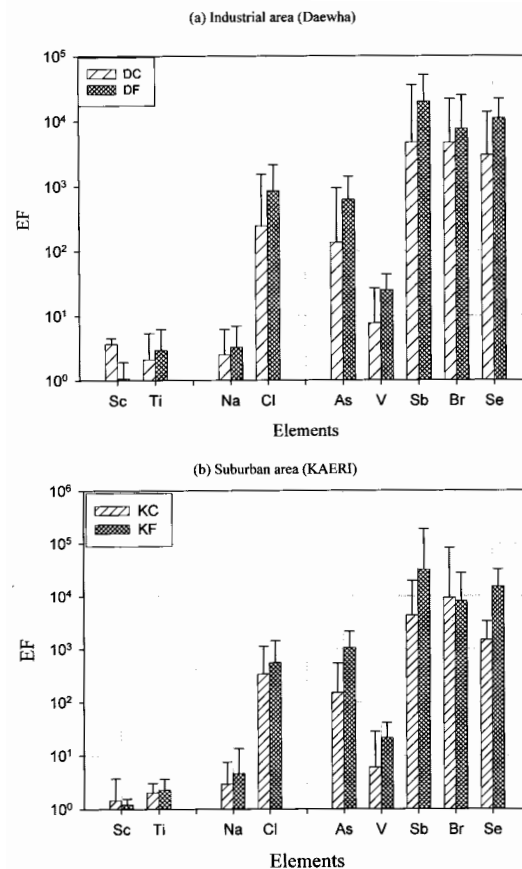


Figure 7. Enrichment Factors of the CPM and FPM at the Two Sampling Sites

unique element in soil. In general, most of the crustal elements (Al, Sc, Ti) have EF values close to unity; higher EF values of the elements indicate that they are not of a crustal origin. Therefore, they can be classified into two groups according to the EF values of the measured elements; anthropogenic and crustal origin. The average EF values calculated for the particle size and sampling site are presented in Fig. 7. These values were in the range of $10^0 - 10^4$ and the industrial area showed generally higher values than those of the suburban area. The EF values of the FPM are generally higher than those of the CPM for

anthropogenic elements with respect to the elements of crustal origin. The observed EF values of the pollutant elements are high in both areas, and they are assumed to be anthropogenic elements except V. In the case of Cl of the sea-salt element, it is assumed that there are two kinds of source in both areas. The element of V can not classify as pollutant source due to lower EF value. These consistent trends suggest that these results are applicable for investigating air pollution sources and levels for the evaluation of environmental conditions.

4. Conclusions

To enhance the use of neutron activation analysis and to assess the feasibility of the use of nuclear analytical techniques as a routine monitoring tool for air pollution studies, the concentrations of trace elements in airborne particulate matter were measured with two particle sizes at two regions. The relative error of measured elements using CRM was less than 10% excluding that for As and Se. The annual average mass concentrations of the total PM₁₀ in the suburban and industrial areas were much lower than the value of the Korean air quality criteria. 10 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. The results of APM and elemental are consistent with those of enrichment factors. Therefore, the results are applicable to investigation of air pollution sources and levels for the evaluation of environmental conditions. Thus, air pollution and relevant environmental information obtained from the statistical results of analytical data and neutron activation analysis using a research reactor proved to be a useful tool for environmental pollution

monitoring and management. Further, elemental analysis of a large amount of collected samples was demonstrated to be a cost-effective and beneficial method.

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