

## Apportionment of Air Pollution Sources and Elemental Analysis of Urban Dust by using Instrumental Neutron Activation Analysis

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### 1. Introduction

Airborne particulate matter (APM) which may be accumulated in the lungs by an inhalation consists of various potentially toxic and trace elements and chemical compounds which originate from both man-made and natural sources.[1] Therefore, sampling and analysis of APM which is separated PM<sub>2</sub> and PM<sub>10-2</sub> is the first step to evaluate the air quality and air contamination level. About 30 trace elements in APM can be analyzed at up to  $\mu\text{g/g}$ ~  $\text{ng/g}$  concentration levels by using an instrumental neutron activation analysis (INAA).[2,3] The results can be used for various purposes such as epidemiological studies, source identification and apportionment, a long-range transport and back-trajectory, the trans-boundary air pollution and atmospheric processes and the establishment of a better cost-effective air quality management.[4]

In this study, INAA was applied for a quantitative analysis of the trace elements in the APM samples collected from two different sampling sites in a moderately polluted urban area of Daejeon city in the middle of South Korea during the period of Jan. 2003 to Sep. 2006. From the air monitoring data, a receptor modeling was performed to identify the air pollution sources using the positive matrix factorization (PMF) method.[5]

### 2. Experimental

#### 2.1 Sampling and elemental analysis

Samples were collected from two urban regions, an industrial complex area (Daewha) and suburban (Kaeri) residential area of Daejeon city. For the collection of APM for the fine (<2  $\mu\text{m}$  EAD) and coarse particle (2-10  $\mu\text{m}$  EAD) fractions, the Gent stacked filter unit low volume air sampler with polycarbonate filters ( $\Phi 47$  mm, 0.4 and 8  $\mu\text{m}$  pore size, Nuclepore<sup>®</sup>) was used and the flow rate was adjusted to 18 L/min at the beginning of a sampling and collected for 24 hours. During this period, 335 samples for two fractions 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 a weighing in the above controlled conditions.

Collected APM samples were irradiated with thermal neutrons using the Pneumatic Transfer System (PTS,  $\Phi_{\text{th}} = 2.95 \times 10^{13}$  n/cm<sup>2</sup>·s,  $R_{\text{cd}}=200$ ) at the HANARO research reactor at the Korea Atomic Energy Research Institute. The measurements of the gamma-ray emitted from the nuclides were carried out using a high-purity

Ge detector with a relative efficiency of 25% and a resolution of 1.9 keV (FWHM) at 1332.5 keV of <sup>60</sup>Co with a peak-to-Compton ratio of 45:1. The detector was connected to a personal computer and a 8k multi-channel analyzer (919A MCB, EG&G ORTEC). During the measurement of the activated samples, the dead time was maintained below 10%. Energy and efficiency calibrations were performed using multi-nuclide reference sources (NES-602, 2.54 cm diameter disc type, NEN Products Inc.) that are certified by NIST (National Institute of Standards and Technology, U.S.A.). Gamma Vision software (EG&G ORTEC) was used for the energy and efficiency calibrations, acquisition of the gamma-ray spectra, and the peak analysis. The calculation of the elemental concentration was used for the private program using a Labview code.

#### 2.2 PMF2 for receptor modeling

Basic equation of the PMF 2 model is shown in equation (1). The method is to find the unknown matrix, G and F by a solution of the least square method iteratively

$$X = GF + E \quad (1)$$

where, X(m×n) is the data matrix consisting of the m chemical components analyzed in n samples, G(n×p) is the source contribution for each sample. F(p×m) is the matrix of the source profile. E presents the residual matrix of the calculation, and the main process of the PMF is minimizing the Q-value which is the sum of the square of the residuals ( $e_{ij}$ ) weighted inversely with the error estimates ( $s_{ij}$ ) of the data point. The Q value can be used to determine the optimal number of a factor. The theoretical Q value should be approximately equal to the degree of freedom of datum in the data set. In most cases, however, the calculated Q value is higher than the theoretical Q value because of missing and below detection limit data points.[5]

### 3. Results and Discussion

#### 3.1 Concentration of APM and elements

During the sampling period, the levels of the annual mass concentration of the APM are increased gradually, and the average values of the coarse fraction (DC) and the fine fraction (DF) at the Daewha site were  $24.8 \pm 15.0 \mu\text{g/m}^3$  and  $12.4 \pm 9.7 \mu\text{g/m}^3$ , respectively. Those of the coarse fraction (KC) and the fine fraction (KF) at the Kaeri sampling site were  $13.6 \pm 10.7 \mu\text{g/m}^3$  and  $12.5 \pm 11.6 \mu\text{g/m}^3$ , respectively. Time series of the mass concentrations with the particle size and the sampling site are represented in Figure 1.

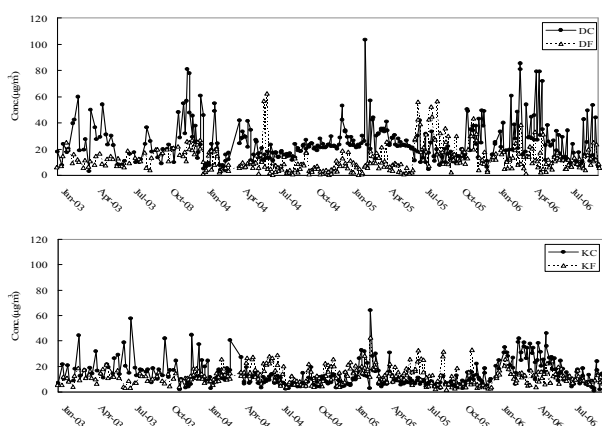
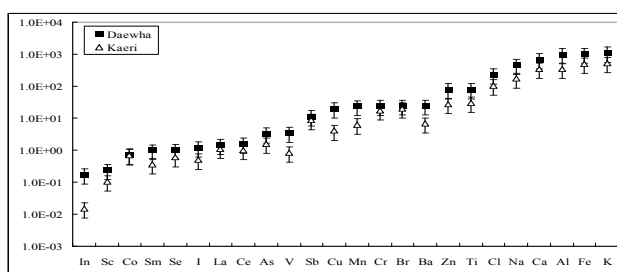
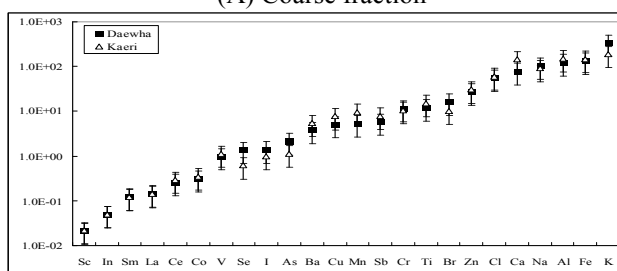


Figure 1. Mass Concentrations of the APM with the Particle Fraction at the Daewha (above) and Kaeri sites (below).

The concentrations of 24 elements, Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cu, Fe, I, In, K, La, Mn, Na, Sb, Se, Sm, Ti, V and Zn were determined by INAA. The total average concentrations of the elements in the APM at the Daewha and Kaeri sites are shown in Figure 2. The concentrations of most elements in the coarse fraction were much higher than the fine fraction at the industrial area, while the concentrations of the anthropogenic originated elements such as As, Br, Cu, I, In, Se, Zn in the fine fraction were higher than those of the coarse fraction at the suburban area.



(A) Coarse fraction



(B) Fine fraction

Figure 2. Elemental Concentration ( $\text{ng}/\text{m}^3$ ) of the APM Samples Collected from Daejeon City.

### 3.3 Source apportionment

Based on the elemental composition data for the APM samples, we attempted to identify the sources, and to assess their contributions to the APM by the positive matrix factorization (PMF2) method. The sources for APM in the both sampling sites were found based on a

Q value, FPEAK, and a scaled residual ( $<\pm 2$ ). Scaled residual values less than  $\pm 2$  were more than 80% in the three data sets. The results of a correlation analysis using observed versus predicted APM mass concentrations indicated that the resolved factors effectively accounted for the total mass.

At the industrial area, the pollution sources of the fine fraction evaluated by PMF2 are 10 factors and the order of the contribution for the sources are as follows ; 1) Metal-alloy (19%), 2) Oil combustion (13%), 3) Coal combustion (14%), 4) Diesel exhaust (13%), 5) Incinerator (11%), 6) Gasoline exhaust (10%), 7) Cu-smelter (8%), 8) Biomass burning (8%), 9) Sea-salt (3%), and 10) Soil dust (1%). And at the suburban area, the pollution sources were 7 factors, and the order of the contribution for the sources were as follows ; 1) Incinerator (31%), 2) Biomass burning (23%), 3) Oil combustion (11%), 4) Gasoline exhaust (10.6%), 5) Diesel exhaust (9%), 6) Soil dust (8%), and 7) Sea-salt (7%).

### 3. Conclusion

For an air pollution monitoring study, APM samples in two particle sizes at two regions were collected during 2003 to 2006 and the concentrations of 24 trace elements were measured by using an instrumental neutron activation analysis. The annual average mass concentrations of the APM in the suburban and industrial areas were smaller than the value of the Korean air quality criteria ( $70 \mu\text{g}/\text{m}^3$ ). Based on the elemental compositions of the APM samples, we tried to identify the sources, and to assess their contributions to APM by positive matrix factorization (PMF2) method. The sources included both natural and anthropogenic ones including metal-alloy, oil combustion, coal combustion, diesel exhaust, incinerator, gasoline exhaust, cu-smelter, biomass burning, sea-salt, and soil dust.

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