

Characterization of Wintertime Atmospheric Aerosols in Seoul Using PIXE and Supplementary Analyzers

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Abstract

Particle Induced X-ray Emission (PIXE) and Elemental Analysis System (EAS) were applied to the investigation of the characteristics and sources of wintertime atmospheric aerosols in Seoul. Atmospheric aerosols were collected by both fine and coarse fractions using a two-stage filter pack sampler from Kon-Kuk University during the winter season of 1999. PIXE was applied to the analysis of the middle and heavy elements with atomic numbers greater than 14 (Si) and EAS was applied to the measurement of the light elements such as H, C and N. The fact that 64.2% of mass of fine particles in Seoul consists of the light elements (N, C, and H) suggests that the measurement of light elements is extremely important. The average mass concentration in Seoul was $38.6 \mu\text{g m}^{-3}$. Elements such as Ca, Fe, Mg, Na, and Ti appeared to have very low Fine/Coarse ratios (0.1~0.4), whereas chemical components related to anthropogenic sources such as Br, V, Pb and Zn were observed to accumulate in the fine fraction. In the Asian Dust Storm (ADS) event, the concentration of soil components increased dramatically. Reconstruction of the fine mass concentrations estimated by a newly revised simple model was fairly in good agreement with the measured ones. Source identification was attempted using the enrichment factor and Pearson's coefficient of correlation. The typical elements derived from each source could be classified by this method.

Key words : light elements, PIXE, Element Analysis System, ADS event, enrichment factor

1. INTRODUCTION

Aerosol studies have been one of the main applications of PIXE analysis ever since it was introduced in the early 1970s. The greatest advantage of PIXE is high sensitivity. It also has advantage such as multi-

element nondestructive technique with a wide range of elements. Various air sampling devices have been devised and adapted for special demands as posed by the PIXE technique giving detection limit of down to ng m^{-3} even for minute samples with the total mass of only several μg . Aerosol samples are typically very thin (order of tens of $\mu\text{g cm}^{-2}$) and therefore allowing for relatively straight forward quantitative analysis.

A large number of studies on the elemental concen-

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tration of atmospheric aerosols using the PIXE analysis have been reported (Kasahara *et al.*, 1996; Wang *et al.*, 1996; Cornille *et al.*, 1990). In most cases, however, characterization of the light elements, which cannot be analyzed by the PIXE has not been performed simultaneously.

More than 80% of atmospheric aerosols are occupied by light elements such as C, N, H and O (Kasahara *et al.*, 1996). Especially, secondary particles like nitrate and organic aerosols generated from gaseous materials consist of light elements. So, it is strongly desirable that the PIXE analysis and light element analysis are practiced at the same time.

In this study, to investigate the characteristics and sources of wintertime atmospheric aerosols in Seoul, PIXE, EAS and IC were applied to the simultaneous measurement of the concentration of various elements involving from light to heavy elements and water-soluble ionic components.

2. EXPERIMENTAL

For sampling of ambient aerosols, two-stage filter pack sampler was operated at a height of 17 m above ground level of the Kon-Kuk University building. The surroundings of this sampling site are residential and commercial areas with some minor point sources such

as textile mill, electronics manufactory and print shops. There are no nearby structures taller than sampling site. Six-lane roads, with usually heavy traffic, are located 0.1 km all around of the sampling site. Sampling period was from Jan. 5 to Jan. 27, 1999. During the sampling period, there was one Asian Dust Storm (ADS) event, which is sandstorm from desert in Central Asian Continent. A two-stage filter pack sampler collected the coarse and fine fraction of the aerosol separately on a first-filter (a 47 mm diameter, 8 μm pore size Nuclepore filter) and second-filter (a 47 mm diameter, 0.4 μm pore size Nuclepore filter), respectively. The sampling duration was 12 hours with the flow rate of 25 l min^{-1} . The 50% cut-off diameter of the first-stage filter with 8 μm pore size at this flow rate was estimated to be about 1.2 μm equivalent aerodynamic diameter (Kasahara *et al.*, 1996).

During the sampling period, the range of windspeed was 0.7~3.6 m s^{-1} , and it was generally blowing from the west. The temperature was around $-3.8\sim 2.8^\circ\text{C}$ and average relative humidity was 56% in sampling period.

For the purpose of simultaneous analysis of elements involving light elements, both PIXE and EAS were applied. Fig. 1 illustrates the schematic diagram of PIXE analysis system. PIXE analysis was performed with a proton beam of 6 mm diameter and 2.0 MeV

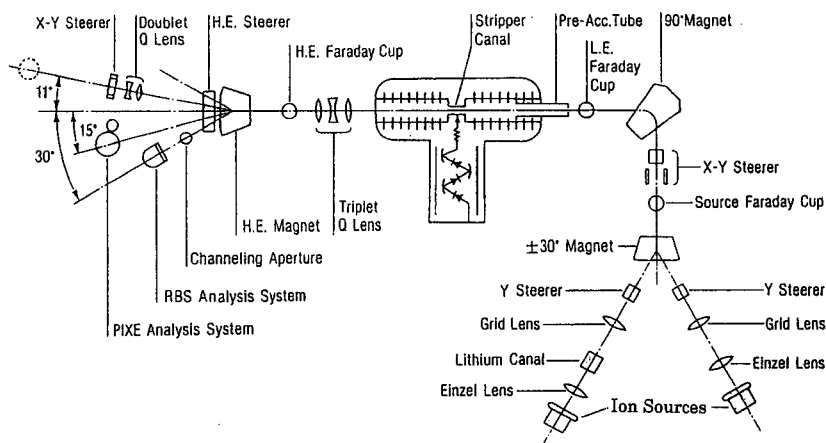


Fig. 1. A schematic diagram of PIXE analysis system employed in this study.

energy from a Tandem Cockcroft accelerator. Beam intensities from 10 to 60 nA were employed and the total doses were about 20 μC .

X-ray with an energy of 14.8 keV emitted from the target were detected by a Si(Li) detector which had a resolution of 152 eV at 5.9 keV. The target and detector were set at 90° and 135° with respect to the direction of the ion beam, respectively. An absorber of 39.3 μm thick Mylar film was set between the target and detector to control counting efficiency of the lighter elements. The count rates for X-rays were kept below 1000 pulses per second. The calibration was carried out with the 18 single element standard samples (2 different mass thickness of 9 elements) at each experimental set up. The sensitivity defined by (PIXE yield per unit dose)/(mass thickness) was obtained theoretically for all objective elements after the sensitivities of the elements adopted, as the standard samples were experimentally determined. The detection limit of the PIXE analysis of atmospheric aerosols depends on the number of factors such as the sort of backing materials, the kind of ion beam energy, the total dose of irradiation and the geometry of the measurement system as well as the sampling conditions of atmospheric aerosols like a sampling area, sampling time and sampling flow rate. The range of the minimum detection limits

for Ca (atomic number, $Z = 20$) and Zn ($Z = 30$) was 0.8–2.6 ng m^{-3} . The more detail analytical procedures and experimental set-ups used for PIXE are described elsewhere (Kasahara *et al.*, 1996).

EAS combined with a high degree of analytical accuracy and a recovery rate of nearly one hundred percent enables a speedy quantitative analysis of C, H, N and S simultaneously in the original sample. Digested samples in the combustion bath at 1150°C condition were detected by each detector which digitize the analogue amplification of the signal via a voltage-to-frequency converter. Fig. 2 shows the schematic diagram of the Elemental Analysis System. Typical spectra of EAS and PIXE were shown in the Fig. 3.

In addition, in order to analyze the water-soluble ionic components the aerosol deposited on each filter was extracted ultrasonically with 10 ml of deionized water.

The extracts were analyzed by ion-chromatograph (Shimadzu LC-10A) to determine mass concentrations of major anions (NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). Cations were analyzed using a Shima-C2 column, 22 mM MSA eluent solution and anions were analyzed Shima-A1 column, 6.6 mM NaOH eluent solution.

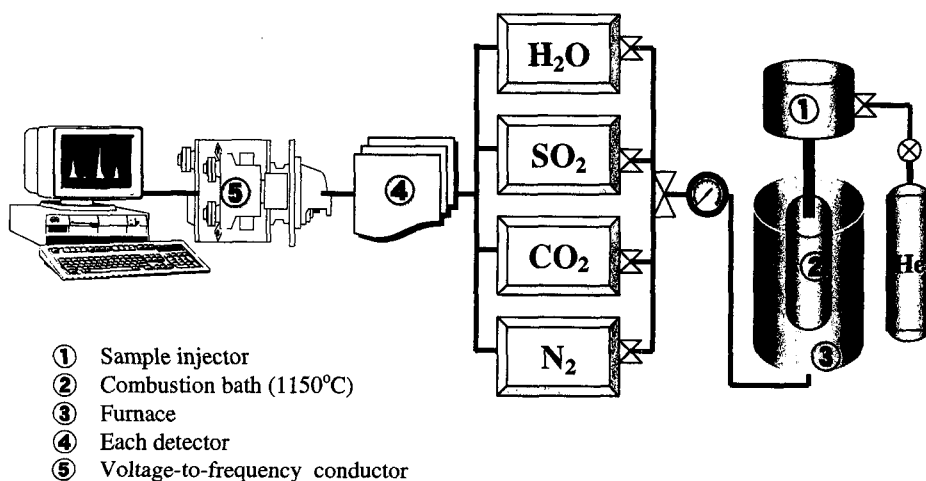


Fig. 2. A schematic diagram of elemental analysis system employed in this study.

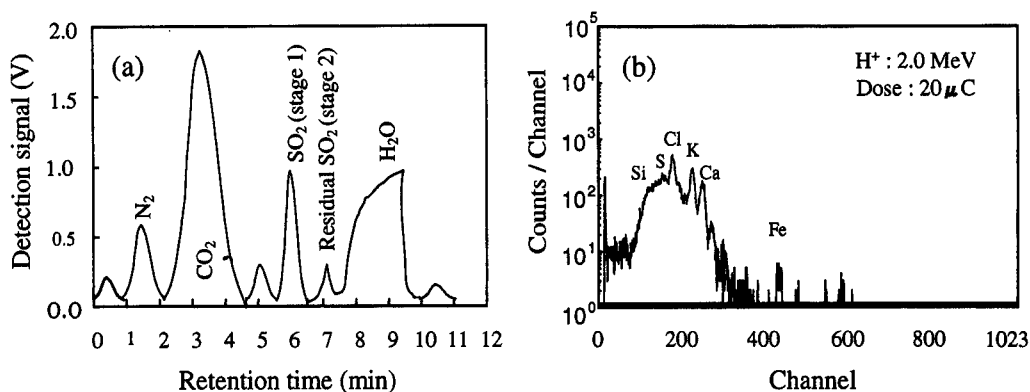


Fig. 3. A diagram of typical spectra for EAS (a) and PIXE (b) analysis.

3. RESULTS AND DISCUSSION

3.1 Aerosols characteristics

In average the sum of N, C and H comprised 64.2% of the mass concentrations in fine particles collected by 2-stage filter pack sampler. The fine/coarse ratio of NH_4^+ , NO_3^- and SO_4^{2-} , an aged aerosol indicator were high (1.55~2.12) (Davis, 1984). According to these results, it is supposed that the carbonaceous materials and ammonium salts such as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are the major components in fine fraction. The pH values determined by pH meter (Horiba Co.) for the bulk aerosol samples extracted with deionized water by ultrasonicator was ranged from 5.8 to 6.4, but pH value during the ADS event was 6.8. This result indicates that the aerosols were normally slightly acidic. On the other hand, those of ADS event were nearly neutralized. There is other considerable evidence to show this fact. The ratio of equivalent concentration of ammonium to sulfate was 1.27. It suggests that appreciable neutralization of H_2SO_4 had occurred. On the other hand, ammonium to sulfate ratio was 0.20 in ADS event. CaCO_3 serves as a neutralizer for strong acid like H_2SO_4 or HNO_3 . Therefore, an upward trend of calcium and bicarbonate ions (HCO_3^-) is most likely the explanation for the downward trend of the hydrogen ions.

One should bear in mind that bulk analysis represents the average value of all particles that had combined and neutralized each other in the sample extracted by the de-ionized water. In the atmosphere, individual particles may remain as acidic or basic state without mixing or neutralization for a long time.

S measured by both PIXE and EAS allowed us to crosscheck the analytical precision of two analytical methods. The agreement between S concentrations determined by PIXE and EAS was very good. A linear regression performed on the analytical results from 22 filter pairs produced the equation $[\text{S}]_{\text{PIXE}} = 0.97[\text{S}]_{\text{EAS}} + 0.08$. This slope and intercept of the line were not significantly different from unity and zero, respectively, and correlation coefficient (r^2) was 0.95. As a check on the quality of the PIXE and Ion chromatography analysis, the S from PIXE can be compared to the SO_4^{2-} from IC. The average ratio of measured S to SO_4^{2-} mass was 0.28 (the ratio of molecular weight is 0.33) and the correlation coefficient between the two measurements was 0.95. This shows that the majority of the particulate S in Seoul was in the form of SO_4^{2-} and that little or no mass was lost in the PIXE analysis.

The ratio of potassium ion concentration of fine to coarse fraction was 1.39. The principle origin of non-soil potassium is thought to be biological and the dominant fine fraction is associated primarily with biomass and wood smoke (Linda *et al.*, 1997).

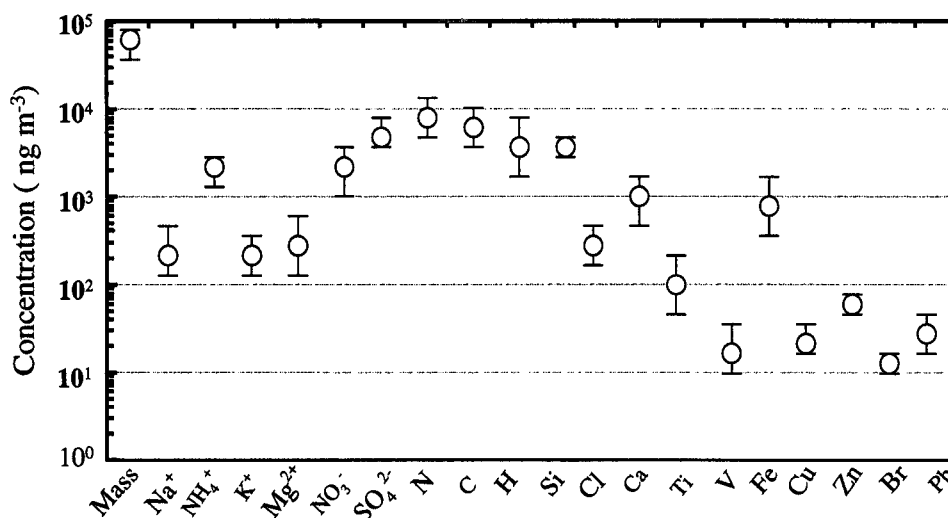


Fig. 4. Average concentrations (fine+coarse) of the chemical components measured in this study.

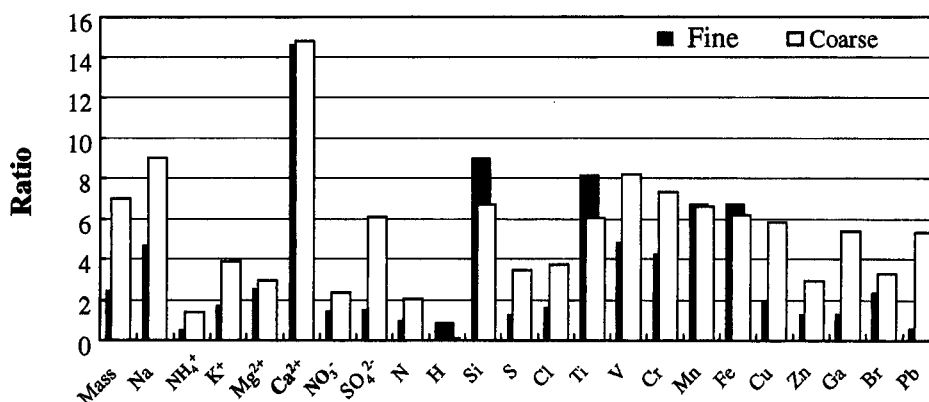


Fig. 5. The ratios of each component in ADS event to in non-ADS day.

Elements such as Ca, Fe, Mg, Na and Ti appeared to be very low ratios (0.1~0.4) of F/C, whereas chemical components relation to anthropogenic sources such as Br, V, Pb and Zn were observed to accumulate in the fine fraction.

Fig. 4 represents the average concentrations of the sum of both fine and coarse fraction of the chemical components. The average mass concentration in Seoul was $38.6 \mu\text{g m}^{-3}$. The mass concentration was about 2 times higher than that of Kyoto measured in December, 1998 by Ma *et al.* (2000). The major components

were classified by two groups, they were ammonium salts components such as NH_4^+ , NO_3^- and SO_4^{2-} , and soil components like Si, Ca, Fe and K.

The ratios of each component in ADS event to in non-ADS day as a function of size fractions are shown in Fig. 5.

As shown in Fig. 5, the ratios of mass concentration in ADS event to in non-ADS day were 2.43 and 6.99 in fine and coarse mode, respectively. And those of every component were above the 1.0. Ca, Si and Ti, that are mainly soil origin components, showed high

ratios. Particularly that of calcium was the highest point (14.78). Although detailed information on the source profiles are desirable, this phenomenon can be caused by such mechanisms as wind action on soil and human activity in urban area. Added to these reasons, inflow of soil components generated in desert and loess areas of China is reasonably considered because the prevailing wind was westerly wind and the typical ADS event was measured during sampling period.

The high ratio of S concentration in ADS event to non-ADS day in coarse fraction was found. On the one hand, S in soils of the desert and loess areas in China was not detected by PIXE (Ma *et al.*, 2000). This reason might be that S is released to the atmosphere in gaseous form and is deposited onto coarse particles through reactions with water vapor and sunlight forming sulfuric acid during the long-range transport. Due to the large available surface area in the coarse fraction compare to that in fine fraction, SO₂ and sulfuric acid deposition rate of the coarse fraction is larger than that of the fine fraction (Iwasaka *et al.*, 1988).

3.2 Simple model for calculation of fine mass

An attempt was made to revise a simple model, which calculate the mass concentration of fine particles. It is possible to estimate the fine mass concentration by the following equation under the assumption which all aerosol species accounted for significant fraction of the mass are measured.

$$\begin{aligned} \text{Calculated mass of fine particles} \\ = 4.125 [S] + 1.20 [OC] + [EC] + 2.857 [N] + [Soil] \\ + [Salt] + [Water] \end{aligned}$$

where, the factor of 1.20 is the ratio of the mass of organic matter to the mass of organic carbon. According to Countess *et al.* (1980), the amount of organics was determined by multiplying the amount of OC by 1.20. The multiplicative factors associated with sulfur and nitrogen are based on the assumptions that sulfates are (NH₄)₂SO₄ and nitrates are NH₄NO₃. It was undoubtedly proved that the main forms of sulfate in this

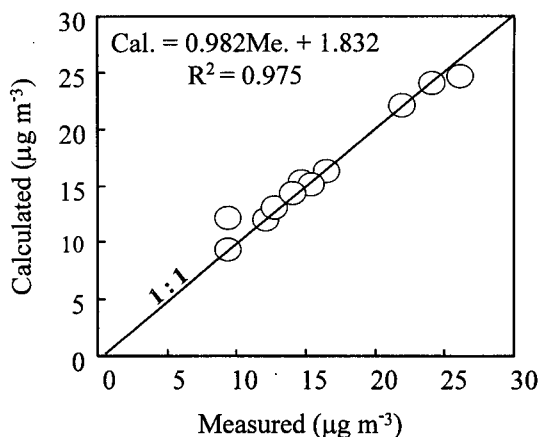


Fig. 6. A plot of measured vs. calculated fine mass.

study were (NH₄)₂SO₄ by use of mole ratio comparison. So, the overestimation of sulfate mass caused by if sulfur is in the forms of NH₄HSO₄ and H₂SO₄ can not be concerned. The masses of sea salt and soil are estimated by 3.27[Na⁺] (Ohta *et al.*, 1990) and by 4.807[Si] (Peter *et al.*, 1990), respectively.

In this study, the amount of water associated with hygroscopic aerosols was disregarded because after the sampling all of filters were equilibrated at 30% relative humidity before weighing. The result is presented in Fig. 6 which circles nearly lied on the 1 : 1 straight line by 0.98 coefficient of determination.

3.3 Source identification

The comparison between the elemental concentration levels of atmospheric aerosol when they are higher than expected in their natural form, according to their proportion in the natural origins, is the simple way to identify their source origin. The degree of enrichment of trace elements in aerosol is given by an enrichment factor, EF.

Over the fast few decades the EF method has been applied by a considerable number of studies (Peter *et al.*, 1990; Gregory *et al.*, 1978). To study the enrichment factor method, atmospheric aerosols may be collected with filtration equipment in order to obtain sufficient amounts of material for quantitative analysis with

reasonable accuracy. Although a large amount of aerosols collected by high-volume sampler is enough for source classification by enrichment factor method, it is quite unsatisfactory to identify as the function of particle size. While the amount of aerosol collected by cascade impactors is usually insufficient for the accurate determination of many important elements (Fred *et al.*, 1980). In these points of view, 2-stage filter packs method used in this study must be suitable for application of the enrichment factor method.

To quantify enrichment, Rahn (1976) proposed the use of enrichment factors, which is defined as :

$$EF_x = \frac{C_{x,p} / C_{ref,p}}{C_{x,c} / C_{ref,c}}$$

where, $C_{x,p}$ and $C_{ref,p}$ are the concentration of the element and of a suitably chosen reference element in the atmospheric aerosol, respectively, and $C_{x,c}$ and $C_{ref,c}$ are the concentration of the element and of a reference element in the natural sources such as soil and sea water.

The soil and marine components are based on the data reported by Peter A. Si and Na were considered as the reference elements of soil and marine, respectively (Peter *et al.*, 1990).

Fig. 7 shows the enrichment factors calculated for the coarse particles. In the crustal enrichment factors, relative to Si and Peter's average soil composition, the EFs were close to 1.0 for many elements such as Mg, Mn, Fe and Ni (Peter *et al.*, 1990). Added to this, the

correlation coefficients between these components were very high ($r = 0.73 - 0.93$). The anthropogenic components such as S, Cu, Ga, Br and Pb had very high EF values. EF based on the marine derived Cl was 7.0 in Seoul. However, in the fine particle, Cl measured in Seoul should be explained by derivation from the auto exhaust particles and refuse combustion. Significantly high concentration of Cl derived from motor vehicle and refuse in Washington, D.C. aerosols was reported by Gregory *et al.* (1978).

There is further evidence about this explanation. Pearson's correlation coefficients (significant level: 0.05 in both sides) between Cl and Br and between Cl and Zn were 0.88 and 0.81, respectively.

Table 1 summarizes the source indicator elements presumed by enrichment factors, Pearson's coefficients of correlation and the concentration ratios of each element relative to trace elements.

V and Zn were treated as the trace elements of oil and refuse, respectively, in this work. Ni and S were closed related with V. Their correlation coefficient to

Table 1. A portionment of major elements for some sources in Seoul area.

Sources	Elements [†]
Soil	Si, Ca, Ti, Fe, K
Marine*	Na, Cl
Oil**	V, Ni, S
Refuse	Zn, K, Cl

[†]: Al was not measured

*: coarse particle

** : fine particle

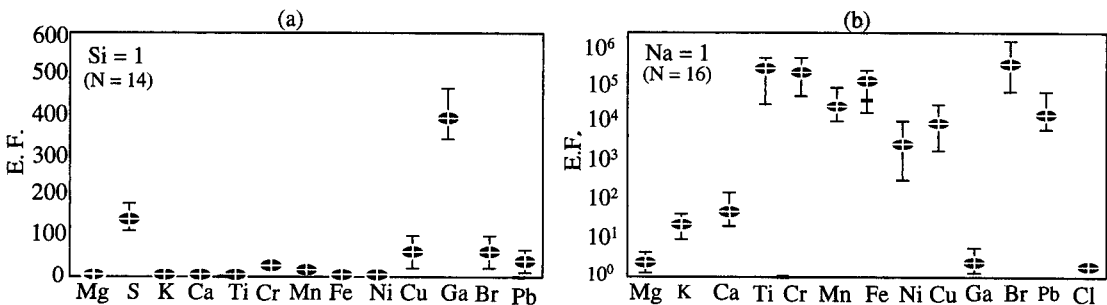


Fig. 7. Enrichment factors calculated for the coarse particles ((a): crustal E.F., (b): marine E.F.).

V were 7.67 and 4.85, respectively. In addition to, the concentration ratios of Ni to V were similar to that of the oil components measured in-stack and plume measurements by Mroz (1976). They are 0.37 and 0.41 in Seoul and in oil components, respectively. Also, correlation coefficients between Zn and K were very high (0.85).

4. CONCLUSIONS

This study was intended as an investigation of characteristics and sources of atmospheric aerosol including the light elements in Seoul. The sum of N, C and H accounted for 64.2% of fine fraction mass concentration in Seoul. So, we reasonable conclude that the PIXE analysis and light elements analysis must be performed simultaneously. The average mass concentration in Seoul was $38.6 \mu\text{g m}^{-3}$. pH values for the bulk aerosol samples was ranged from 5.8 to 6.4, but pH value in the ADS event was 6.8. Elements such as Ca, Fe, Mg, Na and Ti appeared to be very low ratios (0.1 ~ 0.4) of Fine/Coarse, whereas chemical components relation to anthropogenic sources such as Br, V, Pb and Zn were observed to accumulate in the fine fraction. The concentration ratios of the components originated from soil in the ADS event to those in the non-ADS days were high, and especially calcium had dramatically high ratio of 14.8. It was possible to estimate the fine mass concentration by simple model. The plotted squares are mostly lied on the 1 : 1 straight line of calculated vs. measured mass with determination coefficient of 0.98. The typical elements derived from each source could be classified by enrichment factor method and Pearson's coefficient of correlation.

REFERENCES

- Cornille, P. and W. Maenhaut (1990) Sources and characteristics of the atmospheric aerosol near Damascus, Syria. *Atmospheric Environment* 24A, 1083-1093.
- Countess, R.J., G.T. Wolff, and S.H. Cadle (1980) The Denver winter aerosol: a comprehensive chemical characterization. *J. Air Pollut. Control Ass.*, 30, 1194-1200.
- Davis, B.L. (1984) X-ray diffraction analysis and source apportionment of Denver aerosol. *Atmospheric Environment*, 18, 2197-2208.
- Dzubay, T.G., R.K. Stevens, C.W. Lewis, D.H. Hern, W.J. Courtne, J.W. Tesch, and M.A. Mason (1982) Visibility and aerosol composition in Houston, Texas. *Envir. Sci. Technol.*, 16, 514-525.
- Fred, C.A., J.V.C. Marc, and J.V.E. Pierre (1980) Enrichment of trace elements in remote aerosols. *Envir. Sci. Technol.* 14, 1002-1005.
- Greenberg, R.R. (1976) A study of trace elements emitted on particles from municipal incinerators. Ph.D. Thesis, University of Maryland.
- Gregory, S.K., E.C. Carl, and E.G. Glen (1978) Chemical element balances and identification of air pollution sources in Washington, D.C.. *Atmospheric Environment* 12, 1143-1153.
- Holler, R., M. Kasahara, C.J. Ma, K. Gotoh, and Y. Iwasaka (2000) Climate-relevant optical and chemical properties of the urban aerosol of Nagoya. submitted to *Atmospheric Research*.
- Iwasaka, Y., M. Yamamoto, R. Imasu, and A. Ono (1988) Transport of Asian dust (KOSA) particles: importance of weak KOSA events on the geochemical cycle of soil particles. *Tellus* 40B, 494-503.
- John, J.P. and E.J. Robert (1976) Multielement size characterization of urban aerosols. *Envir. Sci. Tech.*, 10, 1124-1127.
- Johnson, B.J., S.C. Huang, M. Lecave, and M. Proterfield, (1994) Seasonal trends of nitric acid, particulate nitrate, and particulate sulfate concentrations at a southwestern U.S. mountain site. *Atmospheric Environment* 28, 1175-1179.
- Kasahara, M., C.J. Ma, and S. Tohno (2000) Characterization of atmospheric aerosols using PIXE, EAS, and IC. Extended abstract of PM 2000: Particulate Matter and Health, Carlestone, USA, Jan. 24-28, 1/36-1/37.
- Kasahara, M., J.H. Park, and S. Chatani (1996) Size distribution and solubility of 15 elements in atmospheric aerosols. *International Journal of PIXE* 6, 299-310.
- Kasahara, M., K.C. Choi, and K. Takahashi (1990) Source contribution of atmospheric aerosols in Japan by chemical mass balance method. *Atmospheric Envi-*

- ronment 24A, 457-466.
- Kasahara, M., S. Tohno, S. Akashi, and C.J. Ma (1999) Single particles analysis? Its importance in aerosol research. 1st Asia Aerosol Conference, Nagoya, Japan, Jul. 27-29, 136-137.
- Linda, Y.Z. and A.H. Martin (1997) Size-resolved airborne particles and their morphology in central Jakarta. *Atmospheric Environment* 31, 1167-1172.
- Ma, C.J., H.K. Kim, K.C. Hwang, S.I. Lee, K.C. Cho, and M. Kasahara (2000) Characterization of ammonia and related components at urban and rural sites in Korea. submitted to *Int. J. of Analytical Science*.
- Ma, C.J., M. Kasahara, R. Höller, and T. Kamiya (2000) Characterization of single particles and bulk aerosol samples in Japan during the Asian dust ? storm period. *Atmospheric Environment* (in press).
- Ma, C.J., M. Kasahara, S. Thono and H.G. Yeo (1999) A Study on the characteristics and sources of the winter time atmospheric aerosols in Kyoto and Seoul using PIXE and supplementary analysis. 1st Asia Aerosol Conference, Nagoya, Japan, Jul. 27-29, 330-331.
- Ma, C.J., M. Kasahara, S. Thono, and K.C. Hwang (2000) Characterization of the winter atmospheric aerosols in Kyoto and Seoul using PIXE and EAS analyses. *Atmospheric Environment* (in press).
- Mroz, E.J. (1976) The study of the elemental composition of particulate emissions from an oil-fired power plant. Ph. D. thesis, Uvni. of Maryland.
- Ohta, S. and T. Okita (1990) A chemical characterization of atmospheric aerosols in Sapporo. *Atmospheric Environment* 24A, 815-822.
- Ohta, S. and T. Okita (1984) Measurements of particulate carbon in urban and marine air in Japanese areas. *Atmospheric Environment* 18, 2439-2445.
- Peter, A.S. and V. Constantine (1990) Characterization and source identification of respirable particulate matter in Athens, Greece. *Atmospheric Environment* 24A, 203-211.
- Pierson, W.R. and W.W. Brachaczek (1988) Coarse- and fine-particle atmospheric nitrate and HNO₃(g) in Claremont, California, during the 1985 nitrogen species methods comparison study. *Atmospheric Environment* 22, 1665-1668.
- Pilinis, C., J.H. Seinfeld, and D. Grosjean (1989) Water content of atmospheric aerosols. *Atmospheric Environment* 23, 1601-1606.
- Rahn, K.A. (1976) The chemical composition of the atmospheric aerosol. Technical report. University of Rhode Island.
- Shaw, R.W., R.K. Stevens, M. Bowermaster, J.W. Tesch, and E. Tew (1982) Measurements of atmospheric nitrate and nitric acid : the denuder difference experiment. *Atmospheric Environment* 16, 845-853.
- Wang, X. and Z. Guanghua (1996) Some characteristics of the aerosol in Beijing. *International J. of PIXE* 6, 361-365.
- Willison, M.J., A.G. Clarke, and E.M. Zeki (1985) Seasonal variation in atmospheric aerosol concentration and composition at urban and rural sites in Northern England. *Atmospheric Environment* 19, 1081-1089.