

Characterization of size-resolved aerosol components using proton induced X-ray emission, inductively coupled plasma optical emission spectrometry and ion chromatography

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Abstract—Size-resolved aerosol monitoring for PM₁₀, PM_{2.5}, and PM_{1.0} was performed to qualify and quantify the elements and ions by using proton induced X-ray emission (PIXE), inductively coupled plasma optical emission spectrometry (ICP-OES), and ion chromatography (IC) analysis. Time-resolved aerosol samplings based on 2-hour and 14-hour intervals were carried out during daytime and nighttime, respectively. Physical and chemical properties of size-resolved aerosols were investigated to characterize air quality in the national park area of Gyeongju, Korea. The PIXE and ICP-OES methods made elemental mass of Al, Si, S, K, Ca, Ti, Cr, Fe, Sr, and Pb. And ions of Na⁺, NH₄⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻ were analyzed by the IC method. The mass concentrations of Si, S, Ti, and Pb determined by PIXE showed relatively good correlation with those determined by ICP-OES. But Fe and Sr had worse correlations with an average R² of 0.4703 and 0.4825, respectively. The PIXE method was a good alternative to measure chemical species of Al, Si, S, K, Ca, Ti, Cr, and Pb for size-resolved aerosols except Fe and Sr in this study. The average relative errors of size-resolved elements for 2-hour and 14-hour interval collections were 10.1±5.7% (0.1-28.3%) and 9.9±7.7% (1.3-38.4%). Ammonium sulfates (AS), mineral dust (MD), and sea salt (SS) aerosols were reconstructed from the elements determined by PIXE and ICP-OES and ions obtained by IC. The mass concentration of MD was calculated with crustal elements of Al, Si, Ca, Ti, and Fe, which are associated with soil erosion. The average relative error of MD was the lowest value of 0.8% in the PM₁₀ regime and the highest value of 10.0% in the PM_{1.0} regime. The average relative errors of AS for PM₁₀, PM_{2.5}, and PM_{1.0} determined by PIXE, ICP-OES, and IC showed relatively lower values of 0.8-5.7%, 1.7-5.9%, and 3.3-8.3%, respectively. The average mass concentrations of AS, MD, and SS of PM₁₀, PM_{2.5}, and PM_{1.0} except submicron SS determined by PIXE were comparable to those determined by ICP-OES and IC within the acceptable relative errors.

Key words: PIXE, ICP-OES, Aerosol, Element

INTRODUCTION

Elements of particulate matters in trace amounts in the atmosphere have an effect on human health, atmospheric light attenuation, and radiative forcing [1-3]. It is, therefore, important to quantify the concentration of the elements for the determination of the chemical composition of aerosol species such as sulfates, sea-salt, and soil dust. A nondestructive, highly sensitive, and multi-elemental analytical method is required to provide the information associated with trace elements. Proton induced x-ray emission (PIXE) is suitable for quantifying the trace elements with a sensitivity of a few parts per million (ppm) [4]. Meanwhile, inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and atomic absorption spectroscopy (AAS) have been mainly used to analyze the trace elements for atmospheric particles. These techniques have intrinsic problems such as time-consuming sample preparation and a method destructive to the original sample. Therefore, comparison of measurement data determined by PIXE with those determined by ICP-MS and/or ICP-AES has been performed in order to adapt in the field of atmospheric environment in terms of evaluating measurement data determined by PIXE [5,6]. It was reported that the analytic values

except for some elements determined by ICP-MS and ICP-AES were generally consistent with those determined by PIXE [7]. And PIXE analysis can provide information of a mass concentration on a small amount of aerosol sample collected from time-resolved aerosol monitoring [8]. In this study, we analyzed time-resolved aerosol samples collected using cyclone samplers in the size ranges 0-1.0, 0-2.5, and 0-10 μm to qualify and quantify the elements using PIXE and inductively coupled plasma-optical emission spectrometry (ICP-OES). ICP-OES is based on the light detection emitted at element-specific characteristic wavelengths from thermally excited atoms or ions using a spectrometer. In this study, physical and chemical properties of size-resolved aerosols determined by PIXE, ICP-OES, and IC were investigated to evaluate air quality in the national park area of Gyeongju, Korea.

EXPERIMENTAL

Intensive aerosol monitoring was conducted at the atmospheric monitoring station of Gyeongju University located at the Seoak section of Gyeongju national park area of Korea. The monitoring station was situated about 4 km from downtown; thus direct artifacts from specific stationary or mobile sources were avoided.

Size-resolved aerosol measurements were performed 28 April-9 May 2008. Time-resolved aerosol samplings based on 2-hour (from 8 A.M. to 6 P.M.) and 14-hour (from 6 P.M. to 8 A.M.) intervals

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were carried out each sampling day. During the intensive monitoring periods, size-resolved aerosol collections for $PM_{1.0}$ ($D_p < 1.0 \mu\text{m}$), $PM_{2.5}$ ($D_p < 2.5 \mu\text{m}$), and PM_{10} ($D_p < 10 \mu\text{m}$) were conducted using a set of URG (University Research Glassware) model URG-2000-30EHB $PM_{1.0}$, model URG-2000-30EH $PM_{2.5}$, model URG-2000-30ENB PM_{10} cyclones, respectively.

PIXE method was introduced to detect the elements of Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Se, Sr, Cd, and Pb for size-resolved aerosols. The PIXE spectra for size-resolved aerosol samples were obtained using a 1-mm-diameter, 4-to-5-nA beam, 3.0-MeV proton beam from a 3-MV Tandemron accelerator at the Electrostatic Accelerator Research Center, National Center for Inter-university Research Facility, Seoul National University. The X-rays were detected with an Si (Li) detector. The spectral peak area for each element was extracted by using the analysis program Win-QXAS (IAEA) and converted to relative concentrations by comparing it to an NIST (National Institute of Standards and Technology) standard reference material SRM1648 [9].

To detect the trace elements using the ICP-OES, each sampled polycarbonate filter was divided in half and one of them put into a 60 ml Teflon digestion vessel. 5 ml of nitro-hydrochloric acid (HNO_3/HCl) was added into the vessel, followed by addition of 1 ml of HF for Si detection and was capped to prevent the solution from being volatilized. The vessel was heated for 24 hours. The filter was removed from the vessel after cleaning with a 1% nitric acid, and then the solution was volatilized by a heater. The concentration solution was diluted by adding 20 ml of 1% nitric acid into the vessel. Twelve species (Na, Al, Si, S, K, Ca, Ti, Cr, Fe, Ni, Sr, Pb) were analyzed by the School of Environmental Science and Engineering in Gwangju Institute of Science and Technology (GIST) using a PerkinElmer Optima™ 5300 DV ICP-OES. And the other half filter was used to analyze ions of Na^+ , NH_4^+ , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} by ion chromatography (IC). They were detected by using a GAT (gamma analysen technik GmbH) model DKK-TOA IA-300 ion chromatograph after being extracted with 10 ml of distilled water. The sampling and analytic methods for size-resolved aerosol collection in this study are summarized in Table 1.

RESULTS AND DISCUSSION

To investigate the variability of elemental mass data of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ analyzed using the PIXE, ICP-OES, and IC method, 66 size-resolved aerosol sets were obtained at two-hour and fourteen-hour sampling intervals during the intensive monitoring period. Temporal variations of mass concentrations of the size resolved aerosols are illustrated in Fig. 1. The average mass concentrations of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were measured to be 73.9 ± 29.2 , 40.6 ± 16.1 ,

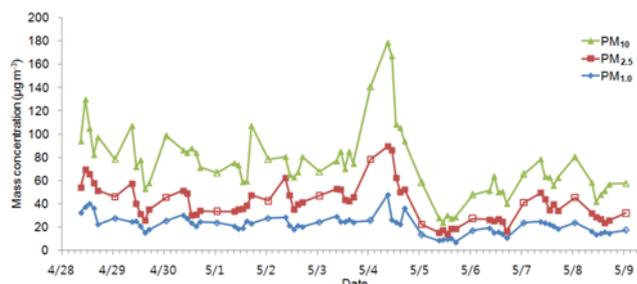


Fig. 1. Temporal variation of the mass concentrations of size-resolved aerosols of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ during the intensive monitoring period.

and $22.1 \pm 7.6 \mu\text{g m}^{-3}$ during the intensive monitoring period, respectively. Fractional contributions of $PM_{2.5}$ to PM_{10} and $PM_{1.0}$ to $PM_{2.5}$ were estimated to be 55.0 ± 9.2 and $54.4 \pm 9.4\%$, respectively. During that period, PM_{10} and $PM_{2.5}$ did not attain the annual PM_{10} and $PM_{2.5}$ national air quality standard of 50 and $25 \mu\text{g m}^{-3}$. The size-resolved aerosols caused serious haze in the national park area of Gyeongju. The minimum values of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were 24.3 , 14.3 , and $7.1 \mu\text{g m}^{-3}$ and the maximum values were 178.4 , 89.3 , and $47.9 \mu\text{g m}^{-3}$, respectively. These broad ranges of data sets can provide better understanding of variability of the elemental mass concentrations from the three analytic methods.

The average mass concentrations of trace elements of size-resolved aerosols analyzed using the PIXE and ICP-OES methods are summarized in Table 2. Major elements in the PM_{10} regime were Al, Si, S, Ca, Fe, and Pb. The average mass concentrations of the crustal elements of Al, Si, Ca, and Fe dramatically decreased in the $PM_{1.0}$ regime, but large amount of sulfur existed in the $PM_{1.0}$ regime. The average mass concentration of sulfur in the $PM_{1.0}$ regime accounted for 37-41% of that in the PM_{10} regime. The mass concentrations of sulfur for PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were $2,554 \pm 1,609$, $2,094 \pm 1,439$, and $1,048 \pm 760 \text{ ng m}^{-3}$ for the PIXE method and $2,691 \pm 1,520$, $2,198 \pm 1,428$, and $983 \pm 821 \text{ ng m}^{-3}$ for the ICP-OES method, respectively. The relative errors of the average mass concentrations of trace elements for size-resolved aerosols determined by the PIXE method to those determined by the ICP-OES method ranged from 1.0 to 25.6% during the intensive monitoring periods. In the PM_{10} regime, the relative errors for Al, Si, S, and Ti were calculated to be less than 5%, but those for K, Ca, Cr, Fe, Sr, and Pb were slightly higher than them. The elements of relative errors less than 5% were Al, S, and Fe in the $PM_{2.5}$ regime and K in the $PM_{1.0}$ regime. The relative errors of the average mass concentration data between PIXE and ICP-OES were found to be larger when the size of the particles became smaller, as summarized in Table 2. In addition, the average

Table 1. Sampling and analytic methods for size-resolved aerosol monitoring in this study

| Instrument | Particle size | Analytical method & specification | Sampling interval |
|------------------------|-------------------------|--|--------------------------|
| URG $PM_{1.0}$ cyclone | $D_p < 1.0 \mu\text{m}$ | Gravimetric analysis (mass) | 2-hour (8 A.M.-6 P.M.), |
| URG $PM_{2.5}$ cyclone | $D_p < 2.5 \mu\text{m}$ | Proton induced X-ray emission (Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Se, Sr, Cd, and Pb) | 14-hour (6 P.M.-8 A.M.), |
| URG PM_{10} cyclone | $D_p < 10 \mu\text{m}$ | Inductively coupled plasma-optical emission spectrometry (Na, Al, Si, S, K, Ca, Ti, Cr, Fe, Ni, Sr, Pb) | and 24-hour |
| | | Ion chromatography (Na^+ , NH_4^+ , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} , etc.) | |

Table 2. Comparison of average elemental mass concentrations analyzed using the PIXE and ICP-OES methods during the intensive monitoring period

| Type | Element | PIXE | | | ICP-OES | | |
|-----------------------|---------|------------------|-------------------|-------------------|------------------|-------------------|-------------------|
| | | PM ₁₀ | PM _{2.5} | PM _{1.0} | PM ₁₀ | PM _{2.5} | PM _{1.0} |
| (ng m ⁻³) | | | | | | | |
| Total | Al | 2385±1547 | 1080±881 | 108±130 | 2345±1290 | 1092±787 | 123±149 |
| | Si | 5263±3503 | 1270±1101 | 136±135 | 5212±3202 | 1389±1291 | 145±145 |
| | S | 2554±1609 | 2094±1439 | 1048±760 | 2691±1520 | 2198±1428 | 983±821 |
| | K | 544±564 | 442±525 | 94±160 | 612±502 | 512±463 | 96±143 |
| | Ca | 1945±1356 | 394±230 | 86±38 | 2131±1425 | 425±240 | 81±55 |
| | Ti | 537±476 | 140±150 | 47±70 | 563±380 | 169±144 | 53±86 |
| | Cr | 184±230 | 50±68 | 16±21 | 206±258 | 67±83 | 20±32 |
| | Fe | 1479±1335 | 555±597 | 79±83 | 1354±1123 | 548±491 | 87±97 |
| | Sr | 8±2 | 2±1 | 1±1 | 8±3 | 3±1 | 1±1 |
| | Pb | 1542±1261 | 971±840 | 264±301 | 1435±1061 | 885±751 | 270±314 |
| 2-hr | Al | 2362±1599 | 1080±881 | 95±126 | 2249±1261 | 1073±783 | 111±146 |
| | Si | 5257±3678 | 1270±1098 | 112±115 | 5262±3295 | 1362±1295 | 118±130 |
| | S | 2416±1598 | 1950±1393 | 952±685 | 2555±1406 | 2062±1275 | 849±534 |
| | K | 530±581 | 437±549 | 75±95 | 609±518 | 515±485 | 85±114 |
| | Ca | 1830±1377 | 386±226 | 88±37 | 2007±1432 | 407±230 | 84±56 |
| | Ti | 518±490 | 136±151 | 33±40 | 546±371 | 166±135 | 40±47 |
| | Cr | 188±249 | 49±72 | 14±17 | 209±278 | 68±90 | 16±13 |
| | Fe | 1399±1295 | 553±644 | 70±77 | 1247±864 | 525±480 | 82±100 |
| | Sr | 8±2 | 2±1 | 1±0 | 8±3 | 2±1 | 1±1 |
| | Pb | 1442±1187 | 910±818 | 221±246 | 1323±927 | 830±743 | 238±257 |
| 14-hr | Al | 2501±1314 | 1045±791 | 174±133 | 2827±1388 | 1191±834 | 185±157 |
| | Si | 5291±2593 | 1499±1126 | 258±168 | 4964±2820 | 1527±1325 | 280±141 |
| | S | 3245±1548 | 2813±1513 | 1529±956 | 3373±1930 | 2882±1965 | 1655±1498 |
| | K | 616±491 | 464±404 | 189±326 | 624±433 | 500±355 | 151±243 |
| | Ca | 2522±1127 | 432±258 | 79±35 | 2750±1277 | 514±281 | 66±48 |
| | Ti | 633±408 | 157±149 | 120±126 | 645±433 | 188±187 | 114±177 |
| | Cr | 163±96 | 54±50 | 26±35 | 190±119 | 60±42 | 43±71 |
| | Fe | 1879±1521 | 567±285 | 124±101 | 1889±1947 | 662±550 | 112±76 |
| | Sr | 8±1 | 2±1 | 2±1 | 9±2 | 3±1 | 1±1 |
| | Pb | 2041±1546 | 1272±918 | 482±447 | 1994±1503 | 1160±765 | 429±501 |

relative errors of size-resolved elements for 2-hour and 14-hour interval collections were 10.1±5.7% (0.1-28.3%) and 9.9±7.7% (1.3-38.4%). Time-resolved aerosol monitoring produced smaller amount of aerosol sample volumes. There was, however, no apparent difference of the relative errors for results between the 2-hour and 14-hour interval sampling method. Time-resolved chemical species of size-resolved aerosols.

The results plotted in Fig. 2 compare the chemical species Al, Si, S, K, Ca, Ti, Cr, Fe, Sr, and Pb in the PM₁₀, PM_{2.5}, and PM_{1.0} regimes obtained by the PIXE method to those obtained by the ICP-OES method during the intensive monitoring period. Scatter plots and Pearson's R² correlation coefficients show the differences between them. The best correlation between the two analytic methods was for Al with R²s of 0.7134 for PM₁₀, 0.6959 for PM_{2.5}, and 0.7496 for PM_{1.0}, and the worst ones were Fe and Sr with an average R² of 0.4703 and 0.4825, respectively. The elements of Si, S, Ti, and Pb show relatively good correlation between the both methods. The correlation coefficients for larger particles of PM₁₀ and PM_{2.5} were

relatively higher than that for PM_{1.0}, as described in Fig. 2. For all trace elements except Fe and Sr the ICP-OES results were slightly higher than the values measured by PIXE in most aerosol size ranges. This is associated with a sample volume between surface detection by PIXE and total detection by ICP-OES [10]. And the results from PIXE are sensitive to surface homogeneity of a sample [11]. The anthropogenic-rich element of S and the crustal elements of Si, Ca, and Ti obtained by PIXE provided better agreement with those obtained by ICP-OES.

The mass ratios (PM_{i,PIXE}/PM_{i,ICP-OES}) of elements for size-resolved aerosols, i (PM₁₀, PM_{2.5}, and PM_{1.0}) determined by PIXE to those determined by ICP-OES are shown in Fig. 3. To prevent statistics from influence by outliers, the data below the 5th percentile and above the 95th percentile were excluded from this analysis. The valid mass ratios of elemental concentrations ranged from 0.3 to 2.1 in the PM₁₀ regime, from 0.2 to 2.2 in the PM_{2.5} regime, and from 0.2 to 2.6 in the PM_{1.0} regime. The mass ratios of Al, Si, S, Ca, and Sr showed relatively narrow deviations. This result was consistent

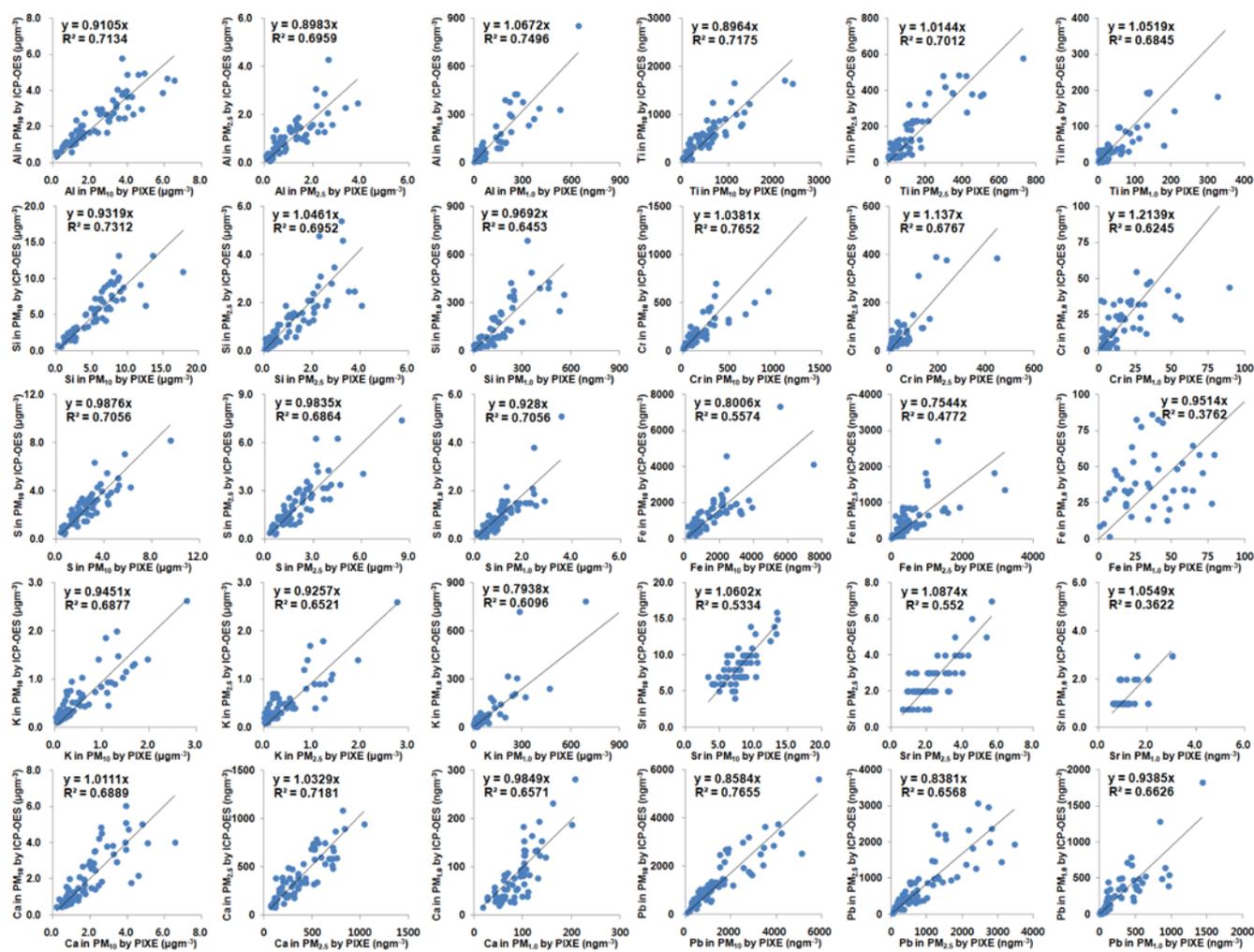


Fig. 2. Scatter plots of elemental mass concentrations determined by the PIXE method versus by the ICP-OES method. The results of linear regressions show slopes and Pearson's R^2 correlation coefficients.

with the results from their correlation coefficients except Sr. The correlation between PIXE and ICP-OES was poor for Sr, as shown in Fig. 2. The mean mass ratios of Al, Si, S, and Ca were approximately 1.0 in the PM₁₀ and PM_{2.5} regime. However, the mean mass ratios of Sr for PM₁₀, PM_{2.5}, and PM_{1.0} were 0.9 ± 0.2 , 0.9 ± 0.4 , and 0.9 ± 0.3 , respectively. From the results, the PIXE method is a good alternative to measure chemical species of Al, Si, S, K, Ca, Ti, Cr, and Pb for size-resolved aerosols in this study, but we should be cautious in recommendation for the PIXE method for Fe and Sr detection from a wide range of particle size.

The elements can be classified into anthropogenic-related, soil-related, and marine-related sources. Atmospheric sulfur dioxide, which is oxidized from sulfur, is formed as a by-product of the combustion of fossil fuel from power generation and industrial activities. Sulfur dioxide acts as an anthropogenic air pollutant and is converted to sulfates in the atmosphere [12]. One of major sulfate salts is ammonium sulfate. In this study, ammonium sulfate (AS) was reconstructed from S by PIXE or ICP-OES and SO_4^{2-} by IC, as summarized in Table 3 [13]. The other sources were attributed to natural emissions. The trace elements of Al, Si, Ca, Ti, and Fe are mainly associated with atmospheric mineral dust, which comes from soil

erosion [14]. The mass concentration of mineral dust aerosol (MD) was calculated from them. Sea salt aerosols are dominated by evaporation of sea spray droplets and are identified using associated reference elements (Na, Cl) or ions (Na^+ , Cl^-) [15,16]. The sea salt aerosol (SS) was reconstructed from Cl by PIXE, Na by ICP-OES, and Cl by IC in this study.

The average mass concentrations of AS, MD, and SS of size-resolved aerosols during the intensive monitoring period are summarized in Table 4. The mass concentration of MD was largest in the PM₁₀ regime and AS was most abundant in the PM_{2.5} and PM_{1.0} regime. The average mass concentrations of MD for PM₁₀, PM_{2.5}, and PM_{1.0} were determined to be 26.1 ± 13.4 , 7.7 ± 5.1 , and $0.9 \pm 0.7 \mu\text{g m}^{-3}$ by PIXE and 25.9 ± 11.7 , 8.2 ± 4.8 , and $1.0 \pm 0.7 \mu\text{g m}^{-3}$ by ICP-OES, respectively. Relative errors ($(M_{i,j} - M_{i,PIXE})/M_{i,j}$) of *i* (AS, MD, and SS) components for *j* (ICP-OES and IC) methods were calculated. The average relative error of MD was the lowest value of 0.8% in the PM₁₀ regime and the highest value of 10.0% in the PM_{1.0} regime. The average relative errors of MD for 2-hour and 14-hour interval collections ranged from 1.2 to 11.1% and from 1.0 to 8.7%, respectively. The average mass concentrations of MD determined by PIXE were similar to the values determined by ICP-OES

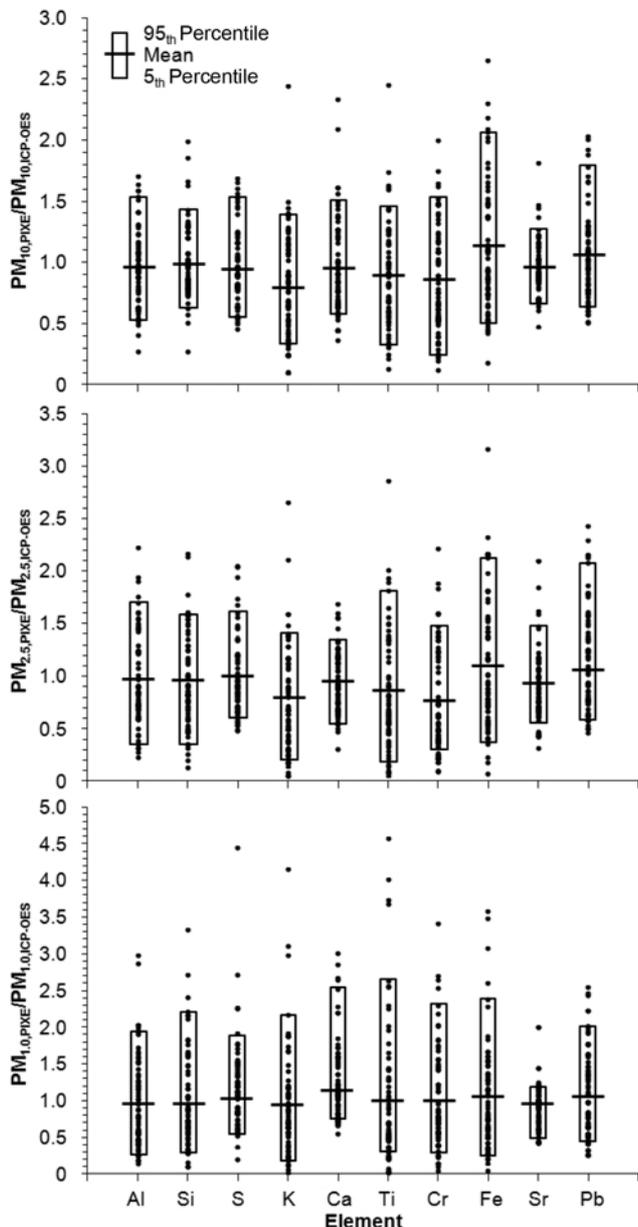


Fig. 3. Mass ratios ($PM_{i,PIXE}/PM_{i,ICP-OES}$) of chemical elements for size-resolved aerosols, i (PM_{10} , $PM_{2.5}$, and $PM_{1.0}$) using the PIXE and the ICP-OES methods.

even though the correlation coefficient of Fe between the both analyses was not good. The average relative errors of AS for PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ determined by PIXE, ICP-OES, and IC showed relatively lower values of 0.8-5.7%, 1.7-5.9%, and 3.3-8.3%, respec-

tively, as summarized in Table 4. The mass concentrations of AS determined by PIXE tended to be almost the same as those determined by ICP-OES and IC. On the other hand, the relative errors of SS among PIXE, ICP-OES, and IC showed relatively higher than the other aerosol components. They were within the range of 3.4-46.6%. The average mass concentrations of SS for PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were determined to be 4.4-5.1, 2.1-2.4 $\mu\text{g m}^{-3}$, and 149-268 ng m^{-3} , respectively. In particular, the relative errors were higher values of 35.0-46.6% in the $PM_{1.0}$ regime, as summarized in Table 4. The lower SS values from PIXE were estimated to be sensitive to surface homogeneity of the submicron aerosols. However, the relative errors of SS in the PM_{10} and $PM_{2.5}$ regime were lower within the range of 3.4-29.5%. The average relative errors of SS for PM_{10} and $PM_{2.5}$ were 5.8 and 12.7%, respectively. The average mass concentrations of AS, MD, and SS of size-resolved aerosols except submicron SS determined by PIXE were similar to those determined by ICP-OES and IC. On the basis of these results, AS accounted for 14.1-15.0% of PM_{10} , 20.7-22.1% of $PM_{2.5}$, and 18.1-20.4% of $PM_{1.0}$ during the intensive monitoring period at the national park area of Gyeongju. And contributions of MD to PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were 35.0-35.3%, 23.1-24.6%, and 4.1-4.5%, respectively. SS accounted for 6.0-7.4% of PM_{10} , 2.8-3.2% of $PM_{2.5}$, and 0.7-1.2% of $PM_{1.0}$.

CONCLUSION

Chemical and physical characteristics of elements and ions for size-resolved aerosols of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were determined by using the PIXE, ICP-OES, and IC methods in this study. Both analytic methods of PIXE and ICP-OES made elemental masses of Al, Si, S, K, Ca, Ti, Cr, Fe, Sr, and Pb. The anthropogenic-related element of S and the crustal elements of Si, Ca, and Ti obtained by PIXE provided better agreement with those of ICP-OES than other elements. And the relative ratios for Al, Si, S, and Ca were relatively lower. The PIXE data showed appropriate measures for chemical species of Al, Si, S, K, Ca, Ti, Cr, and Pb for size-resolved aerosols except Fe and Sr due to poor correlation between PIXE and ICP-OES in this study. In addition, there was no obvious difference in the relative errors for the analytic data between 2 hour and 14 hour interval aerosol samplings. These chemical species were reconstructed into ammonium sulfates (AS), mineral dust (MD), and sea salt (SS) aerosols with the known equations. The average contributions of ammonium sulfate aerosols to PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ were approximately 15, 21, and 19%, respectively. The average mass concentrations of AS, MD, and SS of PM_{10} , $PM_{2.5}$, and $PM_{1.0}$ except submicron SS determined by PIXE were comparable to those determined by ICP-OES and IC within the acceptable relative errors.

Table 3. Reconstruction equations for aerosol components of ammonium sulfates (AS) and mineral dust (MD), and sea salt (SS) by the PIXE, ICP-OES, and IC methods. A bracket means mass concentration

| Component | Specification | Reconstruction equation | | |
|-----------|------------------------------|---|---------------------------|-----------------------------------|
| | | PIXE | ICP-OES | IC |
| AS | $(\text{NH}_4)_2\text{SO}_4$ | $4.125 \times [\text{S}]$ | $4.125 \times [\text{S}]$ | $1.375 \times [\text{SO}_4^{2-}]$ |
| MD | Mineral dust | $2.20 \times [\text{Al}] + 2.49 \times [\text{Si}] + 1.63 \times [\text{Ca}] + 2.42 \times [\text{Fe}] + 1.94 \times [\text{Ti}]$ | | |
| SS | Sea salt | $1.8 \times [\text{Cl}]$ | $2.5 \times [\text{Na}]$ | $1.8 \times [\text{Cl}]$ |

Table 4. Statistics of the reconstructed AS, MD, and SS aerosol components of size-resolved particles observed for 2 hour (2-hr) and 14 hour (14-hr) intervals using the PIXE, ICP-OES, and IC methods during the intensive monitoring period. Relative errors ($|M_{i,j} - M_{i,PIXE}|/M_{i,j}$) of i (AS, MD, and SS) components for j (ICP-OES and IC) methods are calculated

| Type | Particle size | Analytic method | Mass concentration | | | Relative error | | |
|-------|-------------------|-----------------|-----------------------|-----------|----------|----------------|------|------|
| | | | AS | MD | SS | AS | MD | SS |
| | | | (μg m ⁻³) | | | (%) | | |
| Total | PM ₁₀ | PIXE | 10.5±6.6 | 26.1±13.4 | 5.1±2.9 | | | |
| | | ICP-OES | 11.1±6.2 | 25.9±11.7 | 5.5±3.4 | 5.4 | 0.8 | 7.3 |
| | | IC | 10.4±6.8 | | 4.4±3.7 | 1.0 | | 15.9 |
| | PM _{2.5} | PIXE | 8.6±5.9 | 7.7±5.1 | 2.3±1.0 | | | |
| | | ICP-OES | 9.0±5.8 | 8.2±4.8 | 2.4±1.2 | 4.4 | 6.1 | 4.2 |
| | | IC | 8.4±5.9 | | 2.1±1.6 | 2.4 | | 9.5 |
| | PM _{1.0} | PIXE | 4.3±3.1 | 0.9±0.7 | 149±207* | | | |
| | | ICP-OES | 4.0±3.3 | 1.0±0.7 | 235±123* | 7.5 | 10.0 | 36.6 |
| | | IC | 4.4±3.2 | | 268±222* | 2.3 | | 44.4 |
| 2-hr | PM ₁₀ | PIXE | 9.9±6.5 | 25.6±13.9 | 5.0±3.0 | | | |
| | | ICP-OES | 10.5±5.8 | 25.3±11.7 | 5.5±3.6 | 5.7 | 1.2 | 9.1 |
| | | IC | 10.1±6.9 | | 4.4±3.9 | 2.0 | | 13.6 |
| | PM _{2.5} | PIXE | 8.0±5.7 | 7.6±5.1 | 2.3±1.0 | | | |
| | | ICP-OES | 8.5±5.2 | 8.0±4.6 | 2.5±1.2 | 5.9 | 5.0 | 8.0 |
| | | IC | 8.2±5.9 | | 2.1±1.7 | 2.4 | | 9.5 |
| | PM _{1.0} | PIXE | 3.9±2.8 | 0.8±0.6 | 136±203* | | | |
| | | ICP-OES | 3.5±2.2 | 0.9±0.6 | 231±120* | 11.4 | 11.1 | 41.1 |
| | | IC | 4.1±3.0 | | 243±230* | 4.9 | | 44.0 |
| 14-hr | PM ₁₀ | PIXE | 13.3±6.3 | 28.5±10.5 | 5.7±2.4 | | | |
| | | ICP-OES | 13.9±7.9 | 28.8±12.2 | 5.9±2.4 | 4.3 | 1.0 | 3.4 |
| | | IC | 11.9±6.4 | | 4.4±2.2 | 11.8 | | 29.5 |
| | PM _{2.5} | PIXE | 11.6±6.2 | 8.4±5.2 | 2.5±0.9 | | | |
| | | ICP-OES | 11.8±8.1 | 9.2±5.9 | 2.3±1.0 | 1.7 | 8.7 | 8.7 |
| | | IC | 10.1±5.9 | | 2.2±1.2 | 14.9 | | 13.6 |
| | PM _{1.0} | PIXE | 6.3±3.9 | 1.6±0.7 | 165±221* | | | |
| | | ICP-OES | 6.8±6.1 | 1.7±0.8 | 254±140* | 7.4 | 5.9 | 35.0 |
| | | IC | 6.0±4.0 | | 309±170* | 5.0 | | 46.6 |

* Unit is ng m⁻³

These results showed the differences of aerosol chemistry from proper data comparison in chemical analysis. Further inter-comparison study will assist in data interpretation and provide a better understanding of the analytic data among the PIXE, ICP-OES, and IC methods.

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