CHARACTERIZATION OF ASIAN DUST AEROSOL WITH SINGLE PARTICLE ANALYSIS METHOD

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Asian dusts have been increasingly recognized as important regional phenomena in recent years. Single particle analysis method such as EPMA is unique in providing rich and detailed information on particle size and chemical composition and has been used in Asian Dust studies. In this study the reproducibility of the method and the feasibility of differentiating aerosol samples of different Asian dusts events were evaluated. Acidic constituents of sulfur-containing compounds were also investigated due to its potential health effect.

Aerosol samples used in the study were collected on Nuclepore filters in Beijing during two Asian Dust event, on April 25, 2000 and March 20, 2002 and during a 11-day sampling campaign in March-April, 2002 in Changdao, an island in coastal area in Eastern China. The Superprobe 733 of JEOL of University Antwerp, UIA, was used for automated single particle analysis. The high voltage was 20 KV and the beam current 1 nA. The minimum diameter was set to 0.25 μm for particles analyzed. Elements with atomic number not less than sodium could be detected by the conventional X-ray Energy dispersive detector. Duplicate experiments 425d, 425e, and 425f were carried out for sample of April 25, 2000. And also experiments 320a and 320b for sample of March 20, 2002. For each experiment different part of the filter was analyzed and the number of particles analyzed varied from 350 to 1500. For Changdao aerosol samples 500 particles each were analyzed.

Cluster analysis was performed to classify particles into different particle groups according to the particle chemical composition. Eight major groups were found and the particle number abundance percentage was listed in the Table 1. Aluminosilicate particles (first four rows in Table 1), with a percentage greater than 80%, always dominate. However, one can see that duplicate experiments presented consistent results, while two Asian Dust events appeared different in some way. The aluminosilicates in first row were considerably higher in 425 experiments that that in 320 ones. Silicate in the fourth raw was high in 320 experiments, while absent in 425 ones. Ca-rich particles were found in all experiments, but higher in 320s than 425s. When cluster analysis was applied to the data in Table 1, it indicated that 425s and 320s fall into different groups, respectively. The similarity within group (same sample) is much stronger than that between groups (different samples).

***Table 1.** Particle number abundance percentage of sample 425 and sample 320*

Particle class	425d	425e	425f	320a	320b
Si, Al-K, Mg, Ca, Fe^+	75.8	75.2	73.7	51.2	47.2
Si	13.7	13.3	14.2	18.6	20.2
Si, Al-K, Fe, Sb	1.7	0.7	1.5	3.6	4.6
Si-Fe, K, Ca				9.4	9.2
Ca-rich	5.2	7.3	5.9	10	12.2
Fe-rich	2.0	1.9	1.7	2.8	2.4
Ti-rich	0.6	0.8	1.0	1.8	2
Others	0.9	0.6	1.9	2.6	2.2

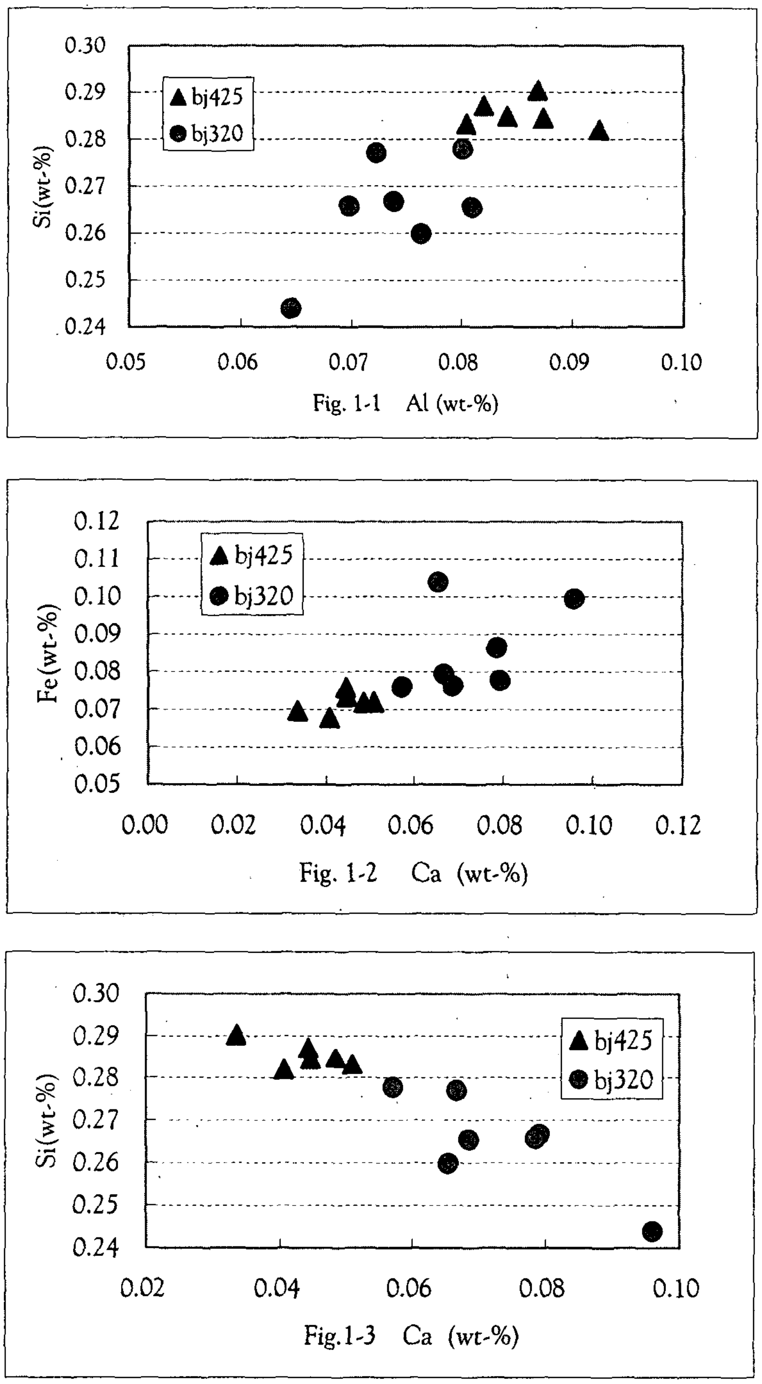

Figure 1. *Average weight fraction of selected elements for Asian Dust aerosol samples on April 25, 2000 and March 20, 2002*

The average weight fractions of Al, Si, Fe and Ca were calculated for those two aerosol samples. As shown in Figure 1, each data points were obtained based on several hundreds single particle analyses with EPMA. And a variation exits for repeated measurements on the same sample. The difference in chemical composition turned out obvious, as separated data groups in Figure 1. For example, weight fraction of Si is 0.2652 ± 0.0114 in bj320 and 0.2854 ± 0.0030 in bj425; and Ca is 0.0731 ± 0.0127 in bj320 and 0.0437 ± 0.0061 in bj425, respectively.

Our results indicate that single particle analysis with EPMA generates reproducible data for Asian Dust samples. Both similarity and difference can be observed between two events on April 25, 2000 and March 20, 2002.

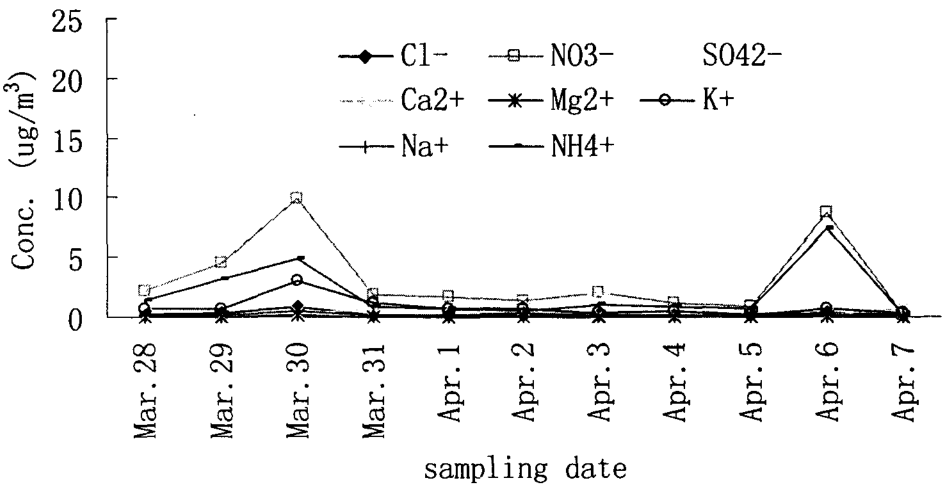

Figure 2. *Temporal variation of ionic species for fine aerosol samples in Changdao, in spring 2002*

During a 11-day sampling campaign in March-April, 2002 in Changdao, an island in coastal area in Eastern China, an Asian Dust event occurred from April 6 to April 8 as shown in Figure 2. There are substantial variations and the highest and lowest sulfate value was found on the first and second day of Asian Dust event, respectively. Ammonium and nitrate data went along with sulfate. Figure 2 presents the fine aerosol data, however, the coarse aerosol data told the same story. It seems that Asian dust aerosols arrived in extremely high concentrations being so efficient in scavenging acidic pollutants and nothing left for the very next day.

As shown in Figure 3, when calculating the ratio between the total sulfur measured with ICP-AES and water-soluble sulfates measured with IC, it is interesting to note that sulfates on April 6 were more water-soluble than April 7, and other ordinary days as well. Usually the ratio varied in the range of 0.6 to 0.8, while on April 6 it reached 1.0, indicating that sulfates were completely soluble.

EPMA single particle analysis method is able to gain additional information. Since particle classes were identified, the major elements detected provide information on possible elemental associations. From Figure 4 one can see in fine aerosol samples S-containing particles were mainly K-S, Ca\K-S, and S-rich. K-S particles were frequently detected in fine aerosol samples, but absent in Asian Dust samples. S-rich particles accounted for 50% fine particles on April 6, but very low next day. As traditional EPMA is able to detect only elements from sodium upwards, S-rich particles are most likely the ammonium sulfate.

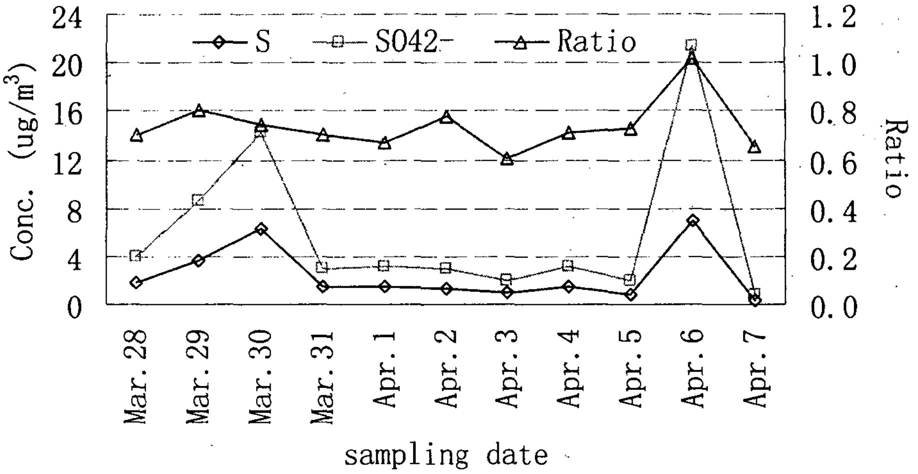

Figure 3. Concentration variation of water soluble sulfates and total sulfur in fine aerosol samples in Changdao, in spring 2002

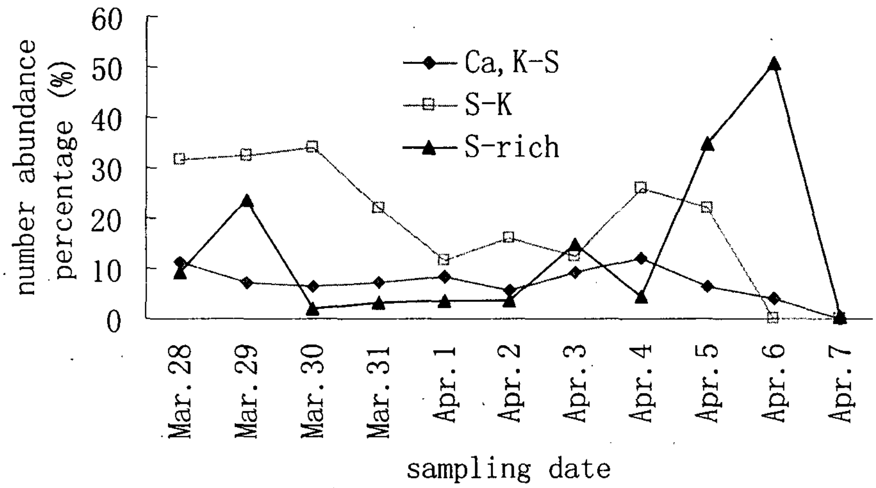

Figure 4. Number abundance percentage (%) of S-containing particles in fine aerosol samples in Changdao in spring 2002

In Table 2 Ion Chromatography data were listed for Asian Dust samples. The anion/cation ratio was usually good for ordinary days, ranging from 0.8 to 1.2, but poor for Asian Dust samples. The value of 1.3 for fine aerosol on April 6 indicates a deficiency of cation, probably the hydrogen ion. It implied a high acidity. For other three samples the ratio deviated to the opposite direction, indicating a deficiency of anion, most likely the bicaronate. Since ammonium concentration was one order of magnitude higher than the sum of other cations measured for fine aerosol on April 6, one can say that both sulfate and nitrate existed as ammonium salts on that day. When compared with its coarse counterpart, one can see the sulfate and nitrate concentration were reduced by about 50% and there were two major cations, calcium and ammonium, a situation no longer possible to make a simple and straightforward conclusion about chemical speciation. On April 7, the second day of the Asian Dust event, the ionic concentration dropped sharply. The relative importance of

Table 2. Data of ionic species for Asian Dust aerosol samples

	Start Date	Equivalent Concentration (neq/m^3)										Ratio (Anion/ Cation)
		Anion			Sum	Cation					Sum	
		Cl^-	NO_3	SO_4^{2-}		Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+		
Fine	Apr.6	11.2	139.5	443.3	594.0	10.3	4.5	16.1	9.3	409.9	450.1	1.3
	Apr.7	5.6	3.3	16.6	25.5	32.0	6.1	7.2	6.1	10.8	62.2	0.4
Coarse	Apr.6	35.2	80.3	212.1	327.5	201.7	31.9	34.3	44.4	130.0	442.3	0.7
	Apr.7	83.7	27.9	88.1	199.7	26.7	45.1	42.4	77.2	64.1	255.4	0.8

ions also changed. Calcium and sodium ions became the highest cations in fine and coarse fractions, respectively.

It seems that Asian Dust event evolutes in composition on its way moving ahead. The front was enriched in sulfur by taking up pollutants in coastal provinces of China where pollution emissions are high. Asian Dust aerosol is dominated by coarse particles and there is mass transfer between fine and coarse fractions. It was observed that in the course of transport ammonium sulfate may converts into other sulfates such as calcium sulfate. Based on single particle analysis data, fine sulfate particles are mainly secondary aerosol, while sulfate in coarse fraction may exist as surface coating due to bigger particle sizes.

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