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Size fractionated speciation of sulfate and nitrate in airborne particulates in Beijing, China

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Abstract

We report on the speciation of sulfate, nitrate with special attention to their ammonium salts during 1999–2000 in Beijing. Higher concentrations in fine particles were observed for ammonium sulfate and other sulfates during winter. Ammonium sulfate concentration ranged from 2.78 to 23.7 $\mu\text{g m}^{-3}$ in fine particles, and ranged from 0.15 to 1.39 $\mu\text{g m}^{-3}$ in coarse particles. Other sulfate concentrations ranged from 1.51 to 11.9 $\mu\text{g m}^{-3}$ in fine particles, and ranged from 0.10 to 1.00 $\mu\text{g m}^{-3}$ in coarse particles. Ammonium nitrate was mainly in fine particles with the highest concentration in December (11.9 $\mu\text{g m}^{-3}$). Other nitrates were mainly distributed in the particles of 2.1–4.7 μm with concentrations ranged between 0.36 and 2.54 $\mu\text{g m}^{-3}$, and the highest concentration of other nitrates was observed in fine particles in January (9.32 $\mu\text{g m}^{-3}$). XRD analysis showed that ammonium sulfates existed in different forms in atmospheric aerosols. The results suggested the importance of heterogeneous formations of sulfate and nitrate in Beijing especially in winter.

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Keywords: Airborne particulates; Speciation; Sulfate; Nitrate

1. Introduction

China is thought to be the largest source of SO_2 emissions in the world (Kato, 1996), and the NO_x emission also increases rapidly due to the rapid growth of vehicular population in recent decades (Galloway, 1989; Akimoto and Narita, 1994; Zhang and Iwasaka, 1999). Part of the emitted SO_2 and NO_x , through heterogeneous and homogeneous reactions, are oxidized to sulfate and nitrate aerosols (Seinfeld, 1986). These acidic aerosols have been recognized as one of the most important pollutants with harmful impact on human health, natural environment and ecological system (Vincent, 1989). Sulfate, nitrate and ammonium are the dominant inorganic aerosol species in $\text{PM}_{2.5}$ (particulate matter with aerodynamic diameter

<2.5 μm) (Zhuang et al., 1999; He et al., 2001; Yao et al., 2002), which more readily penetrate into the lungs and are therefore more toxic to humans than the larger particulate species (PM_{10}) (Lippmann, 1998). Of the species present in atmospheric aerosol, sulfate is considered to be the largest contributor to direct anthropogenic radiative forcing (Charlson and Schwartz, 1992; Adams et al., 2001). Acidic aerosols can react with gaseous ammonia (NH_3) to form completely or partially neutralized ammonium salts such as: ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) (Robarge et al., 2002). The presence of these ammonium salts, especially volatile compounds (NH_4NO_3 and NH_4Cl) in the troposphere has a significant influence upon the atmospheric concentrations of their acid constituents which can be regenerated during transport (Harrison et al., 1990). These acid compounds may cause an intense acid

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deposition on areas far from anthropogenic activities because of the high deposition velocities of HNO_3 and HCl (Beilke, 1985).

Many studies about the sulfate and nitrate in atmospheric aerosols have been carried out in China (Zhang and Iwasaka, 1999; He et al., 2001; Yao et al., 2002; Wang et al., 2002). These studies mainly focus on aerosol size distributions, concentrations, and influences on the environment and source identifications. SO_4^{2-} , NO_3^- and NH_4^+ were observed to be the dominant ionic species in these studies. However, up to now there is little data about the speciation of ammonium sulfate and ammonium nitrate as function of particle size and season. This paper presents the results obtained from the size-fractionated speciation of sulfate and nitrate in airborne particulates, and from the X-ray diffraction analysis. Accordingly, the particulates collected from different sources (such as soils, soot, walkway dusts, etc.) were also analyzed to correlate with the presence of sulfate and nitrate in atmospheric aerosols. Taking advantage of the equilibrium displacement of NH_4NO_3 and NH_4Cl to the gas phase, the annular denuder and thermal desorption system to separate NH_4NO_3 and NH_4Cl from sulfate particles in atmospheric samples were used. This operation circumvented artifacts encountered in aerosol sampling by filter: (1) adsorption of gaseous compounds such as NH_3 , SO_2 and HNO_3 onto aerosols already collected on the filters (Ferm and Sjodin, 1985) and (2) dissociation of ammonium-containing aerosols such as NH_4NO_3 and NH_4Cl within the sampler itself (Forrest et al., 1980; McMurray, 2000).

2. Experimental

Aerosol samplings were performed from March 1999 to January 2000 in Beijing, China. The sampling site was on the roof (15 m above ground level) of the Research Center for Eco-Environmental Science, Chinese Academy of Science, about 150 m from a mail road. The meteorological conditions during sampling are presented in Table 1. The sampling system consisted of four annular denuders and a cascade impactor as shown in Fig. 1. Each denuder consisted of two concentric glass tubes of which the outer tube was 32 cm long and the inner tube was 20 cm in length. The inner diameter of the outer tube was 35 mm and the outer diameter of the inner tube was 33 mm. The air gap between the tubes was 1 mm. Both inner walls of the air gap were coated with gas collection media. The collection solutions for the denuders were as follows: 5% Na_2CO_3 –1% glycerin in 1:1 methanol/water to remove gaseous acids such as SO_2 , HNO_3 , and 10% citric acid in methanol to remove ammonia. Ten milliliter of the solution were put into a denuder tube to coat the inner wall uniformly, and the

Table 1
Summary of weather conditions

Sample	Temp. range (°C)	Temp. average (°C)	RH range (%)	RH average (%)	Wind average (m s^{-1})
15 March	0–6	3	50–84	61	2.5
21 April	4–10	7	40–72	52	2.9
9 July	26–35	30	30–86	47	1.9
26 July	25–40	32	34–85	50	2.3
19 August	25–32	32	40–75	49	4.2
11 September	22–30	26	40–80	52	1.8
18 October	15–27	20	42–75	54	2.7
25 December	–3–4	0	50–90	68	2.1
18 January	–11–1	–6	42–76	55	3.0

excess solution was removed. Then, the wall of the denuder was dried with N_2 gas. Both ends of the tube were capped before using. Predicted annular denuder collection efficiencies were calculated by Possanzini et al. (1983). In this experiment, collection efficiencies were greater than 99.2% for an annular denuder with the dimensions adopted here at an air flow rate of 28.31 min^{-1} for 12 h (Lun et al., 2003).

A cascade impactor (Anderson 200), with a cut size of $11 \mu\text{m}$ at 28.31 min^{-1} and nine-stage filters, were placed downstream of the denuders. Aerosol particles were collected on an 80 mm diameter Teflon membrane (0.5 μm pore size). Under the last stage Teflon membrane, there were two 80 mm Whatman 41 filters impregnated with gas collection media to collect, respectively, HCl , HNO_3 and NH_3 gases evaporated from the Teflon filters. The impregnated filter was prepared by immersing a 80 mm diameter Whatman 41 filter into the collection solution. The solution was 2% Na_2CO_3 –2% glycerin in water for HNO_3 and HCl and 5% phosphoric acid for NH_3 . A Teflon membrane was put between the two impregnated filters in order to avoid the reaction between them. During the process, Whatman 41 filters required careful prewashing to reduce experimental blank levels of Cl^- , NO_3^- , and NH_4^+ . This was accomplished by washing it in an ultrasonic bath with distilled deionized water. After repeated washing, the filters were dried in a vacuum desiccator and then coated with the collection solutions and finally were dried again on last time.

After collection, the samples were separated into three parts. Particles on the first three stages were coarse particles ($11 \mu\text{m} < D_p < 4.7 \mu\text{m}$), those on the next two stages were middle particles ($4.7 \mu\text{m} < D_p < 2.1 \mu\text{m}$), and those on the last four stages were fine particles ($D_p < 2.1 \mu\text{m}$). Each filter was transferred to a stainless steel filter holder together with a Na_2CO_3 -coated paper filter and a phosphoric-coated paper filter. The filter holder was put into a GC oven (70°C), and connected to

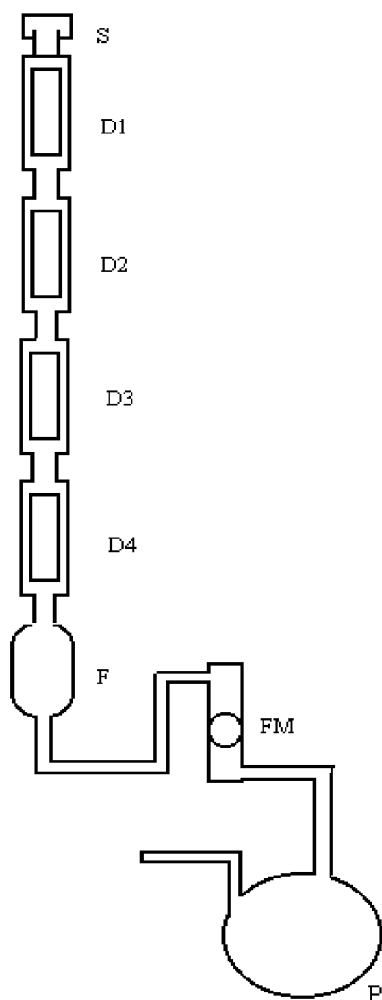


Fig. 1. Sampling assembler. S designated a rain shelter, which had a diameter of 12 cm and was 15 cm long. The inlet of the denuder was 5 cm inside the shelter. D1–D4: glass annular denuders. D1, D2: HNO_3 and SO_2 collection tube coated with K_2CO_3 and glycerin. D3, D4: NH_3 collection tube coated with citric acid. F: cascade impactor. FM: flow meter, P: pump.

the carrier gas entrance. The deposited NH_4Cl and NH_4NO_3 particles were volatilized entirely from the Teflon membrane by passing pure dry nitrogen at 21min^{-1} for 3 h. The released HCl , HNO_3 and NH_3 were collected on the back-up filters. Extraction of filters was ultrasonically carried out for 45 min using 7 ml isopropanol plus 43 ml deionized water for Teflon membranes and 25 ml distilled deionized water for impregnated paper filters. The anions Cl^- , NO_3^- and SO_4^{2-} were analyzed by ion chromatography (DX-120, AS14, 25- μl loop). Ammonium ions were analyzed by the hypochlorite method (Weatherburn, 1967).

Aerosol samples for the XRD analysis was collected separately for 60 days at sampling site when meteor-

ological conditions were relatively constant over a long period of time in order to obtained heavier loads to meet the requirement of XRD analysis. After sampling, the particles were also separated into three parts as described above. The XRD instrument used in the experiment was a SIEMEN D500 diffractometer with Fe K_α radiation at 40 kV, 25 mA.

Samples of street dusts, soils and fly ash were collected at several locations near the sampling site and subsequently suspended in a big chamber by N_2 flux. Detail operation was described elsewhere (Lun et al., 2003). A cascade impactor was connected with the entrance on the top of the chamber to collect samples. The same methodology as the particulate aerosols was used to determine the concentrations of ammonium sulfate, other sulfates, ammonium nitrate and other nitrate.

3. Results

The concentrations of ammonium sulfate and ammonium nitrate are shown in Table 2. The concentrations of other sulfates, nitrates and chlorides for each sampling period are shown in Table 3. The results of the XRD analysis are presented in Table 4.

3.1. Ammonium sulfate and other sulfates

The mean total sulfate concentration during all sampling periods was $1.45\ \mu\text{g m}^{-3}$ in coarse particles, $1.88\ \mu\text{g m}^{-3}$ in middle particles and $15.97\ \mu\text{g m}^{-3}$ in fine particles. The annual average other sulfate concentrations was $0.75\ \mu\text{g m}^{-3}$ in coarse particles, $1.05\ \mu\text{g m}^{-3}$ in middle particles and $6.22\ \mu\text{g m}^{-3}$ in fine particles. Other sulfate concentrations were high during winter (Fig. 3), although the larger conversion rates (2.32% in December and 11.38% in July) (Hu et al., 2002) may be operative during summer because of the higher concentrations of oxidizing species. This result was different from those in Mediterranean (Danalatos and Glavas, 1999; Mihalopoulos et al., 1997; Luria et al., 1996) where higher sulfate concentrations were observed in the summer. Sulfate was the main component of the particulate anions especially in fine particles in Beijing area, which was in agreement with other studies in this region (Wang et al., 1996; He et al., 2001).

Ammonium sulfate concentration ranged from 2.78 to $23.7\ \mu\text{g m}^{-3}$ in fine particles, and ranged from 0.15 to $1.39\ \mu\text{g m}^{-3}$ in coarse particles. Ammonium sulfate existed mainly in fine particles and its concentration was high in winter (Fig. 2).

The thermal-desorption analysis of the source samples showed ammonium salts were detected neither in the soil nor in the fly ash, whereas in the dusts from the street, a few ammonium particles existed, which probably came from the depositions of atmospheric aerosols (Fig. 3).

Table 2

Concentrations of ammonium sulfate, ammonium nitrate in atmospheric aerosols

$\mu\text{g m}^{-3}$	15th March	21st April	9th July	26th July	19th August	11th September	18th October	25th December	18th January	Average
NH_4NO_3	2.72	2.51	1.46	1.50	1.71	1.48	0.89	11.90	9.23	3.71
$(\text{NH}_4)_2\text{SO}_4$										
Coarse	1.39	1.05	0.35	0.30	0.15	0.32	0.26	1.09	1.35	0.70
Middle	1.28	1.32	0.30	0.29	0.26	0.34	0.34	1.43	1.63	0.83
Fine	8.67	15.7	3.27	4.36	5.43	2.78	2.96	20.9	23.7	9.75

Table 3

Concentrations of other sulfates (SO_4^{2-}) and nitrates (NO_3^-) in atmospheric aerosols

$\mu\text{g m}^{-3}$	15th March	21st April	9th July	26th July	19th August	11th September	18th October	25th December	18th January	Average
Coarse										
SO_4^{2-}	1.00	0.96	0.80	0.64	0.10	0.89	0.32	0.81	1.25	0.75
NO_3^-	0.43	0.31	0.86	0.72	0.69	0.36	0.16	0.69	0.79	0.56
Middle										
SO_4^{2-}	1.31	1.24	0.95	1.23	0.24	0.81	0.89	1.61	1.19	1.05
NO_3^-	0.78	0.82	2.54	2.13	0.93	0.97	0.36	0.92	1.21	1.18
Fine										
SO_4^{2-}	4.23	5.78	5.58	10.6	1.51	9.65	6.76	11.9	10.7	6.22
NO_3^-	1.56	0.47	1.02	0.88	0	0.27	0.26	7.61	9.32	2.38

Table 4

Major chemical phases/compounds size-fractionated particles and various sources

Components	Air samples	Soils	Fly ash	Dust on the street
SiO_2	+++	++++	++++**	++
CaCO_3	++	++	++	
FeCO_3	+		++*	
$\text{CaMg}(\text{CO}_3)_2$	+		++	
KCl	*		*	
NH_4Cl	*		**	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	+		++	
CaSO_4				
$\text{Fe}_2(\text{SO}_4)_3$	*		***	
$\text{K}_3\text{Fe}(\text{SO}_4)_2$	*		***	
$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	*			
$(\text{NH}_4)_2\text{SO}_4$	*			
$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$	*			
$(\text{NH}_4)_4(\text{NO}_3)\text{SO}_4$	+			

“*” is for fine particles, and “+” is for coarse particles. The more of these are the higher concentration of this component.

Results of X-ray diffraction analysis (XRD) in Table 4 showed sulfates in the atmospheric aerosols existed in several forms. In fine particles sulfates were mainly

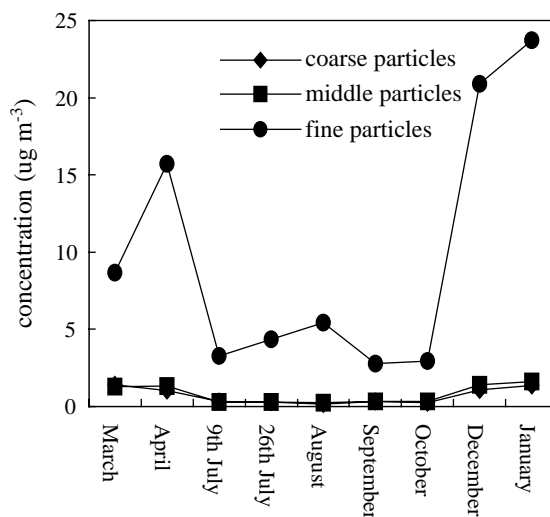


Fig. 2. Seasonal trends of concentrations of ammonium sulfate in atmospheric aerosols.

$\text{Fe}_2(\text{SO}_4)_3$, $\text{K}_3\text{Fe}(\text{SO}_4)_2$, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, of which $\text{Fe}_2(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_2$ came from the fly ash. In coarse particles, ammonium

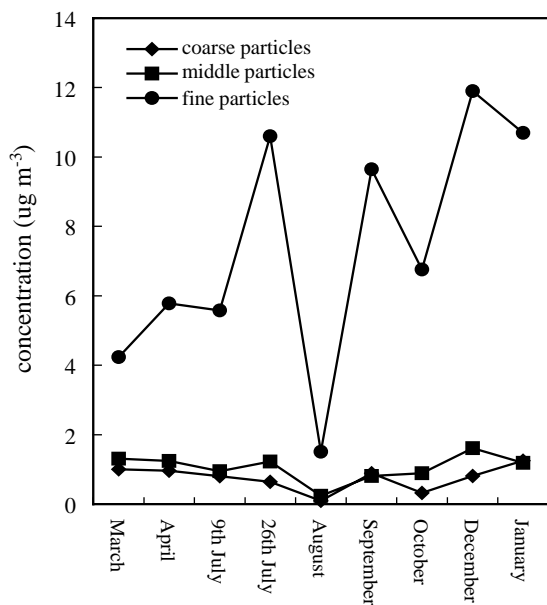


Fig. 3. Seasonal trends of the other sulfates (sulfates except ammonium sulfate) in atmospheric aerosols.

sulfate existed mainly in the form of $(\text{NH}_4)_4(\text{NO}_3)\text{SO}_4$ showing in coarse particles, some ammonium sulfate and ammonium nitrate were in an internal mixture form, as Zhang et al. (2000) pointed out.

3.2. Ammonium nitrate and other nitrates

Because there were some dissociations of ammonium nitrate during sampling, it was difficult to determine their concentrations in different sizes. Here we only obtained the total concentration of ammonium nitrate, which were the sum of the ammonium nitrate from the background filters during field sampling and back-up filters for the thermal desorption. The annual average ammonium nitrate concentration was $3.71 \mu\text{g m}^{-3}$. Ammonium nitrate concentrations, higher in the winter (Fig. 4), were 3–6 times lower than ammonium sulfate concentrations. After complete evaporation of NH_4Cl and NH_4NO_3 from Teflon filters, NO_3^- could be detected on the back-up filters for fine particles, but not on the back-up filters for coarse particles. This result may suggest that ammonium nitrate existed mainly in fine particles. Other nitrates were mainly distributed in the particles of 2.1–4.7 μm . Other nitrate concentrations ranged from 0.16 to 0.79 $\mu\text{g m}^{-3}$ in coarse particles, from 0.36 to 2.54 $\mu\text{g m}^{-3}$ in middle particles, and from 0.24 to 9.32 $\mu\text{g m}^{-3}$ in fine particles. There was an increase in other nitrate concentrations in fine particles in winter (Fig. 4). The annual average percentage of ammonium nitrate in total particulate nitrate was about 41.1% (Table 5).

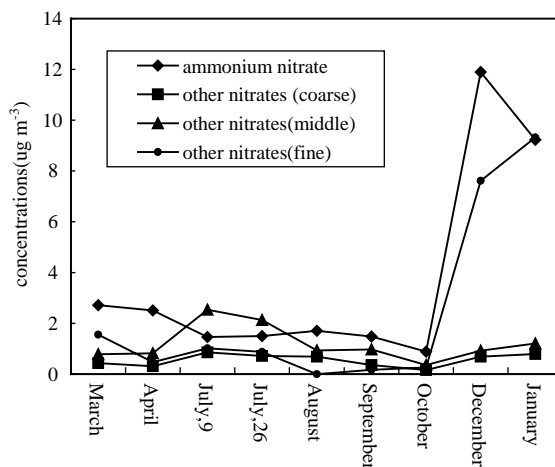


Fig. 4. Seasonal trends of ammonium nitrate and other nitrates in atmospheric aerosols.

Table 5

Percentages of ammonium sulfate (ammonium sulfate/total sulfate) and ammonium nitrate (ammonium nitrate/total nitrate)

Experiments	Ammonium sulfate			Ammonium nitrate
	Coarse	Middle	Fine	
15 March	50.2	41.5	59.9	43.2
21 April	44.2	43.6	66.4	54.9
9 July	23.8	18.8	29.9	20.4
26 July	25.6	14.6	23.0	23.8
19 August	54.5	44.2	72.3	45.0
11 September	20.5	23.6	17.3	41.8
18 October	37.3	21.9	24.1	46.9
25 December	49.4	39.2	56.1	50.0
18 January	43.9	50.0	61.6	38.7
Average	40.5	36.4	53.3	41.1

4. Discussion

As shown in Table 5, ammonium sulfate contributed 40.5% of the total coarse mode sulfate, 36.4% of the middle aerosol sulfate and 53.3% of the fine aerosol sulfate. Since there were no known major emission sources for coarse mode ammonium sulfate, it was thus assumed to come from the reaction of H_2SO_4 and SO_2 with coarse particles or from the accumulation of little ammonium sulfate to the coarse particles. During the heating time, the concentration of ammonium sulfate was higher than that at the other time especially in fine particles (Fig. 2). This result may suggest there were more ammonium sulfate formations in fine airborne particulates, since there were no major differences between the sources in the heating time and the other

time for ammonium sulfate (Yang, 2002). Because of the much higher concentrations of SO₂ and PM_{2.5} in winter (SO₂: about 5–10 times of that in summer; PM_{2.5}: about 2 times of that in summer) (Yang, 2002), there might be more sulphuric acid formed in winter than in summer. Since the concentrations of oxidizing species were relatively lower in winter than in summer, the heterogeneous reactions probably catalyzed by Fe (III), etc. may have great importance. Zhang and Iwasaka (1999) also suggested that the heterogeneous formation of sulfate and nitrate on the surface of aerosols in Beijing.

Studies of the formation of coarse particle nitrate and sulfate aerosol have been done since the 1980s. Gottlieb and Mamane (1989, 1992) investigated the individual sea-salt and mineral particles before and after their exposure to sulfur and nitrogen oxides in a laboratory simulation experiments by using electron microscopic techniques. Their results indicated that sea-salt and minerals reacted with sulfur and nitrogen oxides to form sulfate and nitrate, respectively. Sievering et al. (1995) found that the heterogeneous oxidation of SO₂ by O₃ proceeds rapidly in freshly formed coarse sea-salt aerosol when it contains water due to the initial alkaline nature of the particles. The formation of non-sea-salt sulfate by droplet-phase oxidation of SO₂ in clouds was also suggested to be a major mechanism of coarse mode non-sea-salt sulfate (Kerminen and Wexler, 1995). SO₂ or H₂SO₄ can also react with aqueous carbonates such as dissolved CaCO₃ and MgCO₃ on soil particles to form coarse mode sulfate (Wu and Okada, 1994; De Bock et al., 1994). Using single particle analysis by X-ray spectrometry, Wu and Okada (1994) found that sulfate and nitrate existed on soil particles as a surface layer, suggesting that surface reaction mechanism of these acidic species with soil particles existed. The behavior of nitrate and sulfate in ambient aerosols depends not only on the concentrations of acidic gases and ammonia, but also heavily on the chemical composition of particles and atmospheric conditions (Tang, 1980; Bassett and Seinfeld, 1983). In Beijing, a large emitter of sulfur compounds where dust concentration was very high, heterogeneous reactions were likely to contribute to the coarse mode sulfate considering the initial alkaline nature of the particles. But how these reactions took place and how much they contributed to the whole coarse sulfate were still unknown.

As listed in Table 3, other nitrates existed mainly in the middle particles (2.1–4.7 μm) except in winter. There was an increase in the concentrations of other nitrates in fine particles in winter. The highest concentration of other nitrates in fine particles was 9.32 μg m⁻³ in January, probably due to the low temperatures. The concentration of ammonium nitrate was also high during winter. Because the sources of ammonium nitrate were almost at the same level both in winter and summer (Yang, 2002), the high concentration of ammonium

nitrate in winter may indicate that they were preferably formed during winter. Some researches have shown that ammonium nitrate were likely to form in March (Danalatos and Glavas, 1999), while other studies indicated ammonium nitrates would be formed during winter near Rome (Possanzini et al., 1992; Allegrini et al., 1992). The atmospheric formation of ammonium nitrate also depended on the concentrations of HNO₃ and NH₃, as well as on the chemical composition of particles and atmospheric conditions. The results of XRD analysis suggest that (NH₄)₄(NO₃)SO₄ was the predominant species of coarse ammonium aerosols. This phenomenon was possibly due to the heterogeneous formation of sulfate and nitrate on the surface of soil particles (Seinfeld and Pandis, 1998). The presence of these volatile salts in the troposphere has a significant influence upon the atmospheric concentrations of their acid constituents that can be regenerated during transport and cause acid deposition on areas far from anthropogenic activities.

5. Conclusion

Separate determinations of ammonium sulfate, other sulfates, ammonium nitrate and other nitrates in size-fractionated atmospheric aerosols were conducted in Beijing. Ammonium sulfate was found mainly in fine particles. Its concentrations, which were high in winter, ranged from 2.78 to 23.7 μg m⁻³ in fine particles and ranged from 0.15 to 1.39 μg m⁻³ in coarse particles. The mean percentage of coarse ammonium sulfate in coarse particulate sulfate was about 40.5%, a little lower than that of the fine ammonium sulfate (53.3%). Ammonium sulfate existed in different forms in atmospheric aerosols, for example NH₄Fe(SO₄)₂, (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂ in fine particles, and (NH₄)₄(NO₃)SO₄ in coarse particles. Results suggested that there were heterogeneous formations of sulfate in Beijing especially in winter. Ammonium nitrate was mainly in fine particles with the highest concentration in December (11.9 μg m⁻³). Other nitrates were mainly distributed in the particles of 2.1–4.7 μm with concentrations ranged from 0.36 and 2.54 μg m⁻³. But the highest concentration of other nitrates was observed in fine particles in January (9.32 μg m⁻³). The results suggested the importance of heterogeneous formations of sulfate and nitrate in Beijing especially in winter.

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