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# ATMOSPHERIC AEROSOL SAMPLING BY AN ANNULAR DENUDER SYSTEM AND A HIGH-VOLUME PM<sub>10</sub> SAMPLER

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An Annular Denuder System (ADS) was used to study sampling errors of total PM<sub>10</sub> and soluble ionic species concentrations determined by the high volume PM<sub>10</sub> (HVPM<sub>10</sub>) sampler. Experimental results show that in the HVPM<sub>10</sub> sampler, more alkaline glass fiber filters collect more sulfate and nitrate but less ammonium ion than quartz filters. However, total PM<sub>10</sub> concentrations do not seem to depend on the types of filters. Artifact sulfate concentrations in glass fiber filters of the HVPM<sub>10</sub> sampler are found to exceed those predicted by the Coutant's model. It is suggested that artifact sulfate and nitrate not only occur within filters but also in particle deposits. Chloride ion concentrations in the filters of the HVPM<sub>10</sub> sampler are underestimated significantly due to evaporative loss of ammonium chloride.

## INTRODUCTION

Air pollution caused by suspended particles has been a major concern in Taiwan. Atmospheric sulfate and nitrate species usually constitute a major fraction of particles and are of great interest to researchers because of their potential roles in acid rain, visibility and adverse human health effects. Currently, daily average PM<sub>10</sub> (particulate matter less than 10 μm in aerodynamic diameter) concentrations are regulated by the Taiwan Environmental Protection Agency to be less than 125 μg/m<sup>3</sup>. Normally, glass fiber filters are used in HVPM<sub>10</sub> (high volume PM<sub>10</sub>) samplers to collect atmospheric particles less than 10 μm in aerodynamic diameter. PM<sub>10</sub> concentrations are then determined by weighing before and after 24-h sampling. Before weighing, filters are conditioned according to the standard method in which filters are kept for 24 h in a chamber maintained at 40 ± 5% relative humidity and 20 ± 3° C temperature. The sulfate, nitrate and other species are analyzed afterwards if necessary.

Because of their high alkalinities and pHs, glass fiber filters often absorb SO<sub>2</sub> and HNO<sub>3</sub> gases to form extraneous sulfate and nitrate in collected particle samples (Coutant 1977; Witz and Macphee 1977; Witz and Wendt 1981; Witz et al. 1983; Spicer and Schumacher 1977 1979; Appel et al. 1984). These additional sulfate and nitrate are called positive artifacts, which cause an overestimation of sulfate, nitrate, and possibly PM<sub>10</sub> concentrations.

Negative artifacts can also occur due to evaporative loss and/or chemical reaction during sampling (Klockow et al. 1979; Appel and Tokiwa 1981; Dunwoody 1986; Wang and John 1988; Zhang and McMurry 1992; Koutrakis et al. 1992; Kitto and Harrison 1992). An example of nitrate loss is one due to the reactions of acidic aerosol such as particulate H<sub>2</sub>SO<sub>4</sub> with collected ammonium nitrate on the filter media. This results in evaporation of nitric acid gas and loss of ammonium nitrate. Pressure drop existing in

an aerosol sampling system leads to a decrease in the gas phase concentration of a certain species as air flows through the system. This creates a concentration difference between the air stream and the surface of particle deposit, which serves as a driving force for evaporative mass transfer of volatile species from the deposit surface to the airstream. Again, loss of collected particle materials will occur.

Most of previous studies use filter packs or total suspended particulate samplers to study sampling artifact problems. Field experimental data about sampling accuracy of various soluble ionic species and  $PM_{10}$  concentrations as determined by commercial HVPM<sub>10</sub> samplers are not readily available. In particular, the relationship between sampling errors and  $PM_{10}$  concentrations has never been explored in the open literature. In this study, an ADS system was used to assess the accuracy of a commercial HVPM<sub>10</sub> sampler for atmospheric aerosol sampling. Only soluble ions but not  $H^+$  are studied since  $PM_{10}$  contains coarse basic particles that neutralize fine acidic particles readily. This renders the measurement of  $H^+$  concentration meaningless.

## EXPERIMENTAL METHOD

The experiment used two SA 1200 HVPM<sub>10</sub> samplers (Andersen Samplers Inc.) and an annular denuder system (ADS) (University Research Glassware Inc.) collocated at the Hsin Chu air monitoring station in Taiwan. The experimental period ran from November 1 of 1993 until March 26 of 1994. During the period, the daily average temperature ranged from 13.5 to 30.7°C (average: 21.8°C) and the daily average relative humidity ranged from 60.2 to 96% (average: 75.8%). Sampling inlets of these samplers were the same, which were 15 m above the ground. One of the HVPM<sub>10</sub> sampler used glass fiber filters (Gelman AE type) while the other used quartz filters (Pallflex 2500 QAT-UP). The pHs and alkalinities, as determined according to ASTM D-202 procedures (Coutant 1977), are 8.95 and 0.336  $\mu\text{eq}/\text{cm}^2$  for glass fiber filters and 5.67 and 0.028  $\mu\text{eq}/\text{cm}^2$  for quartz filters, respectively. Before weighing, HVPM<sub>10</sub> filters were conditioned according to the standard method. After weighing, a 4 cm x 4 cm piece was cut from the filter and extracted in de-ioned water as soon as possible to prevent it from evaporation loss of collected materials. The extracts were stored in a clean refrigerator at 4°C until chemical analysis.

The ADS sampling train consists of 1) a Teflon-coated aluminum cyclone with cutoff aerodynamic diameter equal to 10  $\mu\text{m}$  at the flow rate of 4 sL/m (standard liter per minute); 2) four annular denuders; 3) a filter pack

which has a 47 mm Teflon filter (0.5  $\mu\text{m}$  pore size; Whatman WTP) and three 47 mm glass fiber filters (Gelman AE); and 4) a flow controller (model FM-1050-VI, Andersen Inc.) with timer, pump, and rotameter.

Coating and sample extraction procedure of the ADS system followed that described by the U.S. EPA (1989), Koutrakis et al. (1992), and Lee et al. (1993). The first denuder (242 mm in length) was coated with 10 mL of 1 g/L sodium chloride (NaCl) in 1:9 methanol/water solution to collect  $\text{HNO}_3$  and  $\text{SO}_2$ . The second and third denuders were each coated with 10 ml of 10 g/L sodium nitrate ( $\text{Na}_2\text{CO}_3$ ), 10 g/L glycerol in 1:1 methyl/water solution to collect  $\text{HNO}_2$ ,  $\text{HCl}$ , and  $\text{SO}_2$ . The fourth denuder (242 mm in length) was coated with 10 mL of 20 g/L citric acid in methanol to collect  $\text{NH}_3$ .

In the filter pack, the Teflon filter was used to collect particles. Two glass fiber filters were coated with 20 g/L  $\text{Na}_2\text{CO}_3$  in 3:10 methanol/water solution to collect evaporated  $\text{HNO}_3$  and  $\text{HCl}$  gases (Koutrakis et al. 1992). The other glass fiber filter was coated with 20 g/L citric acid to collect evaporated  $\text{NH}_3$ . After the Teflon filter was conditioned and weighed according to the standard method, preparation and extraction of the Teflon filter were performed in a clean ammonia-free box. The extracts were put in a refrigerator at 4°C until chemical analysis.

The concentrations of soluble ionic species  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  were determined by ion chromatography (model 4500 i/SP, Dionex Corp.). Quality assurance of ion chromatography analysis was documented by the U.S. EPA (1989) and was strictly followed in this study.

## RESULTS AND DISCUSSIONS

### *ADS performance on gas collection*

As a check on the performance of the ADS system for gas collection, daily average  $\text{SO}_2$  concentrations were compared between the ADS and a well calibrated  $\text{SO}_2$  analyzer (Model 43A, Thermo Inc.) as shown in Fig. 1. The comparison reveals that the ADS system collects  $\text{SO}_2$  gas efficiently and measured  $\text{SO}_2$  concentrations are nearly the same as actual ambient concentrations.

### *Artifact sulfate concentrations*

The experimental artifact sulfate vs.  $PM_{10}$  concentrations are shown in Fig. 2, where the artifact sulfate is labeled as follows: 1)  $\text{SO}_4^{2-}(\text{g} - \text{ADS})$ : the sulfate concentration difference between the glass fiber filter of the HVPM<sub>10</sub> sampler and the Teflon filter of the ADS; 2)  $\text{SO}_4^{2-}(\text{g} - \text{q})$ : the sulfate concentration difference

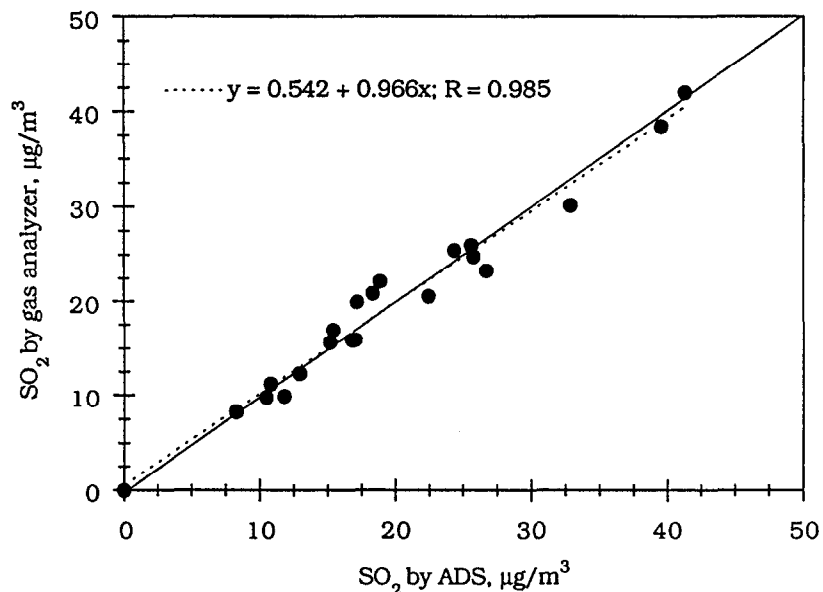


Fig. 1. The comparison of SO<sub>2</sub> concentrations measured by the gas analyzer and the ADS.

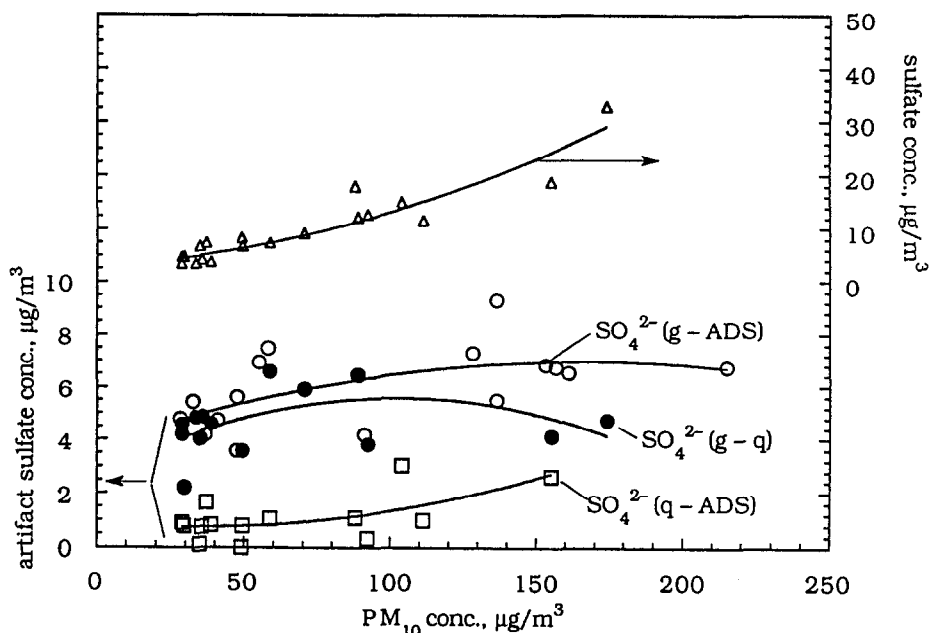


Fig. 2. The relationship between artifact sulfate and PM<sub>10</sub> concentrations. SO<sub>4</sub><sup>2-</sup>(g - ADS): difference between HVPM<sub>10</sub> sampler (glass fiber filter) and ADS; SO<sub>4</sub><sup>2-</sup>(g - q): difference between glass fiber and quartz filters of HVPM<sub>10</sub> sampler; SO<sub>4</sub><sup>2-</sup>(q - ADS): difference between HVPM<sub>10</sub> sampler (quartz filter) and ADS.

between the glass fiber and quartz filters of the HVPM<sub>10</sub> sampler; 3) SO<sub>4</sub><sup>2-</sup>(q - ADS): the sulfate concentration difference between the quartz filter of the HVPM<sub>10</sub> sampler and the Teflon filter of the ADS. In the ADS, backup filters of the filter pack collect no sulfates and there is no need to correct for the sulfate concentration found in the Teflon filter. In Fig. 2, PM<sub>10</sub> concentrations in the x-axis are determined by the HVPM<sub>10</sub> sampler using quartz (case 2 and 3) or glass fiber filters (case 1).

As will be shown later, the PM<sub>10</sub> concentrations are nearly the same whether quartz or glass fiber filters are used in the HVPM<sub>10</sub> sampler.

As shown in Fig. 2, despite the fact that quartz filters of the HVPM<sub>10</sub> sampler are slightly acidic, the artifact sulfate, SO<sub>4</sub><sup>2-</sup>(q - ADS), still exists. The artifact sulfate concentration, which ranges from 0 to 3.04 µg/m<sup>3</sup> (average is 1.07 ± 0.86 µg/m<sup>3</sup>), increases with respect to the PM<sub>10</sub> concentration. The increase of the artifact sulfate

concentration with the  $PM_{10}$  concentration suggests that the formation of sulfate artifact is due to the existence of alkaline coarse particles in the sample, onto which  $SO_2$  gas adsorbs readily and is turned into sulfate. For glass fiber filters of the HVPM<sub>10</sub> sampler, the concentration of the artifact sulfate,  $SO_4^{2-}$  (g – ADS), is high. It ranges from 3.58 to 9.3  $\mu\text{g}/\text{m}^3$  (average is  $6 \pm 1.5 \mu\text{g}/\text{m}^3$ ) and increases slightly with respect to the  $PM_{10}$  concentration. But at high  $PM_{10}$  concentration, artifact sulfate  $SO_4^{2-}$  (g – ADS) remains more or less constant. This suggests that only alkaline particles on the exposed surface of the particle deposit react efficiently with  $SO_2$  gas, whereas those inside the particle deposit do not.

The artifact  $SO_4^{2-}$  (g – ADS) level is much higher than that predicted by the Coutant's model (Coutant 1977) which should be 0.3 – 3.0  $\mu\text{g}/\text{m}^3$ . This is not surprising, since the Coutant's model considers alkalinity in the filter media only, whereas alkaline coarse particles of particle deposits can adsorb and oxidize additional  $SO_2$  gas.

When the artifact sulfate is determined as  $SO_4^{2-}$  (g – q), it ranges from 2.21 to 6.6  $\mu\text{g}/\text{m}^3$  (average is  $4.62 \pm 1.16 \mu\text{g}/\text{m}^3$ ) and remains nearly unchanged with respect to the  $PM_{10}$  concentration (Fig. 2). The latter is to be expected since nearly the same amount of particles are collected by quartz or glass fiber filters, the sulfate artifact,  $SO_4^{2-}$  (g – q), should not increase with the  $PM_{10}$  concentration.

The sulfate concentration measured by the quartz filters of the HVPM<sub>10</sub> sampler is also shown in Fig. 2. The concentration of sulfate (3.43 to 32.8  $\mu\text{g}/\text{m}^3$ ) increases with respect to the  $PM_{10}$  concentration and accounts for 5.62 to 19.2% of the  $PM_{10}$  concentration. However, the percentage of sulfate found in the collected particles does not necessarily increase with increasing  $PM_{10}$  concentration.

#### Artifact nitrate concentrations

The experimental artifact nitrate vs.  $PM_{10}$  concentrations is shown in Fig. 3. Again, three different definitions of artifact nitrate,  $NO_3^-$  (g – ADS),  $NO_3^-$  (g – q) and  $NO_3^-$  (q – ADS) are used. Since nitrate is a volatile species, nitrate concentrations in the Teflon filter are corrected for the volatile loss by adding additional nitrates found in the backup filters of the filter pack (Koutrakis et al. 1992).

As shown in Fig. 3, the nitrate artifact concentration is generally lower than the sulfate artifact concentration. When the  $PM_{10}$  concentration is less than 50  $\mu\text{g}/\text{m}^3$ , the concentration of the artifact nitrate  $NO_3^-$  (q – ADS) is low. It ranges from –0.26 to 1.58  $\mu\text{g}/\text{m}^3$  (average is  $0.37 \pm 0.63 \mu\text{g}/\text{m}^3$ ). Because of higher alkalinity in the glass fiber filter, the corresponding concentration of the artifact nitrate  $NO_3^-$  (g – ADS) is slightly higher. It ranges from 1.42 to 3.27  $\mu\text{g}/\text{m}^3$  (average is  $2.1 \pm 0.69 \mu\text{g}/\text{m}^3$ ).

When the  $PM_{10}$  concentration is higher than 50  $\mu\text{g}/\text{m}^3$ , the artifact nitrate concentration, in general, increases with respect to the  $PM_{10}$  concentration because of alkalinities in the collected coarse particles. But, since volatilization loss of nitrate may also occur during sampling, the artifact level is random, although it remains positive. Considering all data points, the artifact nitrate  $NO_3^-$  (q – ADS) ranges from –0.26 to 8.0  $\mu\text{g}/\text{m}^3$  (average is  $1.62 \pm 2.38 \mu\text{g}/\text{m}^3$ ); the artifact nitrate  $NO_3^-$  (g – ADS) ranges from 0.77 to 10.89  $\mu\text{g}/\text{m}^3$  (average is  $3.25 \pm 2.49 \mu\text{g}/\text{m}^3$ ). The artifact nitrate  $NO_3^-$  (g – q) is small, which ranges from 0.31 to 3.36  $\mu\text{g}/\text{m}^3$  (average is  $1.9 \pm 0.98 \mu\text{g}/\text{m}^3$ ).

The IC analysis of gas phase concentrations in the ADS shows that concentrations of  $HNO_2$  are much greater than  $HNO_3$ . During the experimental period, the average  $HNO_3$  concentration is  $0.67 \pm 0.54 \mu\text{g}/\text{m}^3$  (0 – 2.08  $\mu\text{g}/\text{m}^3$ ) while the average  $HNO_2$  concentration is  $4.29 \pm 2.45 \mu\text{g}/\text{m}^3$  (2.00 – 12.66  $\mu\text{g}/\text{m}^3$ ). Since the concentrations of most artifact nitrate data fall below 4.0  $\mu\text{g}/\text{m}^3$  but well above 0.54  $\mu\text{g}/\text{m}^3$ , it can be concluded that the adsorption of  $HNO_2$  but not  $HNO_3$  gas by alkaline filter media and coarse particles is mainly responsible for the nitrate artifact formation. The role of nitrogen oxide on the formation of nitrate artifact is not clear and remains to be investigated.

The nitrate concentration measured by the quartz filters of the HVPM<sub>10</sub> sampler is also shown in Fig. 3. The concentration of nitrate (0.73 to 27.8  $\mu\text{g}/\text{m}^3$ ) increases with respect to the  $PM_{10}$  concentration and accounts for 2.1 to 16 % of the  $PM_{10}$  concentration.

#### Chloride and ammonium ion concentrations

Based on the experimental data shown in Fig. 4, differences in particulate chloride concentrations between glass fiber filters and quartz filters of the HVPM<sub>10</sub> sampler,  $Cl^-$  (g – q) are found to be small. The average difference is 0.51  $\mu\text{g}/\text{m}^3$ . It means that particulate artifact chloride in the glass fiber filter would be small when the quartz filter is used as a reference. HCl concentrations averaged 3.24  $\mu\text{g}/\text{m}^3$  (0.75 – 6.70  $\mu\text{g}/\text{m}^3$ ) during experimental period.

However, as shown in Fig. 4, the differences in chloride ion concentrations found in the HVPM<sub>10</sub> sampler and ADS system are substantial. In Fig. 4, chloride concentrations in the Teflon filter of the ADS are corrected by those found in the backup filters. The figure shows that  $Cl^-$  (g – ADS) ranges from 0.5 to –15.47  $\mu\text{g}/\text{m}^3$  (average is  $-8.28 \pm 4.26 \mu\text{g}/\text{m}^3$ ) and  $Cl^-$  (q – ADS) ranges from 0.22 to –11.38  $\mu\text{g}/\text{m}^3$  (average is  $-5.76 \pm 3.71 \mu\text{g}/\text{m}^3$ ). Both negative artifacts of  $Cl^-$  (g – ADS) and  $Cl^-$  (q – ADS) increase with increasing  $PM_{10}$  concentration.

As to ammonium ion concentration differences, Fig. 5 indicates that  $NH_4^+$  (g – q) is mostly negative because the

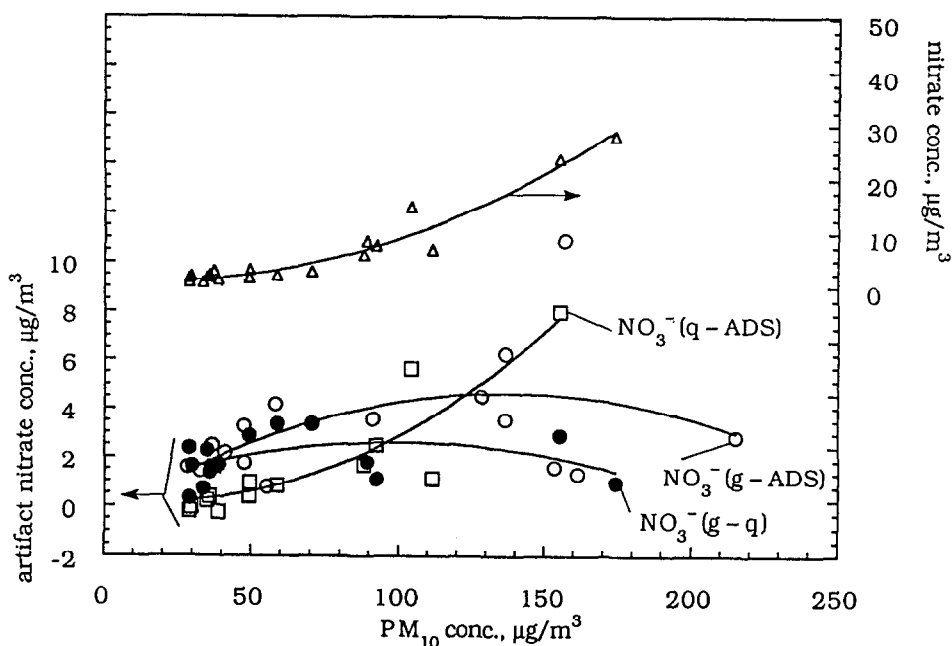


Fig. 3. The relationship between artifact nitrate and PM<sub>10</sub> concentration.

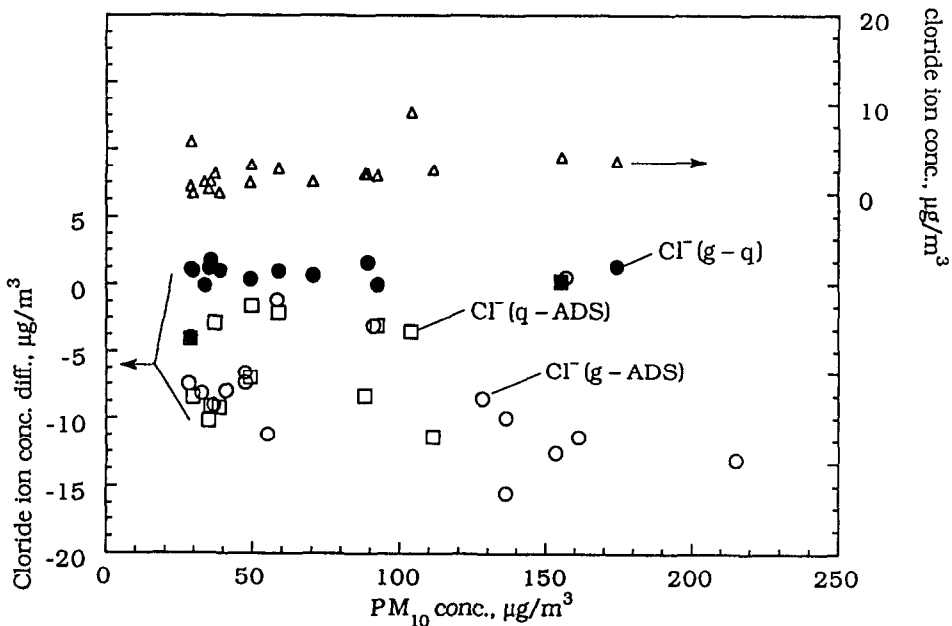


Fig. 4. The relationship between chloride ion concentration difference and PM<sub>10</sub> concentration.

quartz filter is more acidic and thus collects more basic ammonia gas than the glass fiber filter. The average is  $1.92 \pm 1.27 \mu\text{g}/\text{m}^3$  (range: 0.0 to  $\sim -4.18 \mu\text{g}/\text{m}^3$ ).

Loss of ammonium ion in the filters of HVPM<sub>10</sub>, which is expressed as  $\text{NH}_4^+(\text{g} - \text{ADS})$  or  $\text{NH}_4^+(\text{q} - \text{ADS})$ , is also evident as shown in Fig. 5. Ammonium ion concentrations in the Teflon filters of the ADS are also corrected by

those found in the backup filters. The figure shows that  $\text{NH}_4^+(\text{g} - \text{ADS})$  ranges from  $-1.05$  to  $-9.06 \mu\text{g}/\text{m}^3$  (average is  $-4.79 \pm 2 \mu\text{g}/\text{m}^3$ ) and  $\text{NH}_4^+(\text{q} - \text{ADS})$  ranges from  $2.16$  to  $-5.09 \mu\text{g}/\text{m}^3$  (average is  $1.64 \pm 2.19 \mu\text{g}/\text{m}^3$ ).

There are two major mechanisms that can result in losses of ammonium and chloride ions in the HVPM<sub>10</sub> sampler. Equations (1) to (5) show some examples:

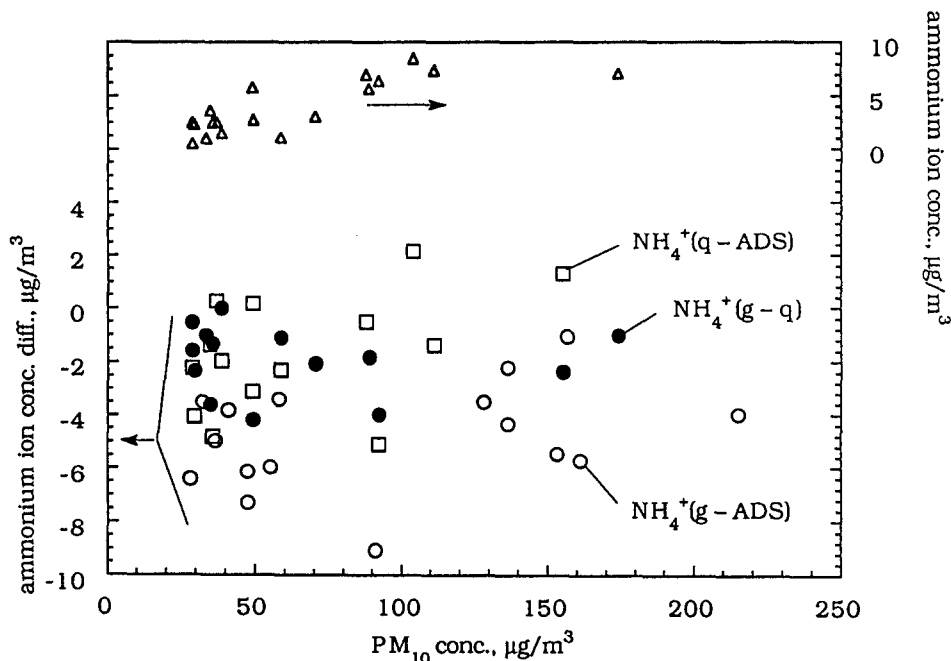
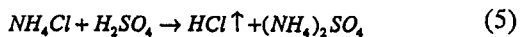
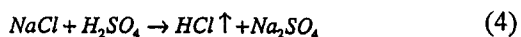
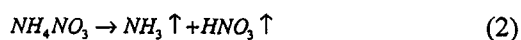
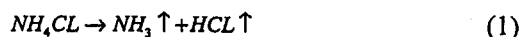


Fig. 5. The relationship between ammonium ion concentration difference and  $PM_{10}$  concentration.



Equations (1) to (3) show that pure evaporative loss of volatile  $NH_4Cl$ ,  $NH_4NO_3$  or  $NH_4A$  ("A" stands for inorganic or organic acid) particles while Equations (4) and (5) show the reaction of chloride particles with acidic particles and subsequent evaporation of hydrogen chloride gas (Kitto and Harrison 1992; Koutrakis et al. 1992). In Equations (4) and (5), acidic sulfate particles could be  $NH_4HSO_4$  or  $(NH_4)_3H(SO_4)_2$ , and chloride particles could be other salts such as  $KCl$  or  $NaCl/Na_2SO_4$  as well. Evaporative loss mechanisms for collected nitrate species in the HVPM<sub>10</sub> sampler are similar to Equations (1) through (5).

By comparing molar concentrations of evaporated gases found on the backup filters of the ADS, as shown in Table 1, one can point out which loss mechanism is more important. If only pure evaporation loss that involves no reactions is important, the molar concentration of ammonium ion will equal to the sum of nitrate and chloride ion. This is the case for fine ammonium particles

(Possanzini et al. 1992). However, the data in Table 1 show that most of ammonium ion concentrations are far less than the sum of chloride ion and nitrate concentrations, and the chloride ion concentration is much higher than the nitrate concentration. This indicates that reactions such as Equations (4) and (5) play more important roles in ammonium and chloride ion losses during HVPM<sub>10</sub> sampling.

Table 1. Comparison of concentrations of volatilized  $Cl^-$  and  $NO_3^-$  with volatilized  $NH_4^+$  found on the back-up filters of the ADS.

Sample no.	$NO_3^-$	$Cl^-$	$NH_4^+$
1	36.81	83.47	509.34
2	3.10	92.9	85.48
3	53.90	58.11	146.94
4	4.32	99.38	32.28
5	0.90	105.86	8.012
6	39.45	285.20	150.39
7	14.75	265.23	121.83
8	8.21	394.37	121.03
9	2.22	350.46	124.81
10	15.64	609.32	250.18
11	2.18	348.72	186.23
12	2.16	345.16	184.36
13	5.94	355.73	274.73
14	19.09	423.37	305.86
15	5.84	349.30	269.77

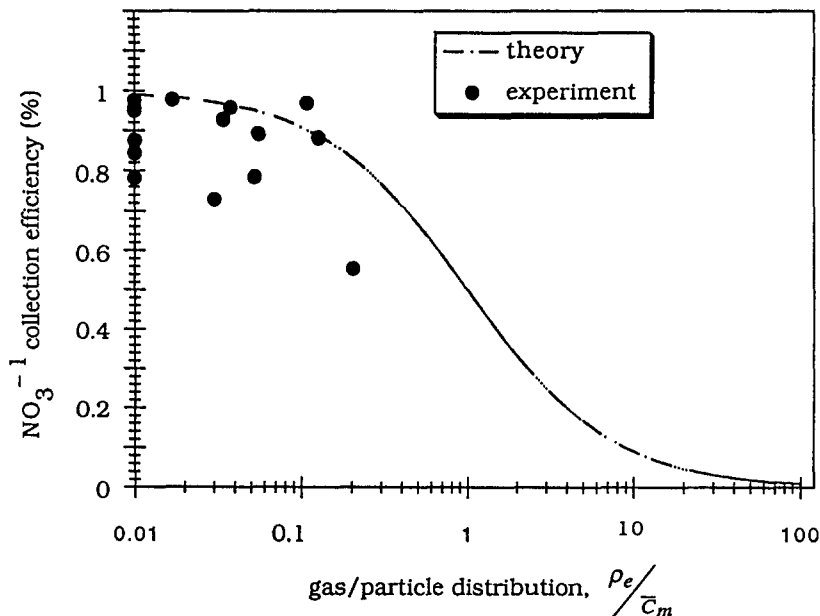


Fig. 6. The comparison of theoretical with experimental nitrate collection efficiency (%) in the denuded Teflon filter.

*Reaction and subsequent loss of volatile species*

To further elucidate the important role of reaction and subsequent loss of volatile species, theory of Zhang and McMurry (1992) is used to calculate the sampling efficiency  $\eta_e$  of volatile particulate species in the denuded Teflon filter and compared with the experimental data. If pure evaporative loss is important, the sampling efficiency  $\eta_e$  of a certain species in the denuder Teflon filter can be calculated as

$$\eta_e = \frac{1}{1 + \bar{\rho}_e / \bar{c}_m} \tag{6}$$

where  $\bar{\rho}_e / \bar{c}_m$  is the ratio of the equilibrium gas phase concentration (averaged over the sampling period) to the measured particle concentration. Here  $\bar{\rho}_e$  is assumed to be equal to the measured gas concentration by ADS.

The experimental sampling efficiency for the denuded filter is obtained by dividing nitrate (or ammonium ion) from the denuded Teflon filter by the true nitrate (or ammonium ion) calculated from the denuded filter pack. The sampling efficiency curve is plotted in Fig. 6 for nitrate and in Fig. 7 for ammonium ion. In these figures, the gas/particles distribution is calculated by dividing the gas phase nitrate (or ammonium ion) concentration from the annular denuder by the nitrate (or ammonium ion) from the denuded Teflon filter. As shown in Fig. 6, for nitrate species, there is considerable scatter in the data with the theoretical collection efficiencies being greater than the experimental data. This indicates that pure evaporative loss does not account for all of the nitrate loss in the

ADS system. Reactions between nonvolatile nitrate and particulate and gaseous strong acid can occur also. It is anticipated that in the HVPM<sub>10</sub> sampler, although the evaporative loss of nitrate species cannot be quantified, a similar conclusion can also be made in regard to nitrate loss. However, since the formation of nitrate artifact is more dominant than the reaction and evaporative loss in the HVPM<sub>10</sub> sampler, nitrate artifact remains positive.

Figure 7 shows that the theory overestimates the losses of particulate ammonium from the denuded Teflon filter. This indicates the evaporated ammonia gases may react with other deposited acidic particles resulting in less evaporative losses as predicted by the theory. A similar phenomenon may exist in the HVPM<sub>10</sub> sampler.

*Comparison of PM<sub>10</sub> concentrations*

It is interesting to compare total PM<sub>10</sub> concentrations determined by the HVPM<sub>10</sub> sampler, that uses different filter media, with that by the ADS system. The latter, denoted as PM<sub>10</sub> (ADS), has included both the PM<sub>10</sub> concentration measured by the Teflon filter and evaporative gas concentrations from backup filters.

It can be seen from Fig. 8, that despite existing differences in ionic species concentrations determined by the HVPM<sub>10</sub> and the ADS system, there is essentially no difference in the PM<sub>10</sub> concentrations. As shown in the figure, whether the glass fiber or quartz filter is used in the HVPM<sub>10</sub> sampler, differences in the PM<sub>10</sub> concentration, denoted as PM<sub>10</sub> (g) – PM<sub>10</sub> (q), are less than 3%, which is

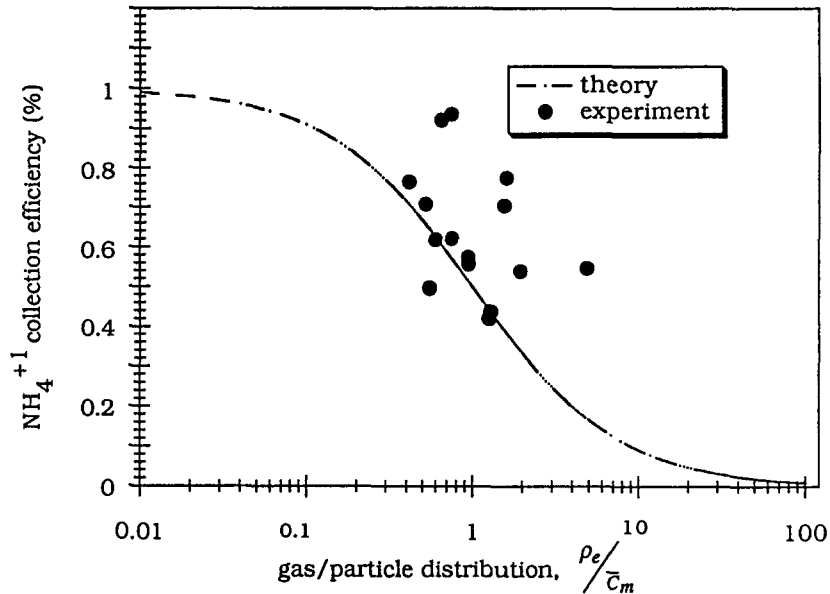


Fig. 7. The comparison of theoretical with experimental ammonium ion collection efficiency (%) in the denuded Teflon filter.

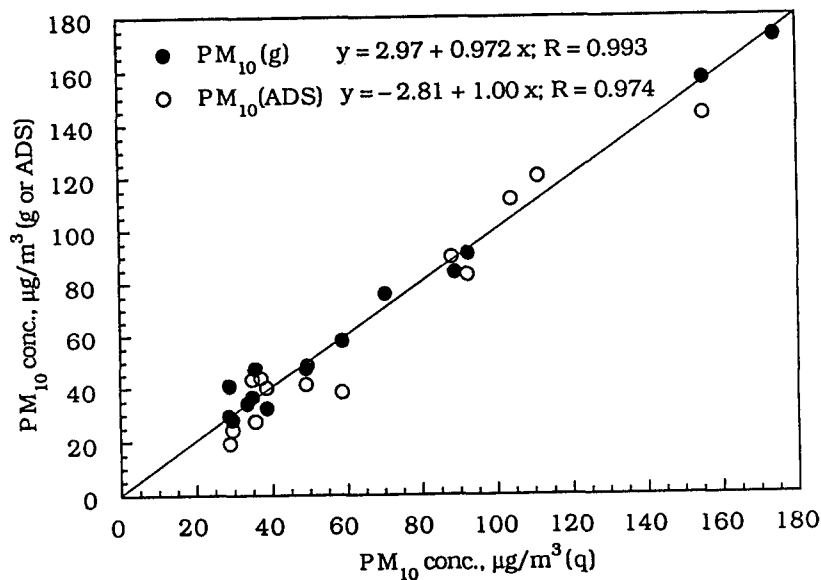


Fig. 8. The comparison of  $PM_{10}$  concentrations determined by two different samplers.  $PM_{10}$  (q: concentration determined by quartz filter of HVPM<sub>10</sub> sampler;  $PM_{10}$  (g): concentration determined by glass fiber filter of HVPM<sub>10</sub> sampler;  $PM_{10}$  (ADS): concentration determined by ADS system which includes evaporative loss.

nearly the same as the experimental errors. The largest differences occur at  $PM_{10}$  concentration less than  $40 \mu\text{g}/\text{m}^3$  when the artifact level accounts for a significant fraction. When the  $PM_{10}$  concentration is high, the artifact level becomes insignificant. Differences in  $PM_{10}$ (ADS) and  $PM_{10}$ (q) are also very small as shown in Fig. 8. It is suggested that positive artifact concentrations found in the HVPM<sub>10</sub> sampler are well balanced by the losses of evaporative species or non-evaporative species due to reaction and evaporation.

## CONCLUSIONS

This paper discusses the magnitude and mechanism of sampling artifact formation in the commonly used HVPM<sub>10</sub> sampler. A collocated annular denuder system has been used to collect gaseous as well as particle species to facilitate this investigation. The following conclusions can be drawn from this study:

1) There are obvious differences in concentrations of ionic species such as sulfate, nitrate and ammonium ion between quartz filter and glass fiber filter of the HVPM<sub>10</sub>



sampler. Concentrations of nitrate and sulfate in the basic glass fiber filter are higher than those in the acidic quartz filter. The concentration of ammonium ion in the glass fiber filter is less than that in the quartz filter.

2) In addition to basic filter media, interactions between acidic gases such as SO<sub>2</sub>, HNO<sub>2</sub>, and HNO<sub>3</sub> and coarse basic particles on the filter of the HVPM<sub>10</sub> sampler also result in the increase of artifact sulfate and nitrate concentration during sampling. The formation of artifact nitrate is mainly due to the retention and subsequent oxidation of HNO<sub>2</sub> rather than HNO<sub>3</sub> by the basic filter media and particle deposit.

3) The concentrations of particulate chloride collected by the filters (glass fiber or quartz) of the HVPM<sub>10</sub> samplers are much lower than actual values. The volatilization of NH<sub>4</sub>Cl and the interaction between nonvolatile chloride species and strong acid particles result in the under-estimation of particulate chloride concentrations in the HVPM<sub>10</sub> sampler.

4) The major volatile ammonium species is found to be NH<sub>4</sub>Cl in the denuded Teflon filter of the ADS. Similar conclusion can be drawn for the HVPM<sub>10</sub> samplers.

5) Despite that differences in ionic species concentrations exist between the HVPM<sub>10</sub> sampler that uses glass fiber or quartz filter and the ADS system, there are virtually no differences in the total PM<sub>10</sub> concentrations determined by these two instruments.

Because that the chemical compositions of particles in the coarse mode are quite different from those in the fine mode, it is expected that the levels and mechanisms of sampling artifacts will be quite different between these two modes. Besides, differences in the total ionic species concentrations have been found to be inadequate to explain the observed differences in the total PM<sub>10</sub> concentrations in different sampling situations, further investigations to cover fine-particle mode as well as organic sampling artifacts are necessary.

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