



ARTIFACTS OF IONIC SPECIES FOR HI-VOL PM₁₀ AND PM₁₀ DICHOTOMOUS SAMPLERS

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Abstract—This study employs two Annular Denuder Systems (ADS₁₀ and ADS_{2.5}) to quantify sampling artifacts of soluble ionic species determined by the high-volume PM₁₀ (hi-vol PM₁₀) sampler using quartz fiber filters and PM₁₀ dichotomous (Dichot) sampler using Teflon filters. According to the experimental results, the percentage of artifact of a species over the actual species concentration is +11, +8 and +15% for PM₁₀^{HV}, PM₁₀^{DICH}, PM_{2.5}^{DICH}, respectively, for sulfate species; -16, -21 and -21% for PM₁₀^{HV}, PM₁₀^{DICH}, PM_{2.5}^{DICH}, respectively, for nitrate species; -24, -32 and -54% for PM₁₀^{HV}, PM₁₀^{DICH}, PM_{2.5}^{DICH}, respectively, for chloride ion species; -17, -21 and -18% for PM₁₀^{HV}, PM₁₀^{DICH}, PM_{2.5}^{DICH}, respectively, for ammonium ion species. For volatile species such as nitrate, ammonium and chloride ions, additional sampling losses due to gas-particle and particle-particle interactions are more important than pure volatilization loss. Amount of positive and negative artifacts is approximately equal and the amount of net artifact does not account for more than 15% of PM₁₀ concentration. © 1998 Elsevier Science Ltd. All rights reserved.

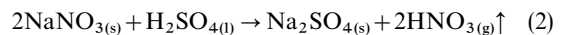
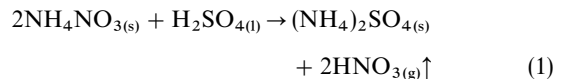
Key word index: Sampling artifact, acidic aerosol, denuder, hi-vol PM₁₀ sampler, dichotomous sampler.

INTRODUCTION

Chemical specification of atmospheric aerosol particles is critical to source apportionment and risk assessment. For chemical analysis purposes, aerosol particles must be collected using impactors or filter samplers. Filter samplers include hi-vol TSP or PM₁₀ samplers, or dichotomous samplers. A number of ambient species are difficult to sample because chemical or physical changes may occur during or after sample collection. These changes cause positive or negative sampling errors, frequently referred to as artifacts, when determining species concentrations.

Sampling errors often occur owing to gas-particle and particle-particle interactions, gas absorption by sampling media or collected particles, and evaporation of collected species due to pressure drop across filter media. For instance, alkaline glass fiber filters can absorb SO₂ gas readily resulting in positive sulfate artifact due to further oxidation (Appel *et al.*, 1979, 1980; Coutant, 1977; Spicer and Schumacher, 1979; Pierson *et al.*, 1976, 1980). Retention of HNO₃ on both quartz and glass filters also occur during ambient sampling (Appel and Tokiwa, 1981; Appel *et al.*, 1984). These phenomena all lead to positive

artifacts. Volatile species such as ammonium chloride and ammonium nitrate become lost due to their dissociation and evaporation when the temperature changes or pressure drop increases during sampling (Appel *et al.*, 1984). Nitrate can also be lost due to chemical interactions between ammonium nitrate and particulate H₂SO₄ and gaseous HCl (Appel and Tokiwa, 1981; Koutrakis, *et al.*, 1992). The mechanisms are as follows:



Similarly, negative chloride artifact is primarily due to the release of HCl by volatilization of ammonium chloride and interaction of particulate chloride with strong acid or gases.

However, due to the coexistence of both positive and negative artifacts, no significant differences in 24-h mass concentration arise between quartz fiber and Teflon filters (Appel *et al.*, 1984). Besides the sampling processes, conditioning of filter samples also leads to a loss of volatile species. PM₁₀ mass concentration is normally determined according to the method described in U.S. EPA (1990) and Chow (1995). Before and after sample collection, filters are conditioned at constant humidity and temperature in

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an enclosed chamber for 24 h. Both conditions in the chamber and storage time are related to sampling errors (Witz *et al.*, 1983, 1990; Witz, 1985; Smith *et al.*, 1978; Dunwoody, 1986), particularly for volatile species. The magnitude of artifacts of various species due to conditioning of filter samples need to be clarified further.

Most of the above studies concentrated primarily on examining artifact formations of sulfate and nitrate in the laboratory. Studying artifact formation under complicated field sampling conditions is of worthwhile interest. In particular, open literature has rarely addressed the formation of chloride and ammonium artifacts and, hence, must be investigated.

In this study, diffusion denuders are used as references to assess the artifact's magnitude and mechanism of artifact formation in the conventionally used hi-vol PM₁₀ and PM₁₀ Dichot samplers in field conditions. Atmospheric acidic aerosol studies have extensively used the denuder technology. Owing to that gases are removed before particles are collected, aerosol artifact formation due to gas-particle interactions can be minimized. In addition, the filter pack's backup filters serve to absorb volatile gases from collected particles on the front Teflon filter. Therefore, actual particle concentrations can be assessed by the filter pack.

EXPERIMENT

Sampling artifacts of hi-vol PM₁₀ (Model SA 1200, Andersen Samplers, Inc., GA, U.S.A.) and PM₁₀ Dichotomous sampler (hereafter will be called as Dichot, Model SA 241, Andersen Samplers, Inc.) were studied. Both samplers are U.S. EPA designated reference methods for PM₁₀ measurement (Chow, 1995). The two samplers were collocated with two annular denuder systems (referred to hereafter as ADS, Model URG-3000, University Research Glassware, NC, U.S.A.) at the Hsin Chu air monitoring station, Taiwan. The two ADSs are the same except one system's inlet is a 10 μm cutpoint cyclone (flow rate: 4.0 ℓ/min , Model URG-2000-30EC) while the other is a 2.5 μm cutpoint cyclone (flow rate: 10.0 ℓ/min , Model URG-2000-30EN). The two ADSs are called as ADS₁₀ and ADS_{2.5}, respectively. The inlets of all samplers were 12.8 m above the ground. The Hsin Chu air monitoring station is located near the center of Hsin Chu city within an area which is 104 square kilometers and population of nearly 340,000. This typical urban city is crowded with cars on the streets and is renowned for its high-tech semiconductor and computer industries. It is located in the northern part of Taiwan, near Taiwan's western coast.

The hi-vol PM₁₀ sampler was operated at a flow rate of 1.13 $\text{m}^3 \text{min}^{-1}$ with quartz filters (Pallflex 2500 QAT-UP, PALL Corp., U.S.A.). If evaluating errors during 24 h conditioning, collected filter samples were conditioned in a 35 cm \times 40 cm \times 45 cm cabinet at RH = 40 \pm 5% and 20 \pm 3°C before chemical analysis. Otherwise, samples were added with deionized water in polyethylene bottles and extracted in an ultrasonic bath immediately after collection. Extracts were stored at 4°C until chemical analysis. The Dichot was operated at a flow rate of 1.67 ℓ/min for coarse particle (aerodynamic diameter greater than 2.5 μm) collection and 15 ℓ/min for fine particle (aerodynamic diameter less than 2.5 μm) collection. Teflon filters (Zeffluor, Gelman

Sciences, U.S.A.) were used. Collected samples were treated for chemical analysis immediately after collection.

Each ADS had four annular denuder tubes to remove the gas species: SO₂, HNO₃, HNO₂, HCl and NH₃ (U.S. EPA enhanced method, 1992). Sampling, extraction and analysis adhered to the U.S. EPA method (1992). In the filter pack, the front Teflon filter was used to collect particles while the second and third nylon filters were used to absorb HCl and HNO₃, which evaporated from particles collected on the front Teflon filter. The fourth glass fiber filter was impregnated with citric acid in ethanol and dried in a vacuum desiccator to collect evaporated NH₃. The filter pack was extracted in an ammonia-free box to prevent acidic aerosol neutralization by ammonia. The front Teflon filter was extracted for pH analysis (Koutrakis *et al.*, 1988) and for anion and cation ions analysis. The second and third filters were extracted with anion eluent to efficiently extract chloride and nitrate (Appel *et al.*, 1988; Hering *et al.*, 1988). Next, the fourth impregnated filter was extracted with distilled deionized water for ammonium analysis. Finally, ions were analyzed by ion chromatography (Model 4500i, Dionex Corp. U.S.A.).

Accuracy and precision of the chemical analysis were determined to be \pm 3% and \pm 2%, respectively. Additional details regarding sampling, extraction and analysis of the ADS can be found in the U.S. EPA method (1992), and the methods described in Koutrakis (1988) and Lee *et al.* (1993).

The experiment ran from 13 October 1994 to 15 April 1995. Nineteen 24 h samples were collected. During the period, the daily average temperature ranged from 19.3 to 28.5°C (average: 23°C) and the daily average relative humidity ranged from 48.8 to 67.2% (average: 59.7%).

RESULTS AND DISCUSSION

For convenience, fine particles and particles less than 10 μm in aerodynamic diameter are denoted herein as PM_{2.5} and PM₁₀, respectively. Superscripts "ADS", "DICH" and "HV" are further used to identify whether samples are measured by ADS, Dichot or hi-vol PM₁₀ samplers, respectively. For instance, fine particles collected by the Dichot are referred to as PM_{2.5}^{DICH}, while the sum of fine and coarse particles is called as PM₁₀^{DICH}. Species concentrations were found to be represented by lognormal distribution functions. Median concentration as well as geometric standard deviation (σ_g) are reported for each ionic species.

Characteristics of aerosols

Fine particles are found to be mostly acidic. Hydrogen ion concentrations in PM_{2.5}^{ADS} range from 0 to 89 nmol m^{-3} (average: 33.4 nmol m^{-3}). According to Koutrakis *et al.* (1992), the amount of acidity neutralized during sampling is equal to the sum of nitrate and chloride concentrations on the nylon filters minus the ammonium concentration on the fourth filter. The percentage of neutralization is calculated from the ratio of the concentration of acidity neutralized to twice the sulfate concentration. The percentage of neutralization in this study varies from 0.3 to 40.6% in fine particles. Molar ratio of H⁺ to sulfate in PM_{2.5}^{ADS} ranges from 0 to 1.65, which according to Koutrakis *et al.* (1988), corresponds to the composition ranging from ammonium sulfate to ammonium bisulfate.

In contrast, H^+ concentrations in PM_{10}^{ADS} are all zero, indicating that the main composition is ammonium sulfate due to severe neutralization of aerosol acidity by alkaline coarse particles and collected ammonia gas.

The molar ratio of $(H^+NH_4^+)/(\text{NO}_3^- + \text{Cl}^- + 2\text{SO}_4^{2-})$ for $PM_{2.5}^{ADS}$ ranges from 0.71 to 1.18 (average: 0.97 ± 0.16). This finding suggests that these species are the major composition of ionic species in fine particle mode. The molar ratio for the PM_{10}^{ADS} ranging from 0.17 to 0.93 (average: 0.48 ± 0.24) is significantly lower than that of $PM_{2.5}^{ADS}$. Such a discrepancy is owing to the existence of large amount of alkali metal or alkaline earth elements such as Na, K, Ca, Mg, Al and Si in coarse particles (Finlayson-Pitts and Pitts, 1986).

Daily concentration ratios of $PM_{2.5}^{ADS}$ to PM_{10}^{ADS} for sulfate, nitrate, ammonium and chloride ions average at 0.81, 0.52, 0.74 and 0.36, respectively. That is, sulfate and ammonium ion are mainly in the fine mode while chloride ion is mainly in the coarse mode. Nitrate is equally divided in fine and coarse modes.

During the experimental period, median gaseous species concentrations are 2.67, 0.58, 20.04, $6.34 \mu\text{g m}^{-3}$ for HNO_2 , HNO_3 , SO_2 and NH_3 , respectively, as measured by the $ADS_{2.5}$. Due to possible coarse particle loss in the denuder tubes of the ADS_{10} system, slightly higher concentrations were measured by the ADS_{10} . The median concentrations are 3.29, 0.69, 22.72, $7.95 \mu\text{g m}^{-3}$ for HNO_2 , HNO_3 , SO_2 and NH_3 , respectively. The effect of coarse particle loss in the ADS_{10} system on the amount of artifacts, and its relative importance as compared to artifact formation due to volatilization and chemical interaction have not yet determined.

Tables 1 and 2 and Fig. 1 summarize experimental results of sampling artifacts. Table 1 compares the ionic species concentration and concentration ratio among PM_{10}^{ADS} , PM_{10}^{DICH} and PM_{10}^{HV} . Table 2 compares the ionic species concentration and concentration ratio among $PM_{2.5}^{ADS}$ and $PM_{2.5}^{DICH}$. Figure 1 compares the species concentrations measured by the hi-vol

Table 2. Species concentration and ratio of species concentration for PM_{10}^{DICH} and $PM_{2.5}^{ADS}$

| Species | Concentration, median (σ_g) range ($\mu\text{g m}^{-3}$) | Concentration ratio, (mean \pm s.d.) |
|--------------|---|--|
| | $PM_{2.5}^{ADS}$ | $PM_{2.5}^{DICH}/PM_{2.5}^{ADS}$ |
| Sulfate | 7.06 (1.89) (2.65–20.94) | 1.15 ± 0.30 |
| Nitrate | 2.82 (2.16) (0.96–10.61) | 0.79 ± 0.17 |
| Chloride ion | 1.73 (1.59) (0.92–4.08) | 0.46 ± 0.16 |
| Ammonium ion | 2.98 (1.84) (1.27–7.80) | 0.82 ± 0.08 |

PM_{10} or $Dichot_{2.5}$ with those measured by the ADS_{10} or $ADS_{2.5}$ for sulfate, nitrate, chloride ion and ammonium ion.

Sulfate artifact

As Table 1 reveals, sulfate concentration measured by the ADS_{10} (range: $3.24\text{--}23.29 \mu\text{g m}^{-3}$, median: $10.3 \mu\text{g m}^{-3}$) is lower than that by the hi-vol PM_{10} . On average, sulfate artifact's concentration is about 11% (range: $2 \sim 37\%$) of the actual sulfate concentration due to absorption of SO_2 by the quartz fiber filter and collected particles in the hi-vol PM_{10} . The sulfate concentration is overestimated by the hi-vol PM_{10} by 0.22 to $3.07 \mu\text{g m}^{-3}$ (average: $1.22 \mu\text{g m}^{-3}$). As Fig. 1a reveals, nearly all measured sulfate concentrations of the hi-vol PM_{10} are higher than those of the ADS_{10} . Two sets of concentrations are well correlated with a very high correlation coefficient.

No significant sulfate artifact occurs during 24 h conditioning at $20 \pm 3^\circ\text{C}$ and $40 \pm 5\%$ RH. Owing to low humidity and enclosed environment in the cabinet, the ambient SO_2 is not adsorbed and oxidized to particulate sulfate on the collected samples. Besides, in this study, samples were conditioned only for 24 h, which is much shorter than in previous studies (Smith

Table 1. Species concentration and ratio of species concentration for PM_{10}^{HV} , PM_{10}^{DICH} and PM_{10}^{ADS}

| Species | Concentration, median (σ_g) (range) ($\mu\text{g m}^{-3}$) | Concentration ratio (mean \pm s.d.) | | |
|--------------|---|---------------------------------------|-------------------------------|--------------------------------|
| | PM_{10}^{ADS} | $PM_{10}^{HVb}/PM_{10}^{HVa}$ | $PM_{10}^{HVa}/PM_{10}^{ADS}$ | $PM_{10}^{DICH}/PM_{10}^{ADS}$ |
| Sulfate | 10.30 (1.79) (3.24–23.29) | 1.00 ± 0.07 | $1.11 \pm .012$ | 1.08 ± 0.16 |
| Nitrate | 6.37 (1.89) (1.83–15.06) | 0.95 ± 0.04 | 0.84 ± 0.15 | 0.79 ± 0.24 |
| Chloride ion | 4.78 (1.28) (2.93–6.79) | 0.94 ± 0.05 | 0.76 ± 0.14 | 0.68 ± 0.20 |
| Ammonium ion | 4.68 (2.06) (1.07–11.36) | 0.92 ± 0.14 | 0.83 ± 0.18 | 0.79 ± 0.21 |

^a Samples were extracted immediately after collection.

^b Samples were conditioned at $40 \pm 5\%$ RH and $20 \pm 3^\circ\text{C}$ for 24 h before extraction.

^c Geometric standard deviation.

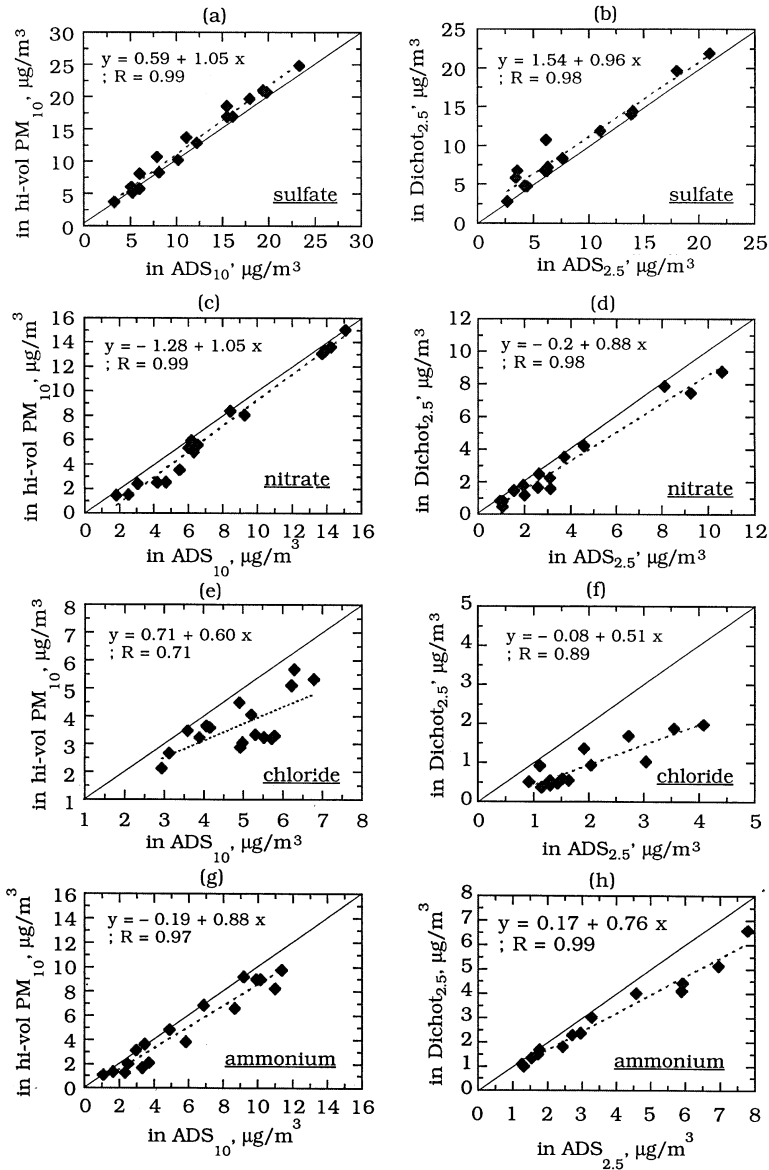


Fig. 1. Comparison of species concentration measured by hi-vol PM_{10} without filter conditioning versus ADS_{10} sampler—(a) sulfate (c) nitrate (e) chloride (g) ammonium; or Dichot $_{2.5}$ versus $ADS_{2.5}$ sampler—(b) sulfate (d) nitrate (f) chloride (h) ammonium.

et al., 1978; Witz *et al.*, 1990); it is reasonable to expect that sulfate artifact formation is not significant during 24 h conditioning.

Sulfate artifact of PM_{10}^{DICH} is only about 3% lower than PM_{10}^{HV} . Roughly 8% of sulfate artifact is formed in PM_{10}^{DICH} due to ambient SO_2 adsorption on collected particles on Teflon filters. The difference in artifact sulfate between PM_{10}^{HV} and PM_{10}^{DICH} indicates that absorption of SO_2 by alkaline particles, subsequently leading to formation of positive sulfate artifact, is more prominent in the hi-vol PM_{10} than in the Dichot. Fine and coarse particles are collected separately in the Dichot. The fact that SO_2 absorption and

oxidation in the acidic environment of the fine particle mass is less likely accounts for why the Dichot has a larger amount of sulfate artifact than that of hi-vol PM_{10} . Quartz filters of the hi-vol PM_{10} are slightly acidic and do not absorb SO_2 .

Table 2 indicates that in fine particles, sulfate concentrations range from 2.65–20.94 $\mu\text{g m}^{-3}$ (median: 7.06 $\mu\text{g m}^{-3}$). Artifact sulfate accounts for roughly 15% of the total sulfate concentration. Fig. 1b depicts that all measured sulfate concentrations of the Dichot $_{2.5}$ exceed those of the $ADS_{2.5}$. Two sets of concentrations are well correlated with a very high correlation coefficient. Exactly why the percentage of

sulfate artifact is higher in $PM_{2.5}^{DICH}$ than in PM_{10}^{DICH} remains unknown. However, several data points with low acidity and low sulfate concentration while having the sulfate artifact percentage as high as 50% of the total sulfate concentration may account for this reason. High sulfate artifact percentage at low acidity corresponds to earlier studies which demonstrated that more acidic environment produced by collected particles or the prior adsorbed acidic gases would tend to inhibit the oxidation of SO_2 by O_2 , O_3 or H_2O_2 because the rate is pH dependent (Witz and Wendt, 1981; Coutant, 1977). Our results and those of Eatough *et al.* (1995) generally suggest that the adsorption and oxidation of SO_2 to sulfate on collected particles is important for both of hi-vol PM_{10} and Dichot samplers.

All samples, including PM_{10}^{DICH} , $PM_{2.5}^{DICH}$ and PM_{10}^{HV} , reflect the importance of artifact formation within particle deposits. In addition, the magnitude of sulfate artifact does not correlate well with the ambient concentration of SO_2 for PM_{10}^{HV} (coefficient of correlation $R = 0.02$) and for the $PM_{2.5}^{DICH}$ ($R = 0.12$). This finding suggests that ambient SO_2 levels alone do not influence the formation of sulfate artifact. This observation is similar to that of Eatough *et al.* (1995) who suggested that thermodynamic equilibrium between SO_2 and adsorbed SO_2 on particles does not control the artifact sulfate formation.

Nitrate artifact

In this study, HNO_3 gas concentration is lower than nitrate concentration. In addition, formation of positive nitrate due to the retention of HNO_3 on collected particles and absorption by filters is not as significant as negative artifact formation due to volatilization loss of nitrate. Consequently, a net nitrate loss during filter sampling in PM_{10}^{HV} , PM_{10}^{DICH} and $PM_{2.5}^{DICH}$.

As Table 1 reveals, on average about 16% of nitrate is lost during hi-vol PM_{10} sampling due to volatilization and chemical reactions. Roughly an additional 5% of nitrate is lost during 24 h conditioning of quartz fiber filter samples. This loss is about one third of the amount occurring during sampling. Figure 1c reveals that nitrate concentrations measured by the hi-vol PM_{10} are always lower than those measured by the ADS_{10} . A good linear relationship between the two sets of concentrations is found.

More loss occurs in PM_{10}^{DICH} than in PM_{10}^{HV} . About 21% of nitrate is lost from PM_{10}^{DICH} due to volatilization and interaction of particulate nitrate. This finding suggests that retention of HNO_3 or nitrogen species on alkaline particles of the hi-vol PM_{10} contributes to around a maximum of 5% positive artifact nitrate.

Amount of negative artifact nitrate in $PM_{2.5}^{DICH}$ is similar to that in PM_{10}^{DICH} . It accounts for about 21% of actual nitrate concentration which ranges from 0.96 to $10.61 \mu\text{g m}^{-3}$ (median: $2.82 \mu\text{g m}^{-3}$). Good linear relationship between two sets of concentrations

measured by Dichot_{2.5} and ADS_{2.5} can be found in Fig. 1d. In addition to the reason stated above, because $PM_{2.5}^{DICH}$ is acidic, it is also reasonable that our experimental data demonstrate that, according to equations (1)–(3), both PM_{10}^{DICH} and $PM_{2.5}^{DICH}$ have more nitrate loss during 24 h sampling than PM_{10}^{HV} .

Chloride ion artifact

As Table 1 indicates, about 24% of chloride is lost on average in PM_{10}^{HV} . Figure 1e also reveals that the negative artifact chloride increases with an increasing chloride concentration. Roughly an additional 5% of chloride is lost from collected samples during 24 h conditioning.

More loss is found in PM_{10}^{DICH} . About 32% of chloride is lost from PM_{10}^{DICH} due to volatilization and chemical interactions. As Table 2 depicts for $PM_{2.5}^{DICH}$, chloride loss is even more severe, i.e. averaging at about 54% of the total chloride concentration; in addition, it increases with an increasing chloride concentration, as shown in Fig. 1f. More losses in $PM_{2.5}^{DICH}$ and PM_{10}^{DICH} than PM_{10}^{HV} imply that the retention of HCl on alkaline particles is more important in the hi-vol PM_{10} than in the Dichot. In addition, more acidity in $PM_{2.5}^{DICH}$ leads to more chemical interactions and more volatile loss.

Since the dissociation constant K_p of NH_4Cl exceeds that of NH_4NO_3 (Seinfeld, 1986; Harrison *et al.*, 1990) and the diffusion coefficient of HCl is larger than that of HNO_3 , it is expected that the percentage of artifact chloride ion over true chloride ion concentration must be greater than the percentage of artifact nitrate over the actual nitrate concentration in either PM_{10}^{HV} , PM_{10}^{DICH} or $PM_{2.5}^{DICH}$. The above experimental data indicate this is actually the case. The percentage of artifact chloride ion is about 1.7 times the percentage of artifact nitrate in both PM_{10}^{HV} and PM_{10}^{DICH} , while the percentage of artifact chloride is about 2.5 times the percentage of artifact nitrate in $PM_{2.5}^{DICH}$.

Ammonium ion artifact

As Table 1 and Fig. 1g demonstrate, the ammonium ion concentration measured by the hi-vol PM_{10} is lower than that by the ADS_{10} . The ratio of concentration measured by the hi-vol PM_{10} to that by the ADS_{10} averages approximately 83%. The average loss is about 17%. An additional 8% loss of ammonium ion occurs during 24 h sampling.

Ammonium ion concentration measured by the Dichot₁₀ is lower than that by the ADS_{10} . Loss of ammonium ion is about 21% in PM_{10}^{DICH} , which is only about 4% more than that in PM_{10}^{HV} . Table 2 and Fig. 1h reveal that ammonium ion concentration measured by the Dichot_{2.5} is lower than that by the $ADS_{2.5}$. Artifact ammonium ion in $PM_{2.5}^{DICH}$ average 18% of ammonium ion concentration. The above data suggest that absorption of NH_3 by acidic particles in $PM_{2.5}^{DICH}$ can reduce ammonium ion loss due to volatilization and chemical interactions in PM_{10}^{DICH} .

Comparison of experimental data with theoretical predictions for volatilization loss

Zhang and McMurry (1992) theoretically analyzed volatilization losses of species from filter and impactor samples during sampling. The sampling efficiency, η_e , for filter sampler can be expressed as

$$\eta_e = \frac{1}{1 + \xi[S + (1 - S)/\delta]\bar{\rho}_e/C_m} \quad (4)$$

where $\xi = \Delta P/(P_0 - \Delta P)$; $\delta = \Delta P/P_0$; ΔP denotes the pressure drop across the filter; P_0 represents the inlet pressure; δ is a dimensionless parameter defined as $\Delta P/P_0$. S , which equals $\bar{\rho}_0/\bar{\rho}_e$, is the average saturation ratio at the sampler inlet; $\bar{\rho}_e$ is the time-average equilibrium gas-phase concentration and $\bar{\rho}_0$ denotes the time-average gas-phase concentration at the sampler inlet. $S = 0$ for denuded filter such as the ADS; $S = 1$ for undenuded filter such as the hi-vol PM_{10} . C_m is the species concentration in particle-phase on the filter. This theory can only predict volatilization loss.

Figure 2 compares the experimental and theoretical sampling efficiencies of nitrate and ammonium ion by the first Teflon filters of the $ADS_{2.5}$ and ADS_{10} sampler. The average equilibrium gas-phase concentration, $\bar{\rho}_e$, is assumed to be equal to the concentration measured by the ADS while C_m is the particle concentration on the Teflon filter of the ADS. A significant portion of the experimental data indicates that the theory of pure volatilization loss for nitrate underestimates the nitrate loss. This observation corresponds to earlier discussion involving particle-particle or particle-gas reactions (equations (1)–(3)) which produce an additional evaporation loss of nitrate during sampling. However, in this study, theoretical sampling efficiencies of ammonium ion are lower than the experimental data. A possible explanation is that

non-volatile ammonium species coexist with volatile ammonium nitrate or ammonium chloride. In this study, the ratio of ammonium ion concentration to that of nitrate averages at 4.65 and 2.50 for $ADS_{2.5}$ and ADS_{10} , respectively. Nonvolatile ammonium salts such as $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4 could also exist in the collected Teflon samples by the $ADS_{2.5}$ and ADS_{10} . These nonvolatile species tend to increase the sampling efficiency of ammonium ion.

Figure 3 compares the theoretical with experimental sampling efficiencies of particulate nitrate for hi-vol PM_{10} and Dichot $_{2.5}$ samplers. Average pressure drops across the filters of the hi-vol PM_{10} and Dichot $_{2.5}$, which are 33 and 104 cm H_2O respectively, are substituted into the corresponding equation to calculate the upper theoretical curves in Fig. 3 assuming $S = 1$. According to these curves, theoretical sampling efficiency assuming pure volatilization loss overestimates experimental data to a great extent. Gas-particle as well as particle-particle interactions account for this discrepancy.

In Fig. 3, lower theoretical curves are calculated assuming $S = 0$ which corresponds to the case of denuded filter samplers. Coincidentally, the theoretical curve becomes more agreeable to experimental data. However, many data points are still below the lower curves, again indicating the importance of additional loss due to chemical interactions.

Influence of artifact on PM_{10} concentration

Assessing whether artifacts involving ionic species influence PM_{10} concentration is of worthwhile interest. Figure 4 sums up the concentrations of positive and negative artifacts and compares them with 24 h average PM_{10} concentrations determined by the Wedding beta gauge PM_{10} monitor (Wedding and Weigand, 1993). Although artifact formation is severe,

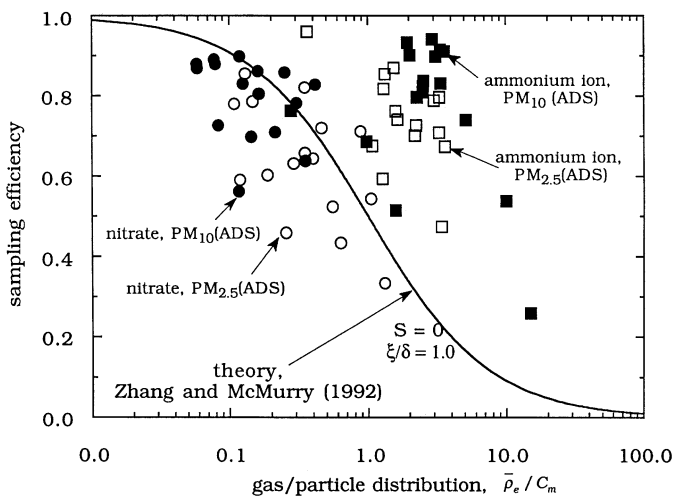


Fig. 2. Comparison of theoretical and experimental sampling efficiencies of nitrate and ammonium ion for PM_{10}^{ADS} and $PM_{2.5}^{ADS}$.

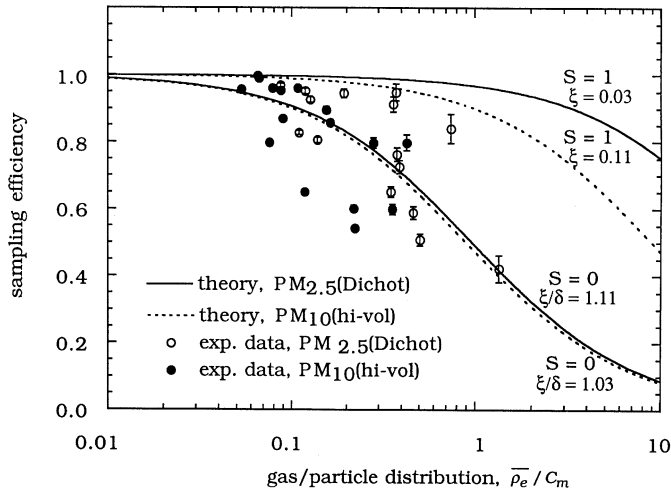


Fig. 3. Comparison of theoretical and experimental sampling efficiencies of nitrate for $\text{PM}_{10}^{\text{HV}}$ and $\text{PM}_{2.5}^{\text{DICH}}$.

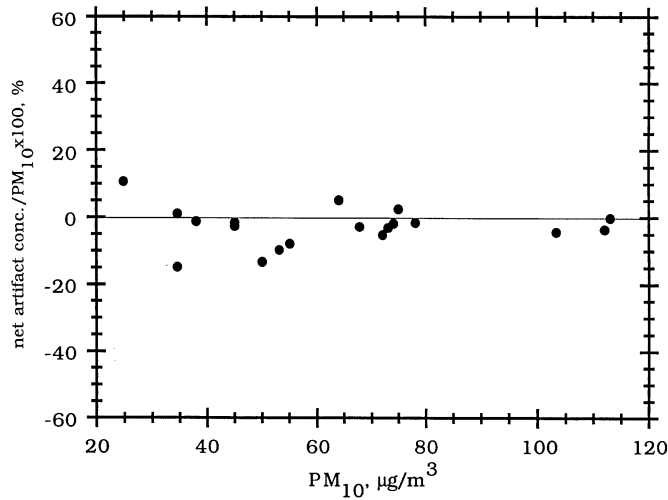


Fig. 4. Percentage of net artifact concentration over PM_{10} concentration.

positive and negative artifacts seem to cancel each other. The amount of net artifact does not account for more than 15% of PM_{10} concentration when PM_{10} is less than $60 \mu\text{g m}^{-3}$. Moreover, the amount of net artifact is less than 10% of PM_{10} concentration when PM_{10} exceeds $60 \mu\text{g m}^{-3}$.

CONCLUSIONS

This study employs diffusion denuders to assess the sampling artifact of ionic species in the widely used Andersen hi-vol PM_{10} and PM_{10} Dichot samplers in field conditions. The high-volume PM_{10} sampler used quartz fiber filters and PM_{10} dichotomous sampler used Teflon filters.

Experimental results indicate that the percentage of positive sulfate artifact over the actual sulfate concentration is 11, 8 and +15% for $\text{PM}_{10}^{\text{HV}}$, $\text{PM}_{10}^{\text{DICH}}$, $\text{PM}_{2.5}^{\text{DICH}}$, respectively. Apparently, SO_2 is absorbed by alkaline particles collected on filters during sampling since both quartz and Teflon filters do not absorb SO_2 . For nitrate species, the percentage of negative artifact over the actual nitrate concentration is -16, -21 and -21% for $\text{PM}_{10}^{\text{HV}}$, $\text{PM}_{10}^{\text{DICH}}$, $\text{PM}_{2.5}^{\text{DICH}}$, respectively. More loss in the Dichot suggests that retention of HNO_3 or nitrogen species on alkaline particles of the hi-vol PM_{10} may be important and interactions of nitrate species with acidic gases or particles is significant.

Loss of chloride ion is the most severe among the species investigated. The percentage of negative

chloride ion artifact concentration over the actual chloride ion concentration is -24 , -32 and -54% for PM_{10}^{HV} , PM_{10}^{DICH} , $PM_{2.5}^{DICH}$, respectively. More loss in PM_{10}^{DICH} than PM_{10}^{HV} suggests that retention of HCl on alkaline particles may be more important in the hi-vol PM_{10} than in the $Dichot_{10}$. Also chemical interactions that release HCl are significant in the $Dichot_{2.5}$. The percentage of negative ammonium ion artifact concentration over the actual ammonium ion concentration is -17 , -21 and -18% for PM_{10}^{HV} , PM_{10}^{DICH} , $PM_{2.5}^{DICH}$, respectively, for ammonium ion species. The above data suggest that the absorption of NH_3 by acidic particles in $PM_{2.5}^{DICH}$ can reduce ammonium ion loss due to volatilization and chemical interactions in PM_{10}^{DICH} .

Regarding artifact formation due to 24 h conditioning at $20 \pm 3^\circ C$ and $40 \pm 5\%$ RH of hi-vol PM_{10} samples, no sulfate artifact is found. However, for a volatile species, loss is not negligible. During 24 h conditioning, the percentage of artifact concentration of a species over the actual species concentration is about 5, 6 and 8% for nitrate, chloride ion and ammonium ion, respectively.

Theoretical sampling efficiency of nitrate species of the hi-vol PM_{10} and $Dichot$ samplers assuming pure volatilization loss overestimates the experimental data to a great extent. Gas-particle as well as particle-particle interactions account for this discrepancy. For ammonium species, besides involvement in chemical interactions, determining nonvolatile ammonium species concentration is essential to accurately predict volatile loss.

Although artifact formation is severe, the amount of positive and negative artifacts seem to cancel each other. Results in this study reveals that the amount of net artifact does not account for more than 15% of PM_{10} concentration.

Coarse particle losses in the denuder tubes may occur which result in uncertainty in the results reported in this study. In the future study, the impact of particle losses in denuder tubes on sampling errors of different particle species will be assessed.

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