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# Sampling and conditioning artifacts of PM<sub>2.5</sub> in filter-based samplers

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### ABSTRACT

Field studies were conducted at Taiwan National Chiao-Tung University (NCTU) campus to evaluate the evaporation loss of fine particles (PM<sub>2.5</sub>) collected by the multi-filter PM<sub>10</sub>–PM<sub>2.5</sub> sampler (MFPPS), which was collocated with a dichotomous sampler (Dichot, Andersen, Model SA-241), a WINS PM<sub>2.5</sub> sampler (Thermo, Model 2000-FRM), and a tapered element oscillating microbalance with the filter dynamic measurement system (TEOM-FDMS, Thermo, Model 1405-DF). Porous-metal denuder samplers (PDSs) were installed in sampling channels of the MFPPS to measure the concentration of evaporated ion species. Results showed that the evaporation loss in PM<sub>2.5</sub> was severe during sampling, accounting for 5.8–36.0% of the corrected PM<sub>2.5</sub> concentration and the percentage increased with decreasing loaded particle mass and increasing filtration velocity. During 24-h sampling, the evaporated NH<sup>4</sup><sub>4</sub>, NO<sup>3</sup><sub>3</sub> and Cl<sup>-</sup> concentrations accounted for 9.5  $\pm$  6.2, 5.4  $\pm$  3.7, and 2.0  $\pm$  1.3% in corrected PM\_{2.5} concentration, respectively, or  $46.4 \pm 19.2$ ,  $66.9 \pm 18.5$ , and  $74.4 \pm 14.0\%$  in the concentration of each species, respectively. Due to the evaporation loss, PM<sub>2.5</sub> concentrations measured by the WINS, Dichot, and MFPPS were lower than those the TEOM-FDMS by 16.6  $\pm$  9.0, 15.2  $\pm$  10.6 and 12.5  $\pm$  8.8%, respectively. When the MFPPS PM<sub>2.5</sub> concentrations were corrected for the evaporated loss determined by the PDS, good agreement with those by the TEOM-FDMS was achieved.

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### 1. Introduction

PM<sub>2.5</sub> standards have been promulgated in many countries around the world, where USA-designated FRM (federal reference method) samplers are normally used for determining the compliance with the standards. However, the measurement accuracy of the FRM samplers may be influenced by sampling artifacts, since these filter-based samplers only use a single filter to collect sample for gravimetric analysis (Watson and Chow, 2011).

While there are no sampling artifacts exist for elements (Tsai et al., 1997; Chen et al., 2010a, 2010b), positive and negative artifacts occur for organic and inorganic species. Positive artifacts are due to the absorption of gaseous organic carbon (OC) or inorganic gases by the sampling media and collected particles. Several denuders have been developed to absorb these interference gases. For example, the activated charcoal diffusion denuder (Eatough et al., 2001) was used to absorb gas-phase OC; while the annular denuder (Possanzini et al., 1983), coiled denuder (Pui et al., 1990), honeycomb denuder (Koutrakis et al., 1993), and porous-metal denuder (PMD) (Tsai et al., 2001a; Tsai et al. 2001b, 2003; Huang et al., 2001) were used to absorb inorganic acid and basic gases.

Negative artifact is mainly caused by the loss of semi-volatile material (SVM) during sampling. When a denuder is placed upstream of the sampling filter to eliminate the positive artifact, more negative artifact will be induced since the removal of gaseous species disturbs the gas-particle equilibrium and enhances the evaporation of the collected SVM (Zhang and McMurry, 1991; Yu et al., 2006). Although these losses may to some degree be compensated by the water retained in the collected aerosols even the filters are conditioned for 24-h at the controlled relative humidity (RH) of 30-40% (Malm et al., 2011), yet there is lack of experimental validation. One or more backup filters are usually employed to capture the evaporated SVM from the particles collected on the front filter. For example, the carbon impregnated glass fiber filter (CIG) (Eatough et al., 2001) or the XAD impregnated quartz filter (XAD-Q) (Swartz et al., 2003) are used to capture semivolatile organic material (SVOM); semi-volatile inorganic material (SVIM) such as HCl and HNO<sub>3</sub> can be captured by the nylon filter, and NH<sub>3</sub> can be captured by the citric acid coated glass fiber filter (Tsai and Perng, 1998; Tsai et al., 2000).



Technical note







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The factors influencing the extent of evaporation loss from collected particles have been evaluated in many previous studies, such as the upstream particle concentration (Cheng and Tsai, 1997), filter face velocity (V<sub>f</sub>) (Ashbaugh and Eldred, 2004), pressure drop across the filter and the equilibrium ratio of the gas to particle concentrations of the volatile species (Zhang and McMurry, 1991), etc. Ashbaugh and Eldred (2004) evaluated the sampling results of the California Acid Deposition Monitoring Program (CADMP, V<sub>f</sub>: 23.8 cm s<sup>-1</sup>) and the Interagency Monitoring of Protected Visual Environments (IMPROVE,  $V_f$ : 100 cm s<sup>-1</sup>) and concluded that the differences in the face velocity did not affect NH<sub>4</sub>NO<sub>3</sub> volatilization. However, similar study conducted by Malm et al. (2011), who evaluated the sampling results of the IMPROVE sampler and the Chemical Speciation Network (CSN) samplers ( $V_{\rm f}$ : 9.5–23.7 cm s<sup>-1</sup>), suggested that filter face velocities had a potential effect on the extent of OC evaporation loss. Therefore, the effect of filter face velocity on the evaporation loss deserves further investigation to clarify this issue.

In addition to sampling process, SVM may also evaporate from collected particles during subsequent sample storage or conditioning processes. Witz et al. (1990) found when the high-vol PM<sub>10</sub> quartz filter samples were stored at room temperature and in the laboratory air for one week, the losses of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> were 51, 19, and 65%, respectively. However, when the high-vol PM<sub>10</sub> quartz filter samples were conditioned at  $20 \pm 3$  °C and  $40 \pm 5\%$  RH for 24-h, the percentage of the evaporated species concentration over the actual species concentration was less, which was 8, 5, and 6% for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>, respectively (Tsai and Perng, 1998). Since most of the existing PM<sub>2.5</sub> samplers use the Teflon filters to collect particles, it would be of value to evaluate the evaporation loss effect on PM<sub>2.5</sub> concentration using Teflon filters during the conditioning process.

Beside manual denuder samplers mentioned above, a real-time PM monitor named tapered element oscillating microbalance with filter dynamic measurement system (TEOM-FDMS) is also able to correct for the sampling artifacts for an accurate determination of PM concentrations as demonstrated in previous studies (Grover et al., 2005; Clements et al., 2012). In this study, the artifacts of PM<sub>2.5</sub> and ion species during sampling by manual samplers using Teflon filters and subsequent conditioning process were evaluated. The effects of both filtration velocity and loaded particle mass on the extent of the evaporation loss were also examined. Finally, the PM<sub>2.5</sub> concentrations measured by the filter-based samplers were compared with those of the TEOM-FDMS.

### 2. Experimental method

The multi-filter  $PM_{10}$ – $PM_{2.5}$  sampler (MFPPS, Liu et al., 2011) was collocated with other instruments at National Chiao-Tung University (NCTU) campus, Taiwan, from June 2012 to May 2013 for 24-h sampling to evaluate the artifacts of  $PM_{2.5}$  and chemical species. These included a dichotomous sampler (Dichot, Andersen, Model SA-241), a WINS  $PM_{2.5}$  sampler (WINS, Thermo, Model 2000-FRM) and a TEOM-FDMS (Thermo, Model 1405-DF). Detailed operation procedure for each instrument can be seen in the supplementary material. The sampling site in NCTU campus is far away (about 1 km) from a heavy-traffic road and inorganic species dominates at this site as found in our previous work (Liu et al., 2013).

In this study, only four MFPPS PM<sub>2.5</sub> channels were used, and some of the filter cassettes were replaced by the porous-metal denuder sampler (PDS, Tsai et al., 2003). As shown in Fig. 1, when aerosols enter the PDS, acid and basic interference gases are first absorbed by Na<sub>2</sub>CO<sub>3</sub> and citric acid coated porous-metal discs. Then aerosols are collected by the front Teflon filter, and acid and basic



Fig. 1. Schematic of the porous-metal denuder sampler (PDS).

gases evaporated from the particles on the front Teflon filter are captured by the backup Nylon and citric acid coated glass fiber filters, respectively.

To meet different sampling purposes, two configurations for the MFPPS PM<sub>2.5</sub> channels were used as summarized in Table 1. In configuration A. only channel 2 was replaced by the PDS while the other channels used the original Teflon filter cassettes, and the collected samples were used to evaluate the PM<sub>2.5</sub> artifacts during sampling and subsequent conditioning process. To examine the effect of filtration velocity on evaporation loss, the PM<sub>2.5</sub> channels were arranged as configuration B, where all sampling channels were replaced by the PDSs except channel 1. These PDSs were operated at the same flow rate of 4.17 L min<sup>-1</sup> but different filtration velocities (V<sub>f</sub>). The V<sub>f</sub> of the PDS in channel 2 was maintained at the original value of 10 cm  $s^{-1}$  (effective filter diameter: 29.8 mm). For the PDS in channel 3  $(PDS_W)$  and channel 4  $(PDS_D)$ , the front surface of the Teflon filter was covered by a circular plastic sheet with an opening of 20.0 and 14.9 mm in diameter, respectively, to achieve the same filtration velocity as that of the WINS and Dichot, which is 22 and 36 cm  $s^{-1}$ , respectively. The analytical methods of each filter sample are also described in Table 1.

For gravimetric analysis, Teflon filters were weighed by a microbalance (Model CP2P-F, Sartorius, Germany) before and after 24-h sampling after the samples were conditioned for at least 24-h in an environment conditioning room where the RH and temperature were kept at  $40 \pm 2\%$  and  $21 \pm 1$  °C, respectively. The electrostatic charge of the Teflon filters was eliminated by an ionizing air blower (Model CSD-0911, MELSEI, Japan) before weighing. The precision of weighing was determined to be 2 µg by repeated weighing for at least five times.

After gravimetric analysis of the filter samples, an ion chromatograph (IC, Model DX-120, Dionex Corp, Sunnyvale, CA) was used to analyzed ionic species including  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $NH_4^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  for the extraction samples. For the PDS samples, the front Teflon filters were analyzed as described above, while the second nylon filters were extracted with anion eluant to efficiently extract chloride and nitrate. The third citric coated glass fiber filters were extracted with distilled deionized water for ammonium analysis. All of these extracted samples were also analyzed by the IC.

### 3. Result and discussion

The comparison of  $PM_{2.5}$  concentrations measured by the MFPPS ( $PM_{2.5,MT1}$ ,  $PM_{2.5}$  collected on the Teflon filter of the MFPPS and analyzed gravimetrically after 24-h conditioning) with those by the Dichot ( $PM_{2.5,D}$ ) and WINS ( $PM_{2.5,W}$ ) are shown in Fig. S1 of the supplementary material, which shows that  $PM_{2.5,MT1}$  agrees well with  $PM_{2.5,D}$  and  $PM_{2.5,W}$ . In addition, from the aerosol composition data (see Fig. S2 in supplementary material), it is expected that the effect of SVOM evaporation on the  $PM_{2.5}$  measurement accuracy is

Table 1

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Channel	Configuration	Assembly	Analytical method
1	A <sup>a</sup> , B <sup>b</sup>	Teflon filter	Weighed and extracted after 24-h conditioning.
2	A, B	PDS ( $V_{\rm f}$ : 10 cm s <sup>-1</sup> )	All filters were extracted immediately after sampling.
3	Α	Teflon filter	Extracted immediately after sampling.
	В	PDS ( $V_{\rm f}$ : 22 cm s <sup>-1</sup> )	All filters were extracted immediately after sampling.
4	Α	Teflon filter	Weighed after 24, 48, 72, 96 and 120-h, and extracted after
			120-h conditioning.
	В	PDS ( $V_{\rm f}$ : 36 cm s <sup>-1</sup> )	All filters were extracted immediately after sampling.

Configurations of MFPPS PM<sub>2.5</sub> channels for different sampling needs.

<sup>a</sup> Configuration A was used to evaluate the evaporation loss of inorganic species during conditioning process.

<sup>b</sup> Configuration B was used to examine the effect of filtration velocity on evaporation loss of inorganic species.

not as important as that of SVIM at this sampling site. Therefore only the evaporation loss of SVIM was evaluated in this study.

The comparison of ion concentrations in the denuded Teflon

filter (C<sub>ion.MdT</sub>, ion concentration in the front Teflon filter of the PDS)

with those in the un-denuded Teflon filter (Cion,MTO, ion concentra-

tion in the Teflon filter of the MFPPS that is extracted immediately after sampling) and the actual ion concentrations ( $C_{\text{ion, actual}}$ ) is

shown in Fig. 2, in which  $C_{\text{ion, actual}}$  is the sum of  $C_{\text{ion,MdT}}$  and the

concentration of ion species collected on the backup nylon and glass

fiber filters of the PDS in the MFPPS ( $C_{ion,Md(N+G)}$ ). It shows that only

NO $_3^-$  has a higher  $C_{ion,MT0}$  than  $C_{ion,MdT}$  by 21.0  $\pm$  34.55% in average,

while C<sub>ion,MT0</sub> and C<sub>ion,MdT</sub> of other species are very close with an

3.1. Artifacts during sampling

# average difference of less than 6.5% (open symbols in Fig. 2). This indicates that only positive NO<sub>3</sub> artifact exists in the un-denuded Teflon filter due to gaseous HNO<sub>3</sub> absorption by collected particles, accounting averagely for $0.4 \pm 0.4\%$ and $5.0 \pm 6.5\%$ of the "corrected" PM<sub>2.5</sub> concentration measured by the MFPPS (PM<sub>2.5,Mcorr</sub>) and actual NO<sub>3</sub> concentration, respectively. PM<sub>2.5,Mcorr</sub> is PM<sub>2.5,MT1</sub> corrected for the evaporated ion species measured by the PDS installed in the MFPPS, or the sum of PM<sub>2.5,MT1</sub> and C<sub>ion,Md(N+G)</sub> concentrations. It can be also observed that C<sub>ion, actual</sub> is significantly higher than C<sub>ion,MdT</sub> for NH<sup>‡</sup>, NO<sub>3</sub> and Cl<sup>-</sup> species (filled symbols in Fig. 2), indicating that the evaporation loss during sampling is severe for these species. Difference in SO<sup>2</sup><sub>4</sub><sup>-</sup> concentrations is insignificant since it is a non-volatile species. The evaporated NH<sup>‡</sup>, NO<sub>3</sub> and Cl<sup>-</sup> account averagely for 9.5 $\pm$ 6.2, 5.7 $\pm$ 3.6, and 2.0 $\pm$ 1.3% of PM<sub>2.5,Mcorr</sub>, respectively; and 46.4 $\pm$ 19.2, 68.8 $\pm$ 19.9, and



**Fig. 2.** Comparison of the ion concentrations in the denuded Teflon filter ( $C_{ion,MdT}$ ) with those in the un-denuded Teflon filter ( $C_{ion,MT0}$ ) and the actual ion concentration ( $C_{ion, actual}$ ). (a) NH<sub>4</sub><sup>+</sup> (b) NO<sub>3</sub><sup>-</sup> (c) Cl<sup>-</sup> (d) SO<sub>4</sub><sup>2-</sup> (number of samples: 26).



Fig. 3. Percentage of evaporated  $PM_{2.5}$  in  $PM_{2.5,Mcorr}$  versus the number of sample conditioning days (number of samples: 20).

74.4  $\pm$  14.0% of C<sub>ion, actual</sub> of each species, respectively. By summing up all evaporated ion species, total ion loss during sampling is found to account for 17.0  $\pm$  8.0% of PM<sub>2.5,Mcorr</sub> in average.

### 3.2. Evaporation loss during filter conditioning process

To evaluate the evaporation loss of PM<sub>2.5</sub> during filter conditioning, the samples in channel 3 of the MFPPS were analyzed gravimetrically after conditioning for 24, 48, 72, 96, and 120 h. The results are shown in Fig. 3 where the percentage of evaporated mass concentration (y-axis) is calculated based on evaporated PM<sub>2.5</sub> concentration divided by PM<sub>2.5,Mcorr</sub>. The samples of non-volatile TiO<sub>2</sub> (AERODISP<sup>®</sup> P25, Degussa, Germany) and Al<sub>2</sub>O<sub>3</sub> (QF-Al-8000, Sipernat, Japan) particles, which were generated by a small scale powder disperser (SSPD, Model 3433, TSI) and collected on Teflon filters, were also weighed and the results are plotted in the figure for comparison. It can be seen that during the sample conditioning process, the mass of non-volatile metal powder Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> samples did not change while it decreased with conditioning days in PM<sub>2.5</sub> samples. Since Teflon filter samples must be conditioned for at least 24-h before weighing, the evaporated PM<sub>2.5</sub> concentration within the first 24-h was determined by the difference in total ion concentrations obtained immediately after sampling and those after 24-h conditioning, which averages  $3.3 \pm 1.8\%$  of PM<sub>2.5,Mcorr</sub> as will be explained in the next paragraph. For conditioning longer than 24-h, the evaporated PM<sub>2.5</sub> concentration was determined by the difference in PM<sub>2.5</sub> mass concentrations measured after 24-h conditioning and those after the conditioning hours of interest. Results show that PM<sub>2.5,Mcorr</sub> concentrations are further decreased by 5.1  $\pm$  1.7, 6.2  $\pm$  2.5, 7.4  $\pm$  3.3 and 8.5  $\pm$  3.2% after 48, 72, 96, and 120-h conditioning, respectively.

The loss of ion species concentrations after the filter samples were conditioned for 24 and 120-h was also evaluated and the results are shown in Fig. S3 of the supplementary material. Results show that except non-volatile  $SO_4^{2-}$  species, the evaporation loss during conditioning process can be observed for other species. The percentages of evaporated species concentration over Cion, actual account for -4.0  $\pm$  4.3 and -7.6  $\pm$  6.7% for NH\_4^+, -8.0  $\pm$  7.1 and  $-14.3 \pm 11.6\%$  for NO<sub>3</sub>, and  $-4.0 \pm 3.8$  and  $-5.7 \pm 4.7\%$  for Cl<sup>-</sup>, respectively, after the samples were conditioned for 24-h and 120h. By summing up the concentrations of all evaporated species, the total evaporated ion concentration accounts for 3.3  $\pm$  1.8 and 5.4  $\pm$  5.3% of PM<sub>2.5,Mcorr</sub> in average, respectively, after 24-h and 120-h conditioning. It is also found that for the samples conditioned for 120-h, the percentage of total evaporated ion concentration in  $PM_{2.5,Mcorr}$  (5.4  $\pm$  5.3%) is slightly lower than that of total evaporated mass concentration in PM\_{2.5,Mcorr} (8.5  $\pm$  3.2%). This indicates that during conditioning process, other semi-volatile species such as SVOM or the remaining water contained in the collected particles may also lead to evaporate loss. This evaporation loss was estimated as the difference between the total evaporated mass concentration and total evaporated ion concentrations, and was found to be 4.0  $\pm$  3.1% of PM\_{2.5,Mcorr} in average after the samples were conditioned for 120-h.

# 3.3. Effects of filter face velocity and loaded particle mass on the evaporation loss

The evaporated ion concentration during sampling (PM<sub>2.5,Md(N+G)</sub>) measured by the PDSs with different filtration velocities are shown in Fig. 4(a). It can be seen that the evaporated ion concentration increases with increasing  $V_{\rm f}$  and the evaporated ion concentrations measured by the PDS<sub>W</sub> ( $V_{\rm f} = 20 \ {\rm cm \ s^{-1}}$ ) and PDS<sub>D</sub> ( $V_{\rm f} = 36 \ {\rm cm \ s^{-1}}$ ) are higher than those the PDS ( $V_{\rm f} = 10 \ {\rm cm \ s^{-1}}$ ) by 16.3  $\pm$  10.5 and 33.4  $\pm$  11.7% in average, respectively. To further



Fig. 4. Relationship between  $V_{\rm f}$  and (a) evaporated ion concentration or (b) actual ion concentration (number of tests: 6).



**Fig. 5.** Relationship between PM<sub>2.5,MT1</sub> and the fraction of evaporated ion species in PM<sub>2.5,Mcorr</sub> (number of samples: 26).

validate the measurement precision of the PDSs, the actual ion concentrations, or  $C_{\text{ion, actual}}$ , measured by the PDSs are also compared with each other as shown in Fig. 4(b). It can be seen that  $C_{\text{ion, actual}}$  measured by the PDSs are in good agreement in all 6 test runs. The ANOVA tests also show no significant differences (p > 0.05) for all 6 sets of PDS samples. This gives an addition support that the difference in the ion concentrations on the backup filters of the PDSs is mainly caused by the different extent of particle evaporation loss from the particles on the front Teflon filter, rather than the measurement uncertainties.

To evaluate the effect of loaded particle mass on the extent of the evaporation loss, the fraction of  $C_{\text{ion,Md}(N+G)}$  in PM<sub>2.5,Mcorr</sub> is plotted versus PM<sub>2.5,MT1</sub>, as shown in Fig. 5. It shows that the evaporation percentage ranges from 5.8 to 36.0% (average: 16.9  $\pm$  8.0%), and a clear trend of increasing percentage with decreasing PM<sub>2.5,MT1</sub> can be observed. This is because when PM<sub>2.5</sub> mass concentration is low, a thinner particle cake formed on the filter will have a larger mass transfer Sherwood number (*Sh*) resulting in more evaporation loss. In contrast, when PM<sub>2.5</sub> mass

concentration is high, a thicker particle cake is formed during sampling and the evaporation will proceed at a slower rate due to a smaller *Sh* (Cheng and Tsai, 1997).

# 3.4. Comparison of $PM_{2.5}$ concentration by the TEOM-FDMS with those by manual samplers

The comparison of PM2.5 concentrations measured by the TEOM-FDMS (PM<sub>2.5.F(b-r)</sub>, PM<sub>2.5</sub> concentrations determined by the base mode corrected for those by the reference mode.) with  $PM_{2.5,MT1}$  and PM<sub>2.5.Mcorr</sub> is shown in Fig. 6. Base and reference modes are two measurement modes in the TEOM-FDMS, in which the former is used to determine the PM mass concentration that is not corrected for sampling artifacts while the latter is used to determine the sampling artifacts for correction. More detailed operation procedure of the TEOM-FDMS can be seen in section 1 of the supplementary material. It is not surprising to see that PM<sub>2.5,MT1</sub> is consistently lower than PM<sub>2.5,F(b-r)</sub>, because of the evaporation loss of SVM during sampling and filter conditioning processes in the filter-based sampler as mentioned above. Similar results were also found in Grover et al. (2005) who conducted the comparison tests by a FRM sampler and a TEOM-FDMS (Model 8500, Rupprecht & Patashnick, Co., Inc.) at Rubidoux, CA., USA. In average, PM<sub>2.5.MT1</sub> is lower than  $PM_{2.5.F(b-r)}$  by 12.5  $\pm$  8.8%. In comparison the  $PM_{2.5}$  concentrations measured by the FRM sampler were found to be lower than those of the TEOM-FDMS by  $33.7 \pm 9.1\%$  in Grover et al. (2005). Less undermeasurement of PM<sub>2.5</sub> concentrations by the MFPPS than that in Grover et al. (2005) is possibly due to the differences in TEOM-FDMS models, filtration velocities and aerosol chemical composition. This issue deserves further investigation in the future. Similar undermeasurements of PM<sub>2.5</sub> concentrations by the Dichot  $(15.2 \pm 10.6\%)$  and WINS  $(16.6 \pm 9.0\%)$  than those by the TEOM-FDMS also exist as can be seen in Fig. S4 of the supplementary material.

After correcting  $PM_{2.5,MT1}$  for the PDS-determined evaporated ion concentration,  $C_{ion,Md(N+G)}$ ,  $PM_{2.5,Mcorr}$  is obtained and is found to be close to but slightly higher than  $PM_{2.5,F(b-r)}$  by  $5.4 \pm 7.0\%$  as shown in the figure. This is due to the overestimated artifacts determined by the PDS since  $C_{ion,Md(N+G)}$  is the ion concentration evaporated from the particles collected on the denuded Teflon filter, and is higher than that evaporated from the un-denuded  $PM_{2.5,MT1}$  Teflon filter.



**Fig. 6.** Comparison of  $PM_{2.5}$  concentrations measured by the TEOM-FDMS with those by the MFPPS with or without PDS correction (number of samples: 26).



**Fig. 7.** Relationship between the concentration of evaporated ion species measured by the PDS ( $C_{ion,Md(N+G)}$ ) of the MFPPS and that by the TEOM-FDMS ( $PM_{2.5,Fr}$ ) (number of samples: 26).

Finally, to compare the SVM concentrations measured by the PDS and those by the TEOM-FDMS,  $C_{ion,Md(N+G)}$  is plotted versus the reference mode concentrations of the TEOM-FDMS (PM<sub>2.5,Fr</sub>) as shown in Fig. 7. It is observed that the former is lower than the latter by 11.0  $\pm$  8.1% in average, which means that more SVM was evaporated from the TEMO-FDMS than that from the PDS. This is again due to the effect of  $V_f$  on the evaporation loss, since  $V_f$  of the TEOM-FDMS (37.7 cm s<sup>-1</sup>) is about 3.8 times higher than that of the PDS (10 cm s<sup>-1</sup>).

### 4. Conclusion

In this study, the MFPPS collocated with the Dichot, WINS and TEOM-FDMS was employed to evaluate the sampling artifacts of  $PM_{2.5}$  mass and ionic species concentrations and to examine the effects of filtration velocity and loaded mass on the extent of evaporation loss.

Results show that during sampling, the positive artifact is not important for PM<sub>2.5</sub> mass concentration, and exists in NO<sub>3</sub><sup>-</sup> species only, which is  $5.0 \pm 6.5\%$  of actual NO<sub>3</sub><sup>-</sup> concentration. Evaporation losses of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> were evaluated to be  $46.4 \pm 19.2$ ,  $68.8 \pm 19.9$ , and  $74.4 \pm 14.0\%$  of the C<sub>ion, actual</sub> of each species, respectively, and the sum of them were calculated to be  $17.0 \pm 8.0\%$  of corrected PM<sub>2.5</sub> (PM<sub>2.5,Mcorr</sub>) in average. For the filters conditioned for 24-h, the evaporation loss calculated by the difference in total ion concentrations between C<sub>ion,MT0</sub> and C<sub>ion,MT1</sub> was found to be  $3.3 \pm 1.8\%$  of PM<sub>2.5,Mcorr</sub>. For the samples conditioned for 48, 72, 96, and 120-h, the gravimetrically-determined evaporation loss was further increased to  $5.1 \pm 1.7$ ,  $6.2 \pm 2.5$ ,  $7.4 \pm 3.3$  and  $8.5 \pm 3.2\%$  of PM<sub>2.5,Mcorr</sub>, respectively.

The effects of filtration velocity and loaded particle mass on the extent of evaporation loss during sampling were also examined. Results show that the loss increases with increasing  $V_{\rm f}$ , and the evaporated ion species measured by the PDS<sub>W</sub> (20 cm s<sup>-1</sup>) and PDS<sub>D</sub> (36 cm s<sup>-1</sup>) are higher than those by the PDS (10 cm s<sup>-1</sup>) by 16.3  $\pm$  10.5 and 33.4  $\pm$  11.7% in average, respectively. For the effect of loaded particle mass, there is a trend that the evaporation fraction increases with decreasing PM<sub>2.5,MT1</sub> due to the effect of *Sh*.

For the comparison between the TEOM-FDMS and filter-based samplers, the present study shows that the PM<sub>2.5</sub> concentrations measured by the WINS, Dichot, and MFPPS are consistently lower than those the TEOM-FDMS by 16.6  $\pm$  9.0, 15.2  $\pm$  10.6 and 12.5  $\pm$  8.8%, respectively, due to the loss of semi-volatile species during sampling. However, when the MFPPS data are corrected with the evaporated ion concentration measured by the PDS, good agreement with those by the TEOM-FDMS is achieved. It is also found that the concentrations of semi-volatile species measured by the PDS are somewhat lower than those by the TEOM-FDMS by 11.0  $\pm$  8.1% in average due to the effect of lower *V*<sub>f</sub> in the former on the evaporation loss.

In the future, it is worthwhile to conduct similar studies at other sites which may contain more semi-volatile organic species in aerosols such as at the urban site, heavy-traffic roadside or even tunnel environment (Chen et al., 2010b; Zhu et al., 2012) to evaluate the evaporation loss of SVOM in PM<sub>2.5</sub>. In addition, the effects of filtration velocity, loaded particle mass, gaseous and PM<sub>2.5</sub> compositions on the extent of evaporation loss are also deserved to be studied theoretically since these factors normally co-exist and can't be clearly identified by experimental studies alone.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.11.075.

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