



## Performance Test of an Inertial Fibrous Filter for Ultrafine Particle Collection and the Possible Sulfate Loss when Using an Aluminum Substrate with Ultrasonic Extraction of Ionic Compounds

Kyung Hwan Kim<sup>1</sup>, Kazuhiko Sekiguchi<sup>1,2\*</sup>, Shinji Kudo<sup>1</sup>, Kazuhiko Sakamoto<sup>1,2</sup>, Mitsuhiko Hata<sup>3</sup>, Masami Furuuchi<sup>3</sup>, Yoshio Otani<sup>3</sup>, Naoko Tajima<sup>4</sup>

<sup>1</sup> Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

<sup>2</sup> Institute for Environmental Science and Technology, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

<sup>3</sup> Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

<sup>4</sup> Japanese Kanomax Inc., 2-1 Shimizu Suita, Osaka 565-0805, Japan

### ABSTRACT

A sampler using inertial fibrous filters (INF) has been recently developed for ultrafine particle collection by impaction and filtration. This new sampler has a low pressure drop (20–30 kPa) and can separate particles smaller than 0.1  $\mu\text{m}$  with a high sampling flow rate (40 L/min). In this study, sampling performance of the INF sampler was evaluated in comparison with a reference sampler in the field as well as in the laboratory and the possible sulfate ion loss when using aluminum substrates for ion extraction in ultrasonic bath was discovered and investigated. When sampling ultrafine particles ( $D_p \leq 0.1 \mu\text{m}$ ) such as carbonaceous and ionic species both in the field and in the laboratory, the performance of the INF sampler was similar to that of a reference sampler despite differences of sampling mechanism, cut-point diameter, and substrate proving that the INF sampler can be an alternative for ultrafine particle collection. Underestimation of sulfate concentration appeared to be unavoidable in ultrasonic extractions from aluminum substrates regardless of whether the extraction time was 30 or 90 min. The average sulfate loss during aluminum filter extraction was 45% ( $\pm 12\%$ ; min: 12%; max: 94%). Therefore, ultrasonic extraction from aluminum filters should be avoided to obtain unbiased measurements of sulfate concentration in ambient air or other ion extraction methods should be considered to minimize sulfate loss (dissolution of aluminum ions) from aluminum filters with sufficient extraction efficiency of ionic species.

The results of this study indicate that the performance of the INF sampler is almost similar to that of the nano-MOUDI sampler for ultrafine particle collection, while advantageous in terms of convenience, and analysis. Furthermore, the INF sampler can collect amounts of ultrafine particles that are sufficient for chemical analysis in a relatively short time, and the particles can be uniformly collected with a quartz fiber filter.

**Keywords:** Inertial classification; Ultrafine particles ( $\text{PM}_{0.1}$ ); nano-MOUDI; Sulfate loss; Aluminum substrate.

### INTRODUCTION

Ultrafine and nanoparticles present in the air due to natural sources and processes, as well as those resulting from anthropogenic activities have attracted an increasing level of interest in the last decade (Morawska *et al.*, 2008). Interest in ultrafine particles (UFPs) in aerosol science has also increased due to the possible adverse health effects of exposure to high number concentrations. For example, there is a correlation between UFPs and alterations in morbidity

and mortality indices because of respiratory and cardiac effects and there is also a correlation with increased proportion of asthma episodes and hospital admissions. What is more impressive and scientifically challenging is the latest evidence suggesting possible penetration of UFPs to the brain and central nervous system (Oberdorster *et al.*, 2004; Politis *et al.*, 2008). In order to assess the adverse health effect of UFPs, it is necessary to determine their chemical composition. However, various chemical analyses require the collection of a fairly large number of particles in order to obtain milligram quantities and achieve sufficient quantitative accuracy. As a result, collecting a sufficient mass of atmospheric UFPs requires long sampling times (Otani *et al.*, 2007).

Low pressure impactors (LPIs) and micro-orifice uniform

\* Corresponding author. Tel./Fax: +81-48-858-9542  
E-mail address: kseki@mail.saitama-u.ac.jp

deposit impactors (MOUDIs) have been developed and used to sample particles with diameters as small as 0.05  $\mu\text{m}$  (Baron and Willeke, 2005). However, analyzing UFPs is difficult due to the low particle mass at each stage as well as the long sampling times. In addition, for particles that are sensitive to evaporation at low pressure, their size is reduced during the collection process (Biswas *et al.*, 1987), and several studies have demonstrated significant evaporation loss of labile species (Biswas *et al.*, 1987; Zhang and McMurry, 1987; Zhang and McMurry, 1992; Cheng and Tsai, 1997; Chang *et al.*, 1999; Sekiguchi *et al.*, 2008). Analysis of aerosols containing carbonaceous particulates requires optical corrections to minimize charring; however, non-uniform deposition of impactor samples causes the optical charring correction scheme to be uncertain or ineffective (Chow *et al.*, 2004; Huang and Yu, 2008). Because the principal function of the optical (laser reflectance and transmittance) component of the analyzer is to correct for pyrolysis charring of organic carbon compounds into elemental carbon by continuously monitoring the filter reflectance and/or transmittance (via a helium-neon laser and a photodetector) throughout an analysis cycle (DRI standard operating procedure, 2005) thus, if a non-uniform particle deposits on the filter is used for the thermal/optical carbon analysis, there would be potential sample biases making the irregular filter reflectance and/or transmittance during the analysis cycle.

Therefore, inertial fibrous filter (INF) samplers for UFPs collection by impaction and filtration have been recently developed (Otani *et al.*, 2007) that can efficiently collect UFPs in sufficient quantities with uniform deposition with a low pressure drop (20–30 kPa) while the pressure drop of the existing samplers for UFPs collection is 70–80 kPa for LPI (Furuuchi *et al.*, 2010a) and 88 kPa for nano-MOUDI at the lowest stage (Geller *et al.*, 2002). Unlike the sampling technique used for LPI or nano-MOUDI which classifies and collects particles by either increasing the value of the slip correction, (i.e., by going to low pressures in the impactor), or by decreasing the nozzle diameter at relatively low flow rate with several stages in ultrafine particle sizes, the relatively low pressure drop for UFPs collection in the INF sampler could be achieved by utilizing the inertial filter with an optimized filtration velocity and thin fibers achieving a large inertial effect thus much lower probability of evaporation loss of labile species due to the relatively low pressure drop can be expected with the INF sampler. Furthermore, a high sampling flow rate (40 L/min) can be used to collect particles in sufficient quantities for chemical analysis with uniform deposition on a quartz fiber filter. Several studies have already evaluated the sampling mechanism and characteristics of INF sampler (Otani *et al.*, 2007; Eryu *et al.*, 2009; Furuuchi *et al.*, 2010a) whereas the sampler performance test for specific chemical species in comparison with the existing sampler for UFPs collection has not been evaluated yet.

There might be an error which has not been discovered in chemical analysis for ambient particulate matters due to lack of knowledge or understanding between the target compounds and analytical procedures. Some of these errors

in analytical procedure can produce underestimation or overestimation of the actual concentrations of target chemical compounds. The possible sulfate ion loss when using aluminum substrates for ion extraction in ultrasonic bath was discovered from a laboratory comparison experiment in this study. Thus, this sulfate loss as well as eluted aluminum ions in ammonium sulfate standard solution in presence of aluminum substrates as a function of extraction time in ultrasonic bath was also studied in this study.

The objective of this study was to evaluate the sampling performance of INF sampler in comparison with a reference sampler (nano-MOUDI) for ultrafine particle collection under laboratory-controlled conditions and in ambient air for atmospheric particle collection and to assess sulfate ion loss when using aluminum substrates for ion extraction in ultrasonic bath which discovered under laboratory comparison study.

## EXPERIMENTAL

### *Apparatus and Instrumentation*

The INF sampler (Japanese Kanomax, Osaka, Japan) consists of four impaction stages that remove particles with diameters of 10, 2.5, 1.0, and 0.5  $\mu\text{m}$ , respectively onto quartz filters equipped on each impaction stages. The performance evaluation of these four impaction stages has already been evaluated by Furuuchi *et al.* (2010a). In their study, the four impactor stages of  $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}/\text{PM}_{0.5}$  have been successfully devised with a reasonable accuracy in cutoff size and the slope of in the collection efficiency curves. Furthermore, the comparison of particle concentrations in the four impactor stages obtained by the INF sampler and other conventional samplers such as high volume sampler (HV), low volume sampler (LV), low pressure impactor (LPI), and tapered element oscillating microbalance (TEOM) for the ambient particles showed a good agreement and the discrepancies between these samplers are less than  $\pm 15\%$ . The sampler also has one inertial filtration stage composed of unwoven stainless steel fibers to remove particles larger than 0.1  $\mu\text{m}$  after the four impaction stages then consequently particles smaller than 0.1  $\mu\text{m}$  can be uniformly collected on 47 mm quartz filter. Fig. 1 shows a schematic diagram of the INF sampler.

The inside diameter of the filter cartridge is 4.75 mm, and the thickness of the stainless steel fibers (Nippon Seisen Co., Ltd., felt type, SUS-304) is 9.8  $\mu\text{m}$ . The cartridge contains 14 mg of packing fiber. Since the mesh of SUS fibers has a high mechanical strength against compression, the filter structure can be maintained at high filtration velocities (Furuuchi *et al.*, 2010). More detailed information on the development and design of INFs is available elsewhere (Otani *et al.*, 2007; Eryu *et al.*, 2009; Furuuchi *et al.*, 2010a, b).

### *Measurement of Particle Collection using INF Sampler*

The laboratory tests investigating the particle collection of the INF sampler were carried out as a confirmation experiment since development and design of INF sampler

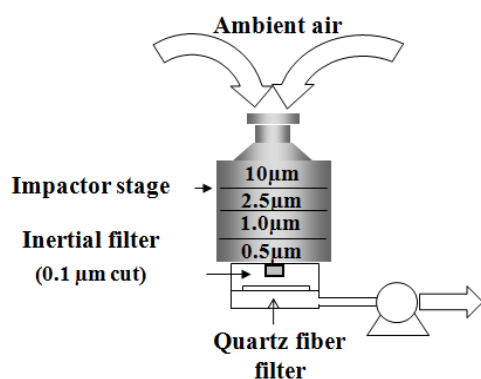


Fig. 1. Schematic of INF sampler and filter cartridge.

have been already evaluated (Furuuchi *et al.*, 2010a). Ammonium sulfate particles ( $0.02 \leq D_p \leq 0.3 \mu\text{m}$ ) were introduced into the system using an atomizer (TSI 3076, Constant Output Atomizer, MN, USA) with a 3.0 mmol/L ammonium sulfate (99.5% purity, Wako, Japan) solution. The particle collection of the INF sampler was estimated using a differential mobility analyzer (DMA) to measure the particle size distribution (TSI 3080, USA) and an ultrafine condensation particle counter (UCPC) to measure the particle number distribution (TSI 3025A, USA). Neither relative humidity nor temperature was controlled, although these parameters were monitored with a thermo-hygrometer (SM-380 multi-hygrometer, Shibaura Electronics, Tokyo, Japan). The temperature was  $27.2^\circ\text{C}$  ( $\pm 0.3^\circ\text{C}$ ) and the relative humidity was  $27.1\%$  ( $\pm 0.4\%$ ).

#### Sampling for the Performance Test of INF Sampler in the Laboratory and the Field

A nano-MOUDI (Nano-Micro orifice uniform deposit impactor, Model 125B, MSP Corporation, MN, USA) was used as the reference sampler in this experiment. The nano-MOUDI operated at 10 L/min using the manufacturer's recommended pump (SV-16, Leybold Sogevac) and classifies particles into the following size intervals: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, 0.056, 0.032, 0.018 and  $0.010 \mu\text{m}$  (MSP, 2004). The pressure drop of each stage was monitored during particle collection in order to prevent possible clogging. Ungreased aluminum (Substrate, foil 47mm, MSP) and quartz fiber (Pallflex 2500 QAT-UP, Pallflex, CT, USA) filters were purchased for nano-MOUDI. Pre-baked aluminum ( $600^\circ\text{C}$  for 3h, (Sardar *et al.*, 2005)) and quartz fiber ( $900^\circ\text{C}$  for 3h as a backup) filters with a 47 mm size were used as sampling substrates in the nano-MOUDI. In addition, pre-baked quartz fiber filters ( $900^\circ\text{C}$  for 3h) were used as sampling substrates in the INF sampler. Carbonaceous and ionic UFP concentrations ( $D_p \leq 0.1 \mu\text{m}$  for INF,  $D_p \leq 0.180 \mu\text{m}$  for nano-MOUDI) were evaluated in this study.

To measure stable and precise data at high particle concentrations, laboratory tests were conducted with ammonium sulfate particles ( $0.02 \leq D_p \leq 0.3 \mu\text{m}$ ) generated by an atomizer after stabilization of the generated particles for more than 1 h by checking the number and size distribution of introduced particles with DMA and UCPC.

The use of Teflon bag with generated particles in a chamber for the performance test enables us to observe the correlation between the two samplers for relatively high concentrations with a controlled environment. A Teflon bag with a volume of  $2 \text{ m}^3$  was used to sufficiently dilute particles in a temperature-controlled room. A detailed experimental setup for the comparison test of samplers in a chamber is shown in Fig. 2. The concentrations of ammonium sulfate solution ranged from 1.5 to 10 mmol/L.

The observed temperature and relative humidity were  $26.3^\circ\text{C}$  ( $\pm 1.0^\circ\text{C}$ ),  $27.2\%$  ( $\pm 0.9\%$ ) respectively. The sampling duration was 3 h for each test, and thus the total sampling volume was  $7.18 \text{ m}^3$  for the INF sampler and  $1.80 \text{ m}^3$  for the nano-MOUDI sampler. Both the INF and nano-MOUDI samplers were started and stopped at the same time.

Field sampling experiments were conducted on the 10<sup>th</sup> floor of the Research and Project Building at Saitama University from May to June, 2009. In order to collect sufficient mass for nano-MOUDI sampler, the sampling duration was 4 days, which corresponds to a total sampling volume of  $220.0 \text{ m}^3$  for the INF sampler and  $55.2 \text{ m}^3$  for the nano-MOUDI sampler. The filter in the INF sampler was exchanged every 23 h with a newly packed filter cartridge. When the filter was being changed, the nano-MOUDI was also stopped and started at the same time.

The ionic compounds were analyzed by ion chromatography (DX-100 Ion Chromatograph, Dionex, CA, USA). Collected particles were extracted from the filters with 15 mL of deionized water in an ultrasonic bath for 90 min at less than  $20^\circ\text{C}$  based on the result of extraction efficiency test. The ion chromatograph was calibrated prior to analysis. Standard solutions were tested prior to running experimental samples to monitor any shift in the calibration response of the instrument. Organic and elemental carbon were analyzed with a DRI thermal optical carbon analyzer (DRI Model 2001, Atmoslytic, Inc., CA, USA) based on IMPROVE protocols (Chow *et al.*, 1993) without optical corrections since optical correction cannot be used with aluminum filters. The limit of detection (LOD) for the methods was defined as the average concentration of the 7 field blanks plus three standard deviation ( $3\sigma$ ) in each analysis procedure.

#### Sulfate Loss Assessment

We carried out an experiment investigating extraction from the quartz fiber and aluminum filters since possible sulfate loss with an aluminum filter extraction in an ultrasonic bath was observed. Filters having a 47 mm size were cut and placed into 30-mL glass bottles, and 15 mL of standard ammonium sulfate solution prepared in the laboratory (sulfate concentrations: 0.80, 0.90, 2.40, 3.70  $\mu\text{g/mL}$ , based on the result obtained in the laboratory comparison experiment) was added to each bottle. The bottles were capped tightly, sealed with parafilm, and then extractions were performed for 30, 60, or 90 min in an ultrasonic bath. The concentrations of the initial standard solution and a solution subjected to the extraction conditions for 90 min in the absence of a filter were also measured. Fig. 3 describes schematic experimental procedure.

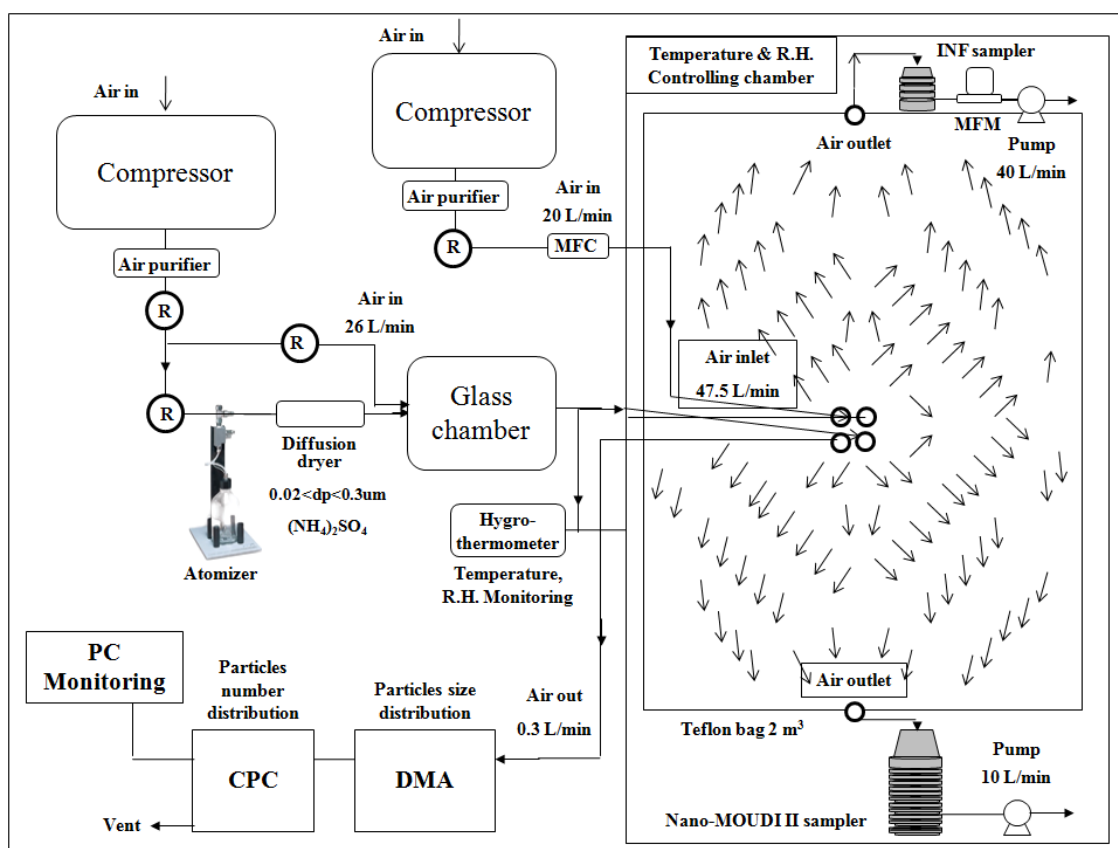


Fig. 2. Schematic of experimental setup for particle collection with INF and nano-MOUDI samplers.

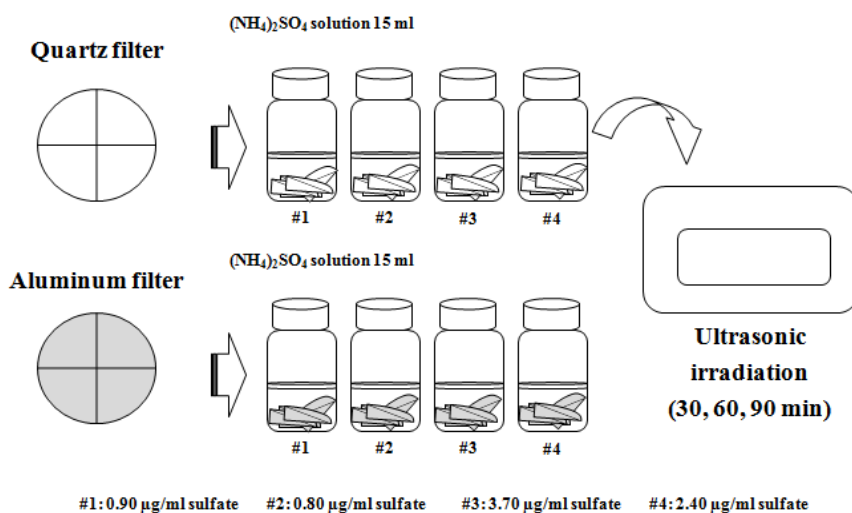


Fig. 3. Experimental procedure for the assessment of sulfate loss in presence of aluminum filters.

After the extraction, each sample was filtered by a PTFE membrane filter (DISMIC<sup>®</sup>-13HP, Advantec, Tokyo). Sulfate and ammonium concentration was analyzed by ion chromatography (Dionex, DX-100) method and each extracted solution described in Fig. 3 was adjusted to 0.1 mol/L nitric acid for the analysis of aluminum and ferrous ions as a confirmation experiment for eluted aluminum ions in the solution by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500cx series).

## RESULTS AND DISCUSSION

### Particle Collection Efficiency

Particle collection efficiency in the INF sampler was determined by measuring particle number concentration at upstream and downstream locations of the test system, and comparing the number particles at upstream and downstream of the test system with an inertial filter cartridge loaded and backup filter unloaded. Particle

penetration (%) was calculated using Eq. (1):

$$\eta = (N_{\text{out}}/N_{\text{in}})100 \quad (1)$$

where the upstream concentrations is  $N_{\text{in}}$  and the downstream concentrations is  $N_{\text{out}}$ .

The measured particle collection values obtained from INF sampler are shown in Fig. 4, although particles with diameters in the range of 0.02–0.04  $\mu\text{m}$  showed a loss of 5–10% within the sampling system. Experimental difficulties may have caused this nanoparticle loss (0.02–0.04  $\mu\text{m}$ ) within the system because there is a stage (space) between the position of backup filter and outlet of INF sampler (Fig. 1). More detailed schematic diagram of INF sampler can be also found elsewhere (Furuuchi *et al.*, 2010a). Nanoparticle ( $D_p < 40 \text{ nm}$ ) loss in this space may cause 5 to 10% loss within the experimental system because of Brownian diffusion. We believe that this loss would be minimized when the filter is loaded. The 50% cut point of INF sampler was approximately 0.07  $\mu\text{m}$  which well corresponds with the data obtained by Furuuchi *et al.* (2010a) whereas that of the nano-MOUDI sampler is between 0.10–0.18  $\mu\text{m}$  for the upper stage of UFPs.

#### **Sampler Performance Test in the Laboratory**

Comparison of the INF sampler with the reference sampler showed high correlations for UFP concentrations of ammonium ( $r^2 = 0.99$ ) and sulfate ( $r^2 = 0.99$ ). A large difference in the ammonium concentration was not observed for the two samplers (slope ( $m$ ) = 1.28), while a large difference in the sulfate concentration (slope ( $m$ ) = 0.33) was observed ( $y$ -axis: nano-MOUDI<sub>UFP</sub>;  $x$ -axis: INF<sub>UFP</sub>). A T-test also showed that there is a statistically difference between sulfate concentrations for UFPs collected by the INF and nano-MOUDI samplers whereas there is no difference between ammonium concentrations for UFPs collected by the two samplers. The observed equivalent ratio between ammonium and sulfate ions can explain the large difference in sulfate concentration for UFPs collected by nano-MOUDI<sub>UFP</sub>. The equivalent ratios observed for INF<sub>UFP</sub> showed similar concentrations of sulfate while the ratios observed for nano-MOUDI<sub>UFP</sub> were almost the same at low concentrations (1–2  $\mu\text{g}/\text{m}^3$ ) but were less than a half at the high concentrations (over 6 or 7  $\mu\text{g}/\text{m}^3$ ), as shown in Table 1 (expressed as  $\mu\text{eq}/\text{m}^3$ ).

#### **Sulfate Loss**

We hypothesized that the sulfate ions in the nano-MOUDI samples might have interacted with aluminum ions ( $\text{Al}^{3+}$ ) since the relatively low sulfate concentrations relative to the ammonium concentrations were observed only when aluminum filters were used. It has been reported that the tendency of an anion to alter the behavior of hydrolyzed metal coagulants was related to its electronegativity as well as its tendency to react with metal ions or positively charged sites on metal hydroxide precipitates (Ge and Zhu 2008).

Thus, if  $\text{Al}^{3+}$  dissolved into the extracted solution from the aluminum filter, it is possible that it interacted with

$\text{SO}_4^{2-}$  to form aluminum sulfate or aluminum hydroxide precipitates. This can explain the reduced sulfate concentration that was observed only when aluminum filters were used in the extraction. The observed low sulfate concentrations are unlikely to be the result of analytical error since the calibration curve was always checked prior to each analysis and the results shown in Table 1 were obtained on the same day.

Fig. 5 shows the observed sulfate (a), ammonium (b), and sulfate loss as a function of extraction time (c) from the two filters, and eluted aluminum concentrations from aluminum filters as a function of extraction time (d).

These results clearly show that sulfate loss occurred only during extraction from the aluminum filters. Only sulfate concentrations decreased as shown in Fig. 5(a), whereas the ammonium concentrations of the initial standard solution and the extraction from the quartz fiber and aluminum filter were almost constant, as shown in Fig. 5(b). Decreased sulfate concentrations were observed when using an aluminum filter regardless of whether the extraction time was 30 or 90 min. Although the rate of sulfate loss was not linearly related to ultrasonic extraction time, the sulfate concentration tended to decrease further when the extraction time lasted 90 min (Fig. 5(c)), possibly due to increased dissolution of  $\text{Al}^{3+}$  from the aluminum filter resulting in the increased removal of sulfate from the solution.

The average sulfate loss was 450.4, 613.9, and 900.5  $\mu\text{g}/\text{L}$  for 30, 60, and 90 min extraction time, respectively while the average eluted aluminum concentrations were 875.2, 161.7, 119.1  $\mu\text{g}/\text{L}$  for 30, 60, and 90 min extraction time, respectively. Sulfate loss tends to increase while the eluted aluminum concentrations inversely decrease with filter extraction time as shown in Fig. 5(d). This can be explained that both sulfate loss and eluted aluminum ions actually increase in all cases, but the observed (decreased) aluminum concentrations indicate that the formed aluminum sulfate or aluminum hydroxide as solid phase (precipitation) in the solution could have already been eliminated by filtering performed right after extraction causing high aluminum concentrations (unreacted aluminum ions) for 30 min extraction and low aluminum concentrations (reacted with sulfate hence eliminated aluminum ions from the solution) for 60 and 90 min extraction. The average sulfate loss from the solution was 45% ( $\pm 12\%$ ; min: 12%, max: 94%).

The equivalent ratios of sulfate and ammonium observed in laboratory tests [Lab test] of the samplers and the filter extraction experiment [Filter test] are compared in Fig. 6.

The linear plots of the data obtained from laboratory tests of the samplers and the filter extraction from the quartz filters had slopes ( $m$ ) that ranged from 0.91 to 0.93, while those from the aluminum filters had slopes ( $m$ ) that ranged from 1.96 to 2.96 ( $y$ -axis: ammonium;  $x$ -axis: sulfate). Accordingly, the observed sulfate concentrations shown in Table 1 were approximately corrected based on equivalent values of ammonium concentration and a high correlation ( $r^2 = 0.99$ ,  $m = 0.98$ ) between the two samplers for sulfate concentration was also observed.

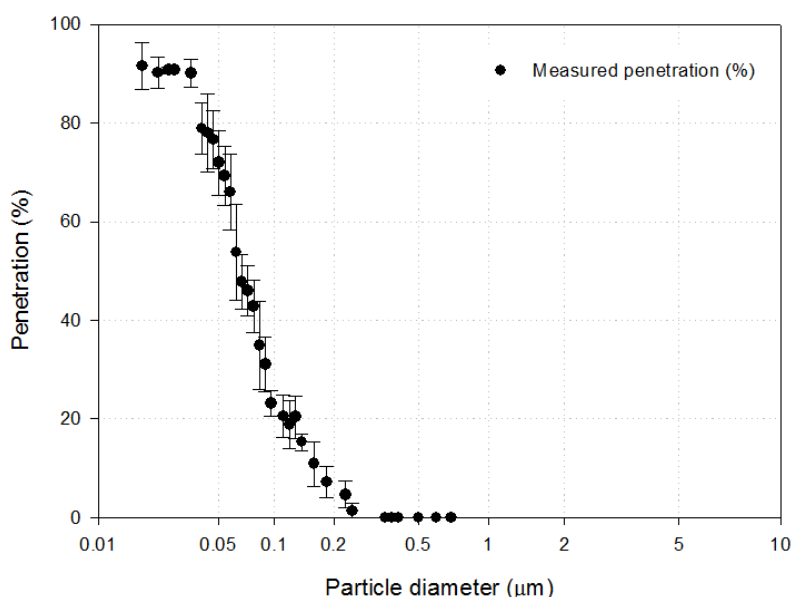


Fig. 4. Particle penetration (%) of INF sampler.

**Table 1.** Equivalent ratios of observed sulfate and ammonium concentrations in laboratory sampling.

| INF <sub>UFP</sub> ( $\mu\text{eq}/\text{m}^3$ ) |                 |                                  | Nano-MOUDI <sub>UFP</sub> ( $\mu\text{eq}/\text{m}^3$ ) |                 |                                  |
|--|-----------------|----------------------------------|---|-----------------|----------------------------------|
| $\text{SO}_4^{2-}$                               | $\text{NH}_4^+$ | $\text{SO}_4^{2-}/\text{NH}_4^+$ | $\text{SO}_4^{2-}$                                      | $\text{NH}_4^+$ | $\text{SO}_4^{2-}/\text{NH}_4^+$ |
| 0.04   | 0.03            | 1.24                             | 0.04  | 0.04            | 1.07                             |
| 0.04   | 0.03            | 1.21                             | 0.04  | 0.04            | 1.07                             |
| 0.04   | 0.03            | 1.22                             | 0.04  | 0.04            | 1.02                             |
| 0.16   | 0.15            | 1.07                             | 0.08  | 0.17            | 0.47                             |
| 0.16   | 0.15            | 1.05                             | 0.08  | 0.17            | 0.48                             |
| 0.16   | 0.15            | 1.05                             | 0.08  | 0.17            | 0.49                             |
| 0.23   | 0.18            | 1.28                             | 0.10  | 0.22            | 0.43                             |
| 0.22   | 0.18            | 1.26                             | 0.10  | 0.23            | 0.43                             |
| 0.22   | 0.18            | 1.26                             | 0.10  | 0.23            | 0.42                             |

Sulfate loss during extraction of ions from the aluminum filter could have affected the actual sulfate concentrations measured in ambient air since some studies (Pryor *et al.*, 2001; Misra *et al.*, 2002; Grose *et al.*, 2006) using a MOUDI have used aluminum filters in ultrasonic extraction for the analysis of ionic compounds. Although using a Teflon filter for ion analysis with MOUDI has been widely used, these filters are sometimes not available for researchers when they have only one MOUDI available for multi-purpose analysis. However, the use of aluminum filters in ion analysis or extraction in an ultrasonic bath must be reconsidered since this can cause underestimation of the sulfate concentration or ion balance in ambient air. The use of INF sampler for UFPs collection has some advantages such as uniform collection, multi-purpose analysis, and relatively less concerns about the loss of ionic species.

#### Sampler Performance Test in the Field

The comparison of the INF sampler with the reference sampler for measuring UFPs in ambient air showed good agreement for OC ( $r^2 = 0.94$ ) and EC ( $r^2 = 0.81$ ),  $\text{NH}_4^+$  ( $r^2 = 0.71$ ), and  $\text{SO}_4^{2-}$  ( $r^2 = 0.95$ ) concentrations despite

differences of sampling mechanism, 50% cut-point diameter, and substrates, as shown in Fig. 7(a). Relatively low concentrations of EC and  $\text{NH}_4^+$  in ambient UFPs may have attributed to the relatively low correlation coefficient values (low absolute concentrations of EC and  $\text{NH}_4^+$  in UFPs collected by a nano-MOUDI). All of the analyzed component concentrations (OC, EC,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ) for the laboratory, field samples were plotted together to observe the overall correlation between the two samplers (Fig. 7(b)). The LODs of OC, EC, sulfate, and ammonium with the INF sampling method were 0.10, 0.01, 0.01, and 0.01  $\mu\text{g}/\text{m}^3$  respectively, while those with the nano-MOUDI sampling method were 0.03, 0.01, 0.02, and 0.01  $\mu\text{g}/\text{m}^3$  respectively. The correlation coefficient was 0.99 ( $p < 0.001$ ), and the average INF/nano-MOUDI ratio was 0.93 ( $n = 44$ ).

#### CONCLUSION

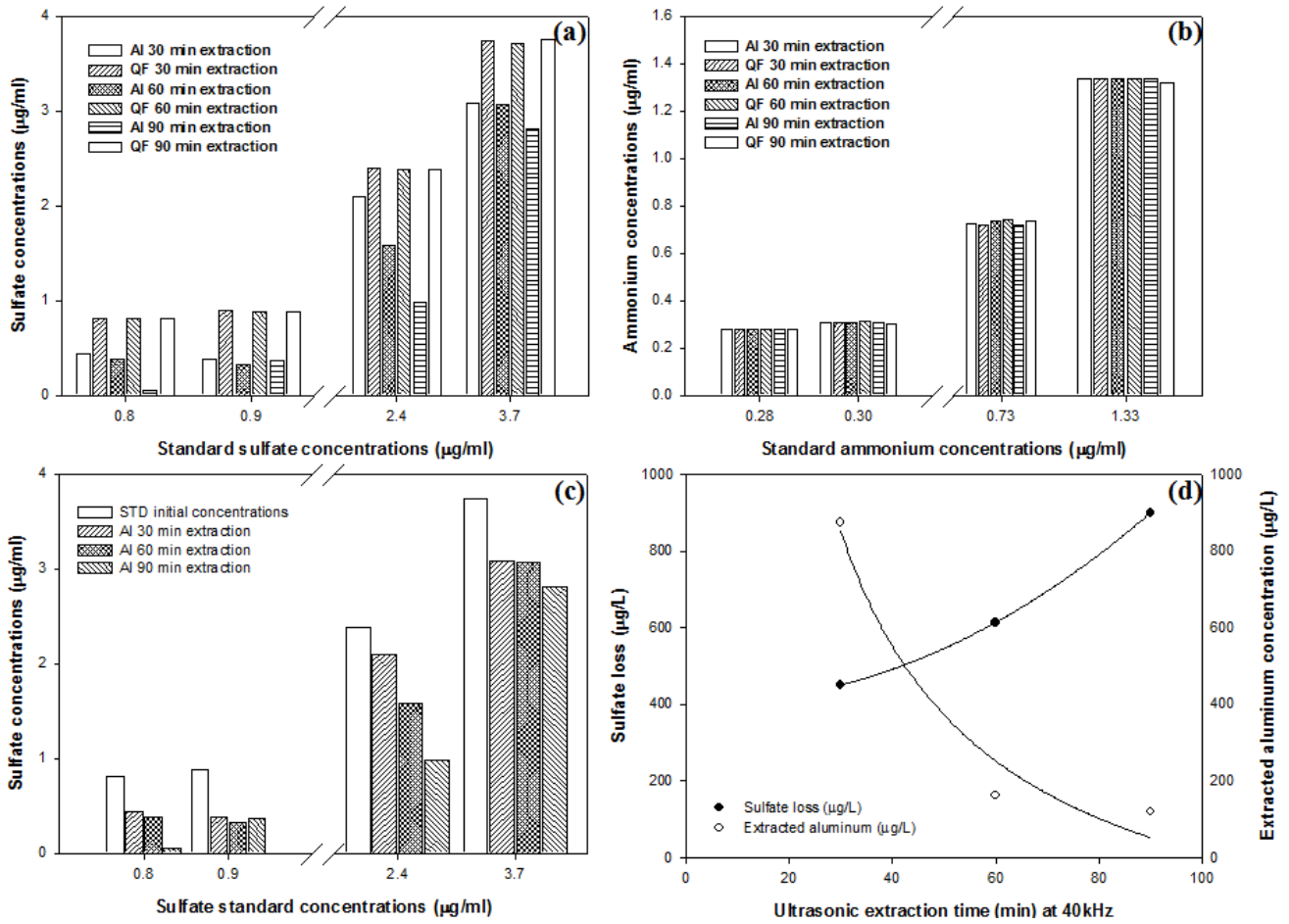
With this INF sampler, it is also possible to measure atmospheric gaseous and particulate phase aerosols simultaneously in combination with an annular denuder technique (Sekiguchi *et al.*, 2009) for UFPs collection.

The sampling performance of an INF sampler was compared with a reference sampler and the possible sulfate loss when using aluminum substrates for ion extraction in ultrasonic bath was investigated in this study. The measured concentrations of the two samplers were in good agreement for carbonaceous and ionic species despite the differences of sampling mechanism, 50% cut-point diameter, and substrate. This study demonstrated that the performance of the INF sampler is almost similar to that of the nano-MOUDI sampler for UFPs collection.

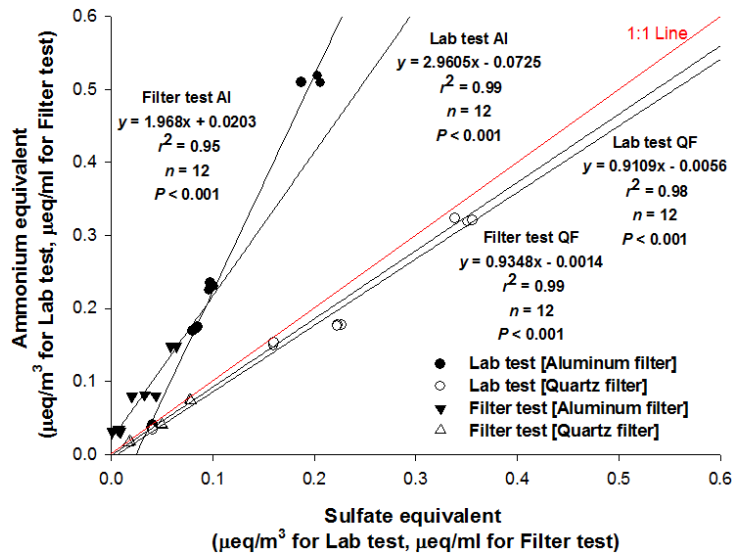
Underestimation of sulfate concentration when using aluminum substrates for ion extraction in an ultrasonic bath was discovered and investigated. Decreased sulfate concentrations appear to be unavoidable when using aluminum filters in ultrasonic extractions, regardless of

whether the extraction time was 30 or 90 min. Therefore, the use of aluminum filters with an ultrasonic extraction

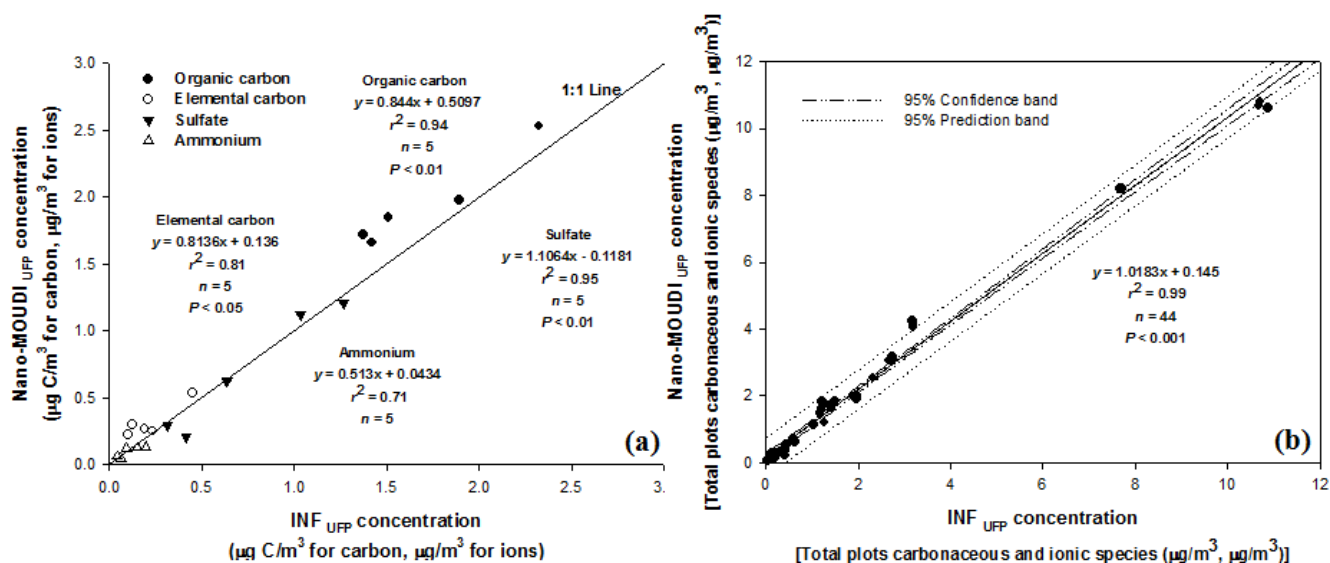
method should be avoided in order to obtain unbiased measurements of sulfate concentrations or other ion



**Fig. 5.** Observed ammonium, sulfate, and aluminum concentrations observed from filter extraction in an ultrasonic bath for 30, 60, and 90 min (AI, aluminum filter; QF, quartz filter); (a) sulfate, (b) ammonium, (c) sulfate loss, and (d) eluted aluminum concentrations.



**Fig. 6.** Equivalent ratios between sulfate and ammonium observed in laboratory sampler comparison (Lab test) and filter extraction (Filter test) data.



**Fig. 7.** Correlation between INF and nano-MOUDI samplers for concentrations of collected carbonaceous and ionic UFPs plotted for (a) each species [Field] and (b) all together [Field + Lab].

extraction methods such as vibration or shaking should be considered as an alternative method to minimize sulfate loss (dissolution of aluminum ions) from aluminum filters with sufficient extraction efficiency of ionic species.

The INF sampler is advantageous in terms of convenience and analysis. Furthermore, it can collect sufficient amounts of UFPs for chemical analysis, especially organic carbon, in a relatively short time. The particles can be uniformly collected with a quartz fiber filter, which simplifies the analysis of carbonaceous particles that require optical corrections.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- Baron, P.A. and Willeke, K. (2005). *Aerosol Measurement: Principles, Techniques, and Applications*, A John Wiley & Sons, Inc: Hoboken, New Jersey, p. 237–241.
- Biswas, P., Jones, C.L. and Flagan, R.C. (1987). Distortion of Size Distribution by Condensation and Evaporation in Aerosol Instruments. *Aerosol Sci. Technol.* 7: 231–246.
- Chang, M.C., Sioutas, C., Kim, S., Jr, H.G. and Linn, W.S. (1999). Reduction of Nitrate Losses from Filter and Impactor Samplers by Means of Concentration Enrichment. *Atmos. Environ.* 34: 85–98.
- Cheng, Y. and Tsai, C. (1997). Evaporation Loss of Ammonium Nitrate Particles during Filter Sampling. *J. Aerosol Sci.* 28: 1553–1567.
- Chow, J.C., Watson, J.G., Chen, A., Arnott, W.P. and Moosmuller, H. (2004). Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. *Environ. Sci. Technol.* 38: 4414–4422.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A. and Purcell, R.G. (1993). The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation and Applications in U.S. Air Quality Studies. *Atmos. Environ.* 27: 1185–1201.
- Eryu, K., Seto, T., Mizukami, Y., Nagura, M., Furuuchi, M., Tajima, M., Kato, T., Ehara, K. and Otani, Y. (2009). Design of Inertial Filter for Classification of  $\text{PM}_{0.1}$ . *Eaorozu Kenkyu* 24: 24–29 (Written in Japanese).
- Furuuchi, M., Choosong, T., Hata, M., Otani, Y., Tekasakul, P., Takizawa, M. and Nagura, M. (2010b). Development of a Personal Sampler for Evaluating Exposure to Ultrafine Particles. *Aerosol Air Qual. Res.* 10: 30–37.
- Furuuchi, M., Eryu, K., Nagura, M., Hata, M., Kato, T., Tajima, N., Sekiguchi, K., Ehara, K., Seto, T. and Otani, Y. (2010a). Development and Performance Evaluation of Air Sampler with Inertial Filter for Nanoparticle Sampling. *Aerosol Air Qual. Res.* 10: 185–192.
- Ge, F. and Zhu, L. (2008). Effects of Coexisting Anions on Removal of Bromide in Drinking Water by Coagulation. *J. Hazard. Mater.* 151: 676–681.
- Geller, M.D., Kim, S., Misra, C., Sioutas, C., Olson, B.A. and Marple, V.A. (2002). A Methodology for Measuring Size-dependent Chemical Composition of Ultrafine Particles. *Aerosol Sci. Technol.* 36: 748–762.
- Grose, M., Sakurai, H., Savstrom, J., Stozenburg, M.R., Watts, W.F., Morgan, C.G., Murray, I.P., Twigg, M.V., Kittelson, D.B. and McMurry, P.H. (2006). Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap. *Environ. Sci. Technol.* 40: 5502–5507.
- Huang, X.F. and Yu, J.Z. (2008). Size Distributions of Elemental Carbon in the Atmosphere of a Coastal Urban Area in South China: Characteristics, Evolution Processes,



- and Implications for Mixing State. *Atmos. Chem. Phys.* 8: 5843–5853.
- Misra, C., Kim, S., Shen, S. and Sioutas, C. (2002). A High Flow very Low Pressure Drop Impactor for Inertial Separation of Ultrafine from Accumulation Mode Particles. *J. Aerosol Sci.* 33: 735–752.
- Morawska, L., Ristovski, Z., Jayaratne, E.R., Keogh, D.U. and Ling, X. (2008). Ambient Nano and Ultrafine Particles from Motor Vehicle Emissions: Characteristics Ambient Processing and Implications on Human Exposure. *Atmos. Environ.* 42: 8113–8138.
- MSP Corporation Website (2004). Model 120 Moudi-II, Model 125B Nano-Moudi-II Brochure. <http://www.scientek.com.tw/upload/NanoMoudi.pdf>.
- Oberdorster, G., Sharp, Z., Atudorei, V., Elder, A., Gelein, R., Kreyling, W. and Cox, C. (2004). Translocation of Inhaled Ultrafine Particles to the Brain. *Inhalation Toxicol.* 16: 437–445.
- Otani, Y., Eryu, K., Furuuchi, M., Tajima, N. and Tekasakul, P. (2007). Inertial Classification of Nanoparticles with Fibrous Filters. *Aerosol Air Qual. Res.* 7: 343–352.
- Politis, M., Pilinis, C. and Lekkas, T.D. (2008). Ultrafine Particles (UFP) and Health Effects. Dangerous. Like no other PM? Review and Analysis. *Global NEST J.* 10: 439–452.
- Pryor, S.C., Barthelmie, R.J., Schoof, J.T., Sorensen, L.L. and Erickson, D.J. (2001). Implications of heterogeneous Chemistry of Nitric Acid for Nitrogen Deposition to Marine Ecosystems: Observation and Modelling. *Water Air Soil Pollut.* 1: 99–107.
- Sardar, S.B., Fine, P.M., Mayo, P.R. and Sioutas, C. (2005). Size-fractionated Measurement of Ambient Ultrafine Particle Chemical Composition in Los Angeles Using the NanoMOUDI. *Environ. Sci. Technol.* 39: 932–944.
- Sekiguchi, K., Ishikawa, N., Yasuhara, M., Sakamoto, K., Otani, Y. and Namiki, N. (2008). Performance Evaluation of an Impactor Filter and its Application to Measurement of Atmospheric Ultrafine Particles. *Eurozoru Kenkyu* 23: 278–288. (Written in Japanese)
- Sekiguchi, K., Kim, K.H., Kudo, S., Sakamoto, K., Otani, Y., Seto, T., Furuuchi, M., Yoshikawa, F., Eahara, K., Hirasawa, M., Tajima, N. and Kato, T. (2009). Evaluation of Multi Channel Annular Denuders for a Newly Developed Ultrafine Particle Sampling System. *Aerosol Air Qual. Res.* 9: 50–64.
- Zhang, X. and McMurry, P.H. (1987). Theoretical Analysis of Evaporative Losses from Impactor and Filter Deposits. *Atmos. Environ.* 21: 1779–1789.
- Zhang, X. and McMurry, P.H. (1992). Evaporation Losses of Fine Particulate Nitrates during Sampling. *Atmos. Environ.* 26: 3305–3312.

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