



# Sources of sampling error for field measurement of nitric acid gas by a denuder system

Hsunling Bai<sup>a,\*</sup>, Chungsyng Lu<sup>b</sup>, Kuan-Foo Chang<sup>b</sup>, Guor-Cheng Fang<sup>c</sup>

<sup>a</sup> Institute of Environmental Engineering, National Chiao-Tung University, 75 Po-Ai Street, Hsinchu 300, Taiwan

<sup>b</sup> Department of Environmental Engineering, National Chung-Hsing University, Taichung 402, Taiwan

<sup>c</sup> Air Toxic and Environmental Analysis Laboratory, Hungkuang Institute of Technology, Sha-Lu, Taichung 433, Taiwan

Received 24 July 2002; received in revised form 18 November 2002; accepted 22 November 2002

## Abstract

Field measurements of atmospheric HNO<sub>3</sub> gas by a denuder system equipped with four annular denuders were conducted in Taiwan. The positive errors from interfering N-compounds as well as the negative errors from incompleteness of the apparent absorption of the HNO<sub>3</sub> gas, as sampled by one NaCl-denuder, were quantitatively determined and the error sources were identified. It is found that the concentrations of positive error and negative error might cancel each other resulting in less difference between the measured and the true HNO<sub>3</sub> concentrations. The atmospheric HNO<sub>3</sub> concentration and the ambient temperature were the major factors that influence the degree of negative errors. The apparent absorption efficiency might decrease to less than 80% if the HNO<sub>3</sub> gas concentration were lower than 0.3 μg m<sup>-3</sup> or the ambient temperature were over 28°C. There are also evidences showed that the positive errors were from both interfering N-containing gases and nitrate-containing particles.

© 2003 Elsevier Science Ltd. All rights reserved.

**Keywords:** Diffusion denuder; Sampling error; Ammonium nitrate; Nitrous acid; Absorption efficiency

## 1. Introduction

Gas-phase nitric acid (HNO<sub>3</sub>) is the end product of NO<sub>x</sub> photochemical reactions and could also be produced by the thermal dissociation of NH<sub>4</sub>NO<sub>3</sub> particles (Possanzini et al., 1999). It is also an important component of acidic deposition (Galloway and Likens, 1981). Therefore, an accurate measurement of HNO<sub>3</sub> gas concentration is needed to understand the N-cycle in the atmosphere.

Annular denuders are widely employed for sampling HNO<sub>3</sub> gas in the atmosphere (Perrino et al., 1990; Febo et al., 1993; Piringier et al., 1997; Possanzini et al., 1999). The sampling mechanism is the diffusion of HNO<sub>3</sub> gas onto the denuder wall coated with reactive substances. Koutrakis et al. (1988) demonstrated the high perfor-

mance of the Harvard-EPA annular denuder system for measuring relatively high concentrations of HNO<sub>3</sub> and HNO<sub>2</sub> gases (about 4.0 μg m<sup>-3</sup>) in the urban of Boston. The differences between the measured and the calculated absorption efficiencies were small in their study. Under well-controlled environments, the absorption efficiencies of the annular denuder for sampling HNO<sub>3</sub> gas could be as high as over 98% (Brauer et al., 1989; Koutrakis et al., 1992).

On the other hand, there are also studies indicated the possibility of sampling errors for HNO<sub>3</sub> measurement using one denuder tube. Durham et al. (1987) conducted a study on the nitric acid–nitrate aerosol measurements by a tubular denuder and compared their experimental data with those predicted by the Gormley–Kennedy equation (Gormley and Kennedy, 1949). The relative errors were in the range of 10–90%. They attributed the deviations to the deposition of interfering N-compounds or the released of HNO<sub>3</sub> gas from NH<sub>4</sub>NO<sub>3</sub> aerosols in

\*Corresponding author. Fax: +886-3-5725958.

E-mail address: hlbai@mail.nctu.edu.tw (H. Bai).

the denuder. Febo et al. (1993) indicated that artifact nitrite might form on NaCl-denuders under high  $\text{NO}_2$  and  $\text{SO}_2$  concentrations so the measurement of both  $\text{HNO}_2$  and  $\text{HNO}_3$  in highly polluted areas with one denuder setup should be prevented. One of the present authors (Bai and Wen, 2000) found that measurement errors of atmospheric  $\text{HNO}_3$  gas by one NaCl-denuder system could be as high as over 80% in Taiwan. By the assumption that the denuder absorption efficiency for  $\text{HNO}_3$  gas is approaching 100%, the sampling errors were mainly from interfering species.

Perrino et al. (1990) evaluated the effect of  $\text{NO}_2$  on  $\text{HNO}_3$  measurements in the field for different coating materials on the denuder wall. The results showed that NaCl coating is the best choice other than the  $\text{Na}_2\text{CO}_3$  coating for reliable determination of  $\text{HNO}_3$  gas. They also indicated that when the particulate  $\text{NO}_3^-$  concentration is at least one order of magnitude greater than gaseous  $\text{HNO}_3$ , a significant error would occur in the measurement of  $\text{HNO}_3$  gas by one NaCl-denuder and hence a differential technique (two-denuder in series) was suggested in Perrino et al. (1990). However, quantified information for the effect of particulate nitrate on the  $\text{HNO}_3$  measurements is limited in the literature. Furthermore, the simultaneous influences of environmental conditions such as nitrate concentration in particles, ambient temperature, and concentrations of N-containing gases may lead to difficulty in addressing their individual effect on the field measurements of  $\text{HNO}_3$  gas. This study intends to estimate the true  $\text{HNO}_3$  concentration in the atmosphere so that positive and negative errors by a denuder system can be further quantified.

## 2. Experimental methods

The measurements of atmospheric  $\text{HNO}_3$  gas were conducted at three sampling sites, Hung-Kuang Institute of Technology (HKIT, Taichung County), National Chung-Hsing University (NCHU, Taichung city) and National Chiao-Tung University (NCTU, Hsinchu city). The HKIT site is located at a heavy traffic highway while the NCHU and NCTU sites are located in campuses. The HKIT and NCHU sites are more close to each other (about 20 km apart) while the NCTU site is about 100 km north of the other two sites.

A denuder system, which was composed of a cyclone (University Research Glassware, URG, Chapel Hill, Inc., USA) followed by four annular denuders (URG-2000-30B), a filter pack, a flow controller and a pump, was employed in this study (USEPA, 1989). The cyclone has a cut-off diameter of 2.5  $\mu\text{m}$ . Four denuders were placed in series coated with 10 ml of 0.1% (w/v) NaCl in 1:9 methanol/water solutions for absorption of  $\text{HNO}_3$  gas (USEPA, 1989; Perrino et al., 1990). After 24-h

sampling, the denuders were extracted with 10 ml de-ionized water. Two filters (Teflon and Nylon) were placed in series to collect particles of  $<2.5 \mu\text{m}$  and were extracted by  $\text{HClO}_4$  and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  solutions, respectively. The Teflon filter was employed to measure nitrate concentration in particles while the Nylon filter was used to evaluate the  $\text{HNO}_3$  gas evaporated from particles collected by the Teflon filter. The airflow rate through the denuder was kept at  $10 \pm 0.21 \text{ min}^{-1}$ .

The extracts for  $\text{NO}_3^-$  analysis were then injected into DIONEX DX-100 ion chromatograph equipped with the AS4A-SC column for samples from NCHU and HKIT sites, and DIONEX 4500I ion chromatograph with the AS4A column for samples from NCTU site. The elute solution was prepared using 1.8 mM  $\text{Na}_2\text{CO}_3 + 1.7 \text{ mM NaHCO}_3$ .

A QA/QC program was performed during sampling and analysis to ensure that the measured artifact source was not from failures of the QA/QC program. This includes leak tests, duplicate samples, spike samples, instrument and method detection limits, and blank tests, etc. However, possible loss at the inlet was not measured and quantified. Replicate results of three identical denuder systems (each equipped with 4 denuder tubes) were installed at the same sampling site. The precision of the samples was then determined by differences between the three systems. The result showed that the first denuder could be within 15% of relative errors while downstream denuders were within 20% of relative errors. Spike analyses showed that the recovery percentages were within  $100 \pm 10\%$  for the first denuders (high concentrations) and within  $100 \pm 25\%$  (low concentrations) for the downstream denuders. One field blank sample was taken for every field sampling, and the concentrations of field blank were well below the instrument detection limits and thus could not be detected by ion chromatograph. The values of instrument detection limits and method of detection limits for nitrate measurement were 0.011 and 0.034  $\mu\text{g m}^{-3}$  at NCHU and HKIT sampling sites and 0.014 and 0.047  $\mu\text{g m}^{-3}$  at a NCTU sampling site. The definitions of above QA/QC parameters agreed with those listed in the EPA manual (USEPA, 1989, 1999) for the annular denuder system.

## 3. Method for estimation of sampling errors

Sampling errors for  $\text{HNO}_3$  measurement by a denuder may be from two major sources. The negative error is from incompleteness of  $\text{HNO}_3$  apparent absorption by the denuder, which leads to an underestimation of  $\text{HNO}_3$  concentration. The positive error is from additional absorption of interferences onto the denuder wall, which results in an overestimation of  $\text{HNO}_3$  concentration.

The measured data by the four denuders were employed to estimate concentrations of true  $\text{HNO}_3$  gas and interference. Since the design and operating conditions of the four denuders are identical, it is assumed that the absorption efficiencies of  $\text{HNO}_3$  gas and interfering species in each denuder are analogous. The  $\text{NO}_3^-$  concentrations collected by each denuder can thus be written as (Koutrakis et al., 1988):

$$\text{1st denuder : } C\eta + C_1 = C_1, \quad (1)$$

$$\text{2nd denuder : } C(1 - \eta)\eta + C_1 = C_2, \quad (2)$$

$$\text{3rd denuder = 4th denuder : } C_1 = C_3 = C_4, \quad (3)$$

where  $C$  and  $C_1$  are the concentrations of estimated true  $\text{HNO}_3$  gas and interfering species, respectively;  $\eta$  is the apparent absorption efficiency of  $C$  for each tube; and  $C_1, C_2, C_3, C_4$  are the measured  $\text{NO}_3^-$  concentrations of the first, second, third and fourth denuders, respectively. Therefore, the collected  $\text{NO}_3^-$  on the third and fourth denuders was due to artifact formation. And by subtracting the average concentrations of the last two denuders from those of the second and first denuders, the estimated true concentration as well as the sampling efficiency of the  $\text{HNO}_3$  gas can be obtained easily.

## 4. Results and discussion

### 4.1. Error estimation

Table 1 shows the measured average  $\text{NO}_3^-$  concentrations of each denuder ( $C_1 - C_4$ ). The calculated data of true  $\text{HNO}_3$  gas concentration ( $C$ ) and apparent absorption efficiency ( $\eta$ ) as well as positive error ( $C_1$ ), negative error ( $C(1 - \eta)$ ) and the overall error concentrations ( $C_1 - C(1 - \eta)$ ) using one NaCl-denuder are also shown

in Table 1. The measured data indicated that the  $\text{HNO}_3$  concentrations collected at the HKIT site were the highest among the three sampling sites, with  $\text{HNO}_3$  gas concentration of over  $1.0 \mu\text{g m}^{-3}$  for all samples and an average concentration of  $4.57 \mu\text{g m}^{-3}$ . This is because that the HKIT site is located at a heavy traffic highway. Besides, it is about 35 km away from the Taichung Power Plant, the largest power plant in the Southeast Asia. On the other hand, most data collected at NCHU and NCTU were usually  $< 1.0 \mu\text{g m}^{-3}$ . The measured nitrate concentrations of the third and fourth denuders were nearly identical for data taken at the three sampling sites that verified the assumption made by Eq. (3).

The calculated results indicated that the apparent absorption efficiencies of  $\text{HNO}_3$  gas ( $\eta$ ) ranged from 64% to 99%, with an average value of 90%. The estimated true  $\text{HNO}_3$  gas concentrations ( $C$ ) were in the range of  $0.16 - 7.45 \mu\text{g m}^{-3}$ , with an average of  $1.96 \mu\text{g m}^{-3}$ . The positive error concentrations ( $C_1$ ) ranged from 0.05 to  $0.31 \mu\text{g m}^{-3}$ , with an average value of  $0.12 \mu\text{g m}^{-3}$ . The negative error concentrations ( $C(1 - \eta)$ ) were in the range  $0.01 - 0.69 \mu\text{g m}^{-3}$ , with an average value of  $0.12 \mu\text{g m}^{-3}$ . The overall error concentrations ranged from  $-0.48$  to  $0.16 \mu\text{g m}^{-3}$ , with only 5 out of 21 samples were negative indicating that the positive error concentration was usually higher than the negative error concentration.

Fig. 1 shows the concentrations of positive and negative errors as a function of estimated true  $\text{HNO}_3$  concentration as measured with one NaCl-denuder. Solid line represents zero error concentration and dash lines indicate regression results. It is seen that the positive error concentrations were usually higher than the negative error concentrations for  $\text{HNO}_3$  concentrations below  $5 \mu\text{g m}^{-3}$ . However, an opposite trend was observed for  $\text{HNO}_3$  concentrations above  $5 \mu\text{g m}^{-3}$ . The

Table 1  
Measured average data at each sampling site and calculated results

Sampling site	$T$ ( $^{\circ}\text{C}$ )	Measured average data				Calculated data				
		$C_1$	$C_2$	$C_3$	$C_4$	$C$	$\eta$	$C_1$	$C(1 - \eta)$	$C_1 - C(1 - \eta)$
HKIT ( $N = 8$ ) 2001	22.6	4.57	0.44	0.21	0.18	4.65	94.7	0.19	0.26	-0.06
NCHU ( $N = 6$ ) 2001	24.6	0.43	0.13	0.08	0.07	0.34	85.5	0.08	0.05	0.02
NCTU ( $N = 7$ ) 1998	22.2	0.52	0.10	0.08	0.07	0.34	85.3	0.07	0.04	0.03
Total average ( $N = 21$ ) (standard deviation)	22.6 (4.00)	1.96 (2.23)	0.23 (0.22)	0.12 (0.08)	0.11 (0.07)	1.96 (2.16)	90.0 (11.5)	0.12 (0.12)	0.12 (0.18)	-0.01 (0.16)

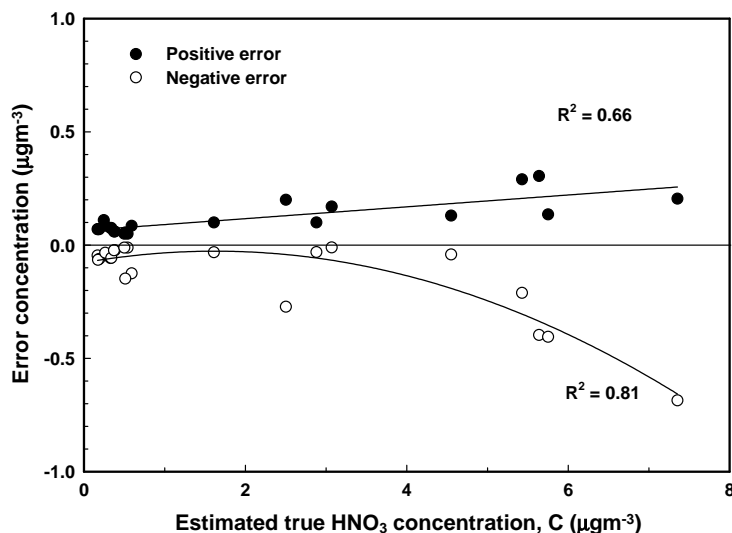


Fig. 1. Concentrations of positive error and negative error as a function of estimated true  $\text{HNO}_3$  concentration when only one NaCl-denuder was employed for  $\text{HNO}_3$  measurement.

concentrations of positive error and negative error, respectively, have a linear ( $R^2 = 0.66$ ) and a second-order polynomial ( $R^2 = 0.81$ ) best-fit relationship with the  $\text{HNO}_3$  concentration.

Both error concentrations were increased as the  $\text{HNO}_3$  concentration increased. The slightly increases in the positive errors with increasing the  $\text{HNO}_3$  concentrations may indicate that the error source could be from the interfering gases such as  $\text{NO}_2$ ,  $\text{HNO}_2$  and PAN. Although we have not measured the concentrations of  $\text{NO}_2$ ,  $\text{HNO}_2$  and PAN, but because both the interfering gases and the  $\text{HNO}_3$  gases are products of  $\text{NO}_x$  chemistry, the contributions of interfering gases increase with increasing nitric acid concentrations seems reasonable. Nevertheless, we did measure the nitrate concentrations in  $<2.5\mu\text{m}$  particles, and it was found that the nitrate in particles increases as the gas-phase nitrate increases. Hence, it is also possible that the positive error could be due to the presence of nitrate particles. On the other hand, the slightly increases in the negative errors with increasing the  $\text{HNO}_3$  gas concentrations are due to the constant  $\text{HNO}_3$  gas absorption efficiency, an assumption that is usually made for estimating the denuder efficiency and will be experimentally checked later in this study.

Fig. 2 shows the relationship between the measured  $\text{NO}_3^-$  concentration collected by one NaCl-denuder and the estimated true  $\text{HNO}_3$  concentration. Solid line represents zero error concentration. As can be seen, most symbols were close to the solid line. This indicated that the concentrations of negative error and positive error might cancel with each other and resulting in slight

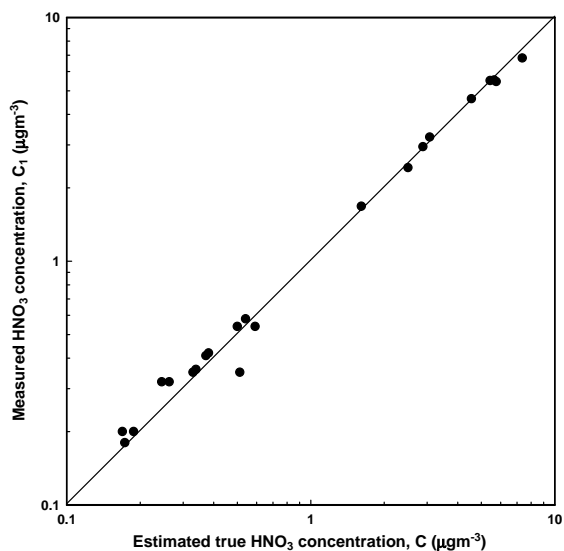


Fig. 2. Relationship between the measured  $\text{HNO}_3$  concentrations collected by the first denuder and the estimated true  $\text{HNO}_3$  concentration.

differences between the measured and the true  $\text{HNO}_3$  concentrations.

Fig. 3 shows the overall relative errors as a function of estimated true  $\text{HNO}_3$  concentration with one denuder. The overall relative error was calculated as the absolute value of overall error concentration divided by the estimated true  $\text{HNO}_3$  concentration. The  $R^2$  value was

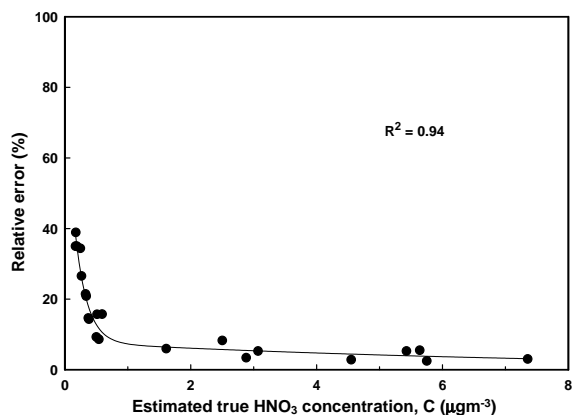


Fig. 3. Percentage relative errors as a function of estimated true  $\text{HNO}_3$  concentration when only one NaCl-denuder was employed.

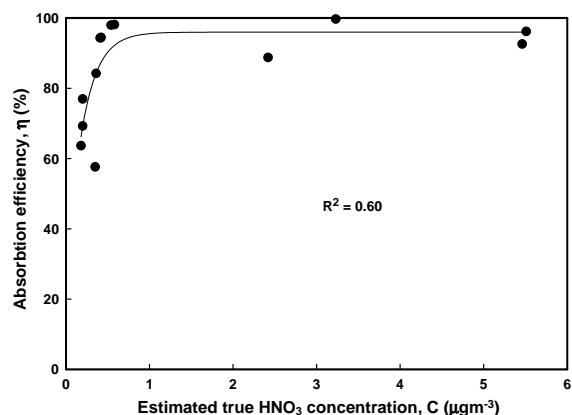


Fig. 4. Apparent absorption efficiencies of  $\text{HNO}_3$  gas as a function of estimated true  $\text{HNO}_3$  concentration.

equal to 0.94 for the best-fit regression. As can be seen, the overall relative error was increased as the  $\text{HNO}_3$  concentration decreased. The relative overall errors might be significant for  $\text{HNO}_3$  concentrations below  $0.3 \mu\text{g m}^{-3}$  and could be as high as 40%. However, as the  $\text{HNO}_3$  concentrations were above  $0.5 \mu\text{g m}^{-3}$ , the overall relative error was decreased to be less than 10%.

#### 4.2. Factors influencing the negative error

The sources of negative error are from incompleteness of apparent absorption of  $\text{HNO}_3$  gas by the denuder. Possible factors that may influence the magnitude of negative error were identified to be the  $\text{HNO}_3$  concentration and the ambient temperature; the results are discussed in the followings.

Fig. 4 shows the apparent absorption efficiencies of  $\text{HNO}_3$  gas as a function of estimated true  $\text{HNO}_3$

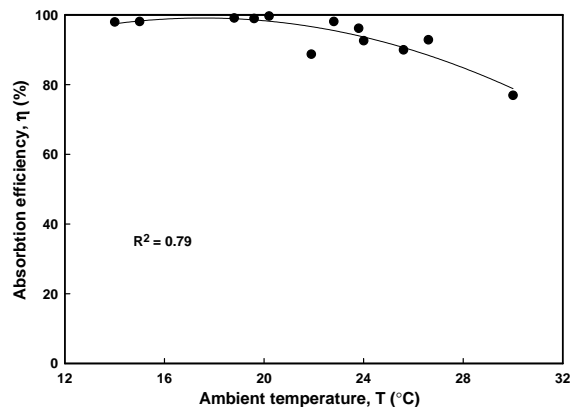


Fig. 5. Apparent absorption efficiencies of  $\text{HNO}_3$  gas as a function of ambient temperature.

concentration. In order to screen out the effect of ambient temperature, only field data sampled in the range of  $20\text{--}25^\circ\text{C}$  were used for plotting Fig. 4. The  $R^2$  value was equal to 0.60 for best-fit regression. It is seen that the apparent absorption efficiency of  $\text{HNO}_3$  gas reached a constant value of around 95% for  $\text{HNO}_3$  concentrations above  $0.5 \mu\text{g m}^{-3}$ . This was in agreement with the hypothesis of Gormley–Kennedy equation (Gormley and Kennedy, 1949) that under the same operating conditions (e.g. the same gas flow rate, temperature, and denuder geometry) the absorption efficiency of a diffusion tube reaches a constant value and is independent of the inlet gas concentration. However, as the  $\text{HNO}_3$  concentrations were less than around  $0.5 \mu\text{g m}^{-3}$ , the apparent absorption efficiency of  $\text{HNO}_3$  gas rapidly decreased as the  $\text{HNO}_3$  concentration decreased. Reid et al. (1988) indicated that the mass diffusivity decreases with decreasing concentration under very dilute solution and causes the decrease of diffusion flux of  $\text{HNO}_3$  gas onto the denuder wall. This might explain the low apparent absorption efficiency of  $\text{HNO}_3$  gas under very low concentration.

It is noted that the non-constant value in the absorption efficiency under low  $\text{HNO}_3$  gas concentration may lead to invalidity of the previous assumption of Eqs. (1) and (2) and resulted in biased of the results discussed in this study. Hence, the regression equation for  $\eta$  as obtained from Fig. 4 ( $\eta = 20.58 + 75.40(1 - 0.057^C)$ ) was substituted into Eqs. (1) and (2). The results showed that the non-constant absorption efficiency only affected by an average of about 11% in estimating the true  $\text{HNO}_3$  gas.

Fig. 5 shows the apparent absorption efficiencies of  $\text{HNO}_3$  gas as a function of ambient temperature. In order to avoid the effect of low  $\text{HNO}_3$  concentration as shown in Fig. 4, only the field data with  $\text{HNO}_3$  concentrations above  $0.5 \mu\text{g m}^{-3}$  were used in plotting

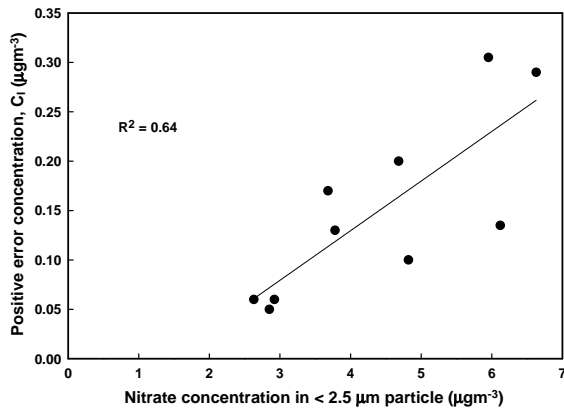


Fig. 6. Positive error concentrations as a function of nitrate concentration in <2.5 μm particles.

Fig. 5. The  $R^2$  value was equal to 0.79 for best-fit regression. It is seen that the apparent absorption efficiency of  $\text{HNO}_3$  gas was decreased as the ambient temperature increased. The apparent absorption efficiency could be as low as 79% at the ambient temperature of 30°C. This may be due to that the solubility of a gas decreases with increasing temperature, as frequently observed in the gas absorption tower (Treybal, 1980).

#### 4.3. Factors influencing the positive error

The sources of positive error are from additional absorption of N-interferences such as the evaporation or diffusional deposition of nitrate-containing particles as well as the absorption of other gaseous N-compounds onto the denuder wall as partially explained in Fig. 1. The possibility of positive errors from nitrate particles is further demonstrated in Fig. 6. As can be seen, the positive error concentration was increased as the nitrate concentration in particles increased. A best-fit linear correlation with the  $R^2$  value of 0.64 was obtained. This indicated that the nitrate-containing particles are one of the major sources of positive error. Both evaporation and diffusional deposition of nitrate-containing particles onto the denuder wall could cause interferences.

## 5. Conclusions

Field study was conducted to evaluate degrees of positive and negative errors as well as possible error sources of one NaCl-denuder system for  $\text{HNO}_3$  measurement. The results indicated that both negative error and positive error could simultaneously exist, but

they might cancel each other and lead to less remarkable overall error concentrations. The negative errors could be important for sampling relatively low  $\text{HNO}_3$  concentrations or at high ambient temperatures. On the other hand, the positive errors could be due to both N-containing gases and nitrate particles. But quantitatively determination on the contribution from either interfering gas or particles is not possible in the present study. This requires further mathematical as well as experimental study.

## Acknowledgements

Support from the National Science Council, Taiwan (NSC89-2211-E-009-058) is gratefully acknowledged.

## References

- Bai, H., Wen, H.Y., 2000. Performance of the annular denuder system with different arrangement for  $\text{HNO}_3$  and  $\text{HNO}_2$  measurements in Taiwan. *Journal of the Air and Waste Management Association* 50, 125–130.
- Brauer, M., Koutrakis, J.M., Wolfson, J.M., Spengler, D., 1989. Evaluation of annular/filter pack system to collect acidic aerosols and gases. *Environmental Science and Technology* 22, 1463–1468.
- Durham, J.L., Spiller, L.L., Ellestad, T.G., 1987. Nitric acid-nitrate aerosol measurements by a diffusion denuder, a performance evaluation. *Atmospheric Environment* 21, 589–598.
- Febo, A., Perrino, C., Cortiello, M., 1993. A denuder technique for the measurement of nitrous acid in urban environments. *Atmospheric Environment* 27A, 1721–1728.
- Galloway, J.N., Likens, G.E., 1981. Acid precipitation: the importance of nitric acid. *Atmospheric Environment* 15, 1081–1085.
- Gormley, P.G., Kennedy, M., 1949. Diffusion from a stream flowing through a cylindrical tube. *Proceedings of the Royal Irish Academic A* 52, 163–169.
- Koutrakis, P., Wolfson, J.M., Slater, J.L., Brauer, M., Spengler, J.D., 1988. Evaluation of annular denuder/filter pack system to collect acidic aerosols and gases. *Environmental Science and Technology* 22, 1463–1468.
- Koutrakis, P., Thompson, K.M., Wolfson, J.M., Spengler, J.D., Keeler, J.L., Slater, J.T., 1992. Determination of aerosol strong acidity losses due to interactions of collected particles: results from laboratory and field studies. *Atmospheric Environment* 26A, 987–995.
- Perrino, C., De Santis, F., Febo, A., 1990. Criteria for the choice of a denuder sampling technique devoted to the measurement of atmospheric nitrous and nitric acids. *Atmospheric Environment* 24A, 617–626.
- Piringer, M., Ober, E., Puxbaum, H., Kromp-Kolb, H., 1997. Occurrence of nitric acid and related compounds in the northern Vienna basin during summertime anti-cyclonic conditions. *Atmospheric Environment* 31, 1049–1057.

- Possanzini, M., De Santis, F., Di Palo, V., 1999. Measurements of nitric acid and ammonium salts in lower Bavaria. *Atmospheric Environment* 33, 3597–3602.
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1988. *The properties of Gases and Liquids*, 4th Edition. McGraw-Hill, New York, USA, pp. 580–581, 611.
- Treybal, R.E., 1980. *Mass-Transfer Operations*, 3rd Edition. McGraw-Hill, New York, USA, p. 277.
- USEPA, 1989. *Compendium, atmospheric research and exposure assessment laboratory: research*. USEPA, Triangle Park, NC (Chapter IP-9).
- USEPA, 1999. *Determination of strong acidity of atmosphere fine particles (<2.5µm)*, Compendium method IO-4. USEPA, Triangle Park, NC.