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Reduction of nitrate losses from filter and impactor samplers by means of concentration enrichment

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Abstract

Sampling errors (artifacts) have greatly affected the precision of the quantitative analysis of volatile species, such as particulate ammonium nitrate. This work presents the effect of the enrichment in concentration of particulate nitrate in reducing volatilization losses in impactors and Teflon filter samplers. During the performance characterization of an ambient fine particle concentrator developed by Sioutas et al. (1995a, Environmental Health Perspectives 103, 172–177, 1995b, Inhalation Toxicology, 7, 633–644, 1977, Journal of Aerosol Science 28, 1057–1071) losses of ambient ammonium nitrate from denuded and undenuded Teflon filter samplers as well as the microorifice uniform deposit impactor (MOUDI) were evaluated in Los Angeles, CA, an area where ammonium nitrate constitutes a major component of ambient fine particulate matter. The field study data were compared to those predicted theoretically for a given set of gas and particulate nitrate concentrations, temperature and relative humidity. Both theoretical and experimental results indicated that the ratio of nitrate gas-to-particle concentration affects significantly the volatilization loss, with higher volatilization losses occurring at higher gas-to-particle concentration values. The concentration enrichment of particulate-phase nitrate resulted in reducing evaporation losses from the MOUDI from 20–50% to less than 10%. Losses of nitrate from denuded Teflon filters were reduced from 60–95% to less than 30%, and for undenuded Teflon filters from 30–80% to less than 5%. Our study concluded that nitrate losses from impactor, denuded and undenuded Teflon filter samplers could be virtually eliminated by placing the sampler downstream of a particle concentrator with a small cutpoint (i.e., 0.1 μm). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nitrate loss; Denuders; Filter samplers; Impactors; Ammonium nitrate; Particle concentrator

1. Introduction

Ambient particulate matter (PM) has been the primary focus of several epidemiological studies, which indicated a strong correlation between adverse respiratory effects and particle concentration levels (Schwartz and Dockery, 1992; Dockery et al., 1993; Ozkaynak et al., 1993). Almost all PM chemical analysis is based on removal of particles from the overwhelmingly larger mass of gases (Appel et al., 1984; Cahill and Wakabayashi, 1992). Since the toxicity of varying forms of the same element can be different, accurate determination of the chemical composition of PM is essential in assessing their health effects on humans. The most commonly used techniques for separating particles from ambient gases are particle collection by filtration and/or impaction. A number of particulate species (called labile species) are difficult to sample because of physical or chemical changes that they undergo during or after collection. Particulate ammonium nitrate and organic carbon are the two most predominant labile PM species. Time-integrated

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sampling of labile species often leads to errors (artifacts), resulting in an underestimation or overestimation of the particulate phase (Coutant, 1977; Appel et al., 1984). Evidence of negative artifacts in particulate nitrate measurements has been discussed extensively in the literature. At least three phenomena lead to these sampling errors: (1) chemical reactions among collected particles, between air stream and collected particles, and between collected particles and sample substrates (Colovos et al., 1977; Appel and Tokiwa, 1983); (2) losses during sample storage (Smith et al., 1978; Dunwoody, 1986; Witz et al., 1990), and (3) volatilization of collected particles during sampling (Eatough et al., 1988; Wang and John, 1988).

Losses of ammonium nitrate during sampling have been attributed to either an increase in pressure drop across the particle-collecting medium or to changes in the solid–gas equilibrium between particulate ammonium nitrate and gas-phase nitric acid and ammonia during sampling. Prediction of nitrate losses due to changes in the solid–gas phase equilibrium has been qualitatively based on the dependence of the dissociation constant of ammonium nitrate on temperature and relative humidity. Although values of the ammonium nitrate dissociation constant in the atmospheric chemistry literature vary (Forrest et al., 1980; Stelson and Seinfeld, 1982; Wexler and Seinfeld, 1991; Mozurkewich, 1993), it is generally accepted that at high temperature or low humidity, the dissociation constant will increase. On the other hand, when relative humidity is 100%, the dissociation constant decreases by several orders of magnitude resulting in negligible evaporation loss. In Southern California, ammonium nitrate is a major fine particle component and the evaporative losses could be severe under conditions of high temperature (e.g., higher than 30°C) and low relative humidity (e.g. less than 40%), both of which are quite common. The increase in pressure drops across filter samplers also leads to a decrease in the free-stream gas-phase concentration. As the vapor concentration over the collected particles is assumed to be at saturation, a differential is created between the free-stream concentration and that over the deposited particles. This partial pressure differential results in evaporative losses due to mass transferring from the deposit surface to the air stream.

Nitrate losses have also been shown to depend on the type of samplers used for particle collection. Both theoretical (Zhang and McMurry, 1987) or experimental (Wang and John, 1988; Zhang and McMurry, 1992; Sioutas et al., 1997; Cheng and Tsai, 1997) studies have demonstrated that nitrate losses in impactors are generally lower than those in filter samplers. Wang and John (1988) found ammonium nitrate evaporative loss is as high as 85–95% at low mass loading (93–208 μg) and is less than 10% when the loaded mass is heavy (more than 2500 μg) in Teflon filters (2 μm pore, Zefluor). Also, evaporation losses from filters are more serious than those from impactor samplers, primarily due to higher deposited particle surface area per mass exposed to airflow in filter samplers than in impactors. The same phenomenon was observed when hot dry air (35$ 5°C, RH" 18$ 2%) was drawn through pre-loaded ammonium nitrate in Berner impactor and filter for a determined time period of 6, 12, and 24 h. Less than 7% loss is found in impactor and 81–95% losses in filter which is not acceptable in filter sampling.

The first systematic theoretical analysis of evaporative losses from both impactor and filter deposits was developed by Zhang and McMurry (1987). In their volatilization loss model, the losses for pure, single-component aerosols can be quantitative expressed in terms of three dimensionless parameters: dimensionless pressure drop, gas-to particle concentration ratio, and dimensionless sampling time. Zhang and McMurry showed that evaporative losses from impactor stages are lower than those from typical filter media. Furthermore, Zhang and McMurry (1992) compared their theory with limited laboratory data reported by Wang and John (1988) and field data obtained in Los Angeles from Southern California Air Quality Study (SCAQS) (John, 1988; Wang and John, 1988; John et al., 1990; Fitz et al., 1989; Coutness, 1989) and at Bryce Canyon (Benner et al., 1987; Eatough et al., 1988). Good qualitative agreement was obtained between the measured and particle sampling efficiencies.

Both the theoretical analysis as well as the comparison with results from laboratory and field studies showed that nitrate losses generally increase as the pressure drop across the sampler increases. Furthermore, these studies indicated that the nitrate gas-to-particle mass distribution affects to a great extent the rate of nitrate volatilization, with higher losses being observed at higher gas-to-particle concentration ratios. Cheng and Tsai (1997) compared experimental losses of pure ammonium nitrate particles during filter sampling with the losses predicted by Zhang and McMurry. Cheng and Tsai showed that severe evaporation loss occurs during the initial particle collection stage, when only few particles are collected on the filter. The formation of a particle cake decreases the rate of evaporation. The upstream particle concentration is one of the most significant factors affecting the evaporation loss of ammonium nitrate particles. When the upstream particle concentration is high, a particle cake will be formed sooner.

This investigation was part of ongoing efforts to characterize the performance of ambient fine particle concentrators developed by Sioutas et al. (1995a,b,1997). Most of the performance characterization of these technologies has been conducted in the East Coast of the US using ambient aerosols enriched in non-volatile species, such as ammonium sulfate. Evaluation of nitrate losses was limited by the very low nitrate concentrations in this area of the US. The present study was conducted in Los Angeles,

CA, an area in which ammonium nitrate constitutes a major component of ambient fine particulate matter (Solomon et al., 1988; Lawson, 1990; Hering et al., 1997). As several of the aforementioned studies have indicated that the nitrate gas-to-particle concentration affects significantly the volatilization loss, this study tested the hypothesis that concentration enrichment of particulate-phase nitrate reduces these losses from impactor as well as denuded and undenuded filter samplers.

2. Methods

2.1. Ambient fine particle concentrator

The human exposure ambient fine particle concentrator used in this study is described in more detail by Sioutas et al. (1995a,b,1997). The concentrator is shown schematically in Fig. 1, along with the instrumentation used for its characterization. Briefly, ambient aerosols are drawn through a preselective inlet that removes particles larger than 2.5 μm in aerodynamic diameter, and then through a series of two virtual impactors that increase the concentration of the fine particles (0.1–2.5 μm particle diameter), each by a factor of about 2.5–3. The inlet is a modified version of the high-volume TE-6001 size selective inlet (SSI) inlet (Tisch Environmental Inc, Cleves, OH), designed to have a cutpoint of 2.5 μm.

Prior to entering the first virtual impactor stage, the ambient aerosol is drawn through a transition piece made of stainless steel. The first virtual impactor stage consists of five slit-nozzle virtual impactors arranged in parallel, operating at an intake flow of 1000 l min^{-1}, each (5000 l min^{-1} total). The virtual impactors operate at a minor-to-total flow ratio of 0.2, thus the concentrated flow of each is equal to 200 l min^{-1}. The minor (concentrated) flows from each of the five virtual impactors are combined and drawn through a plenum and into the second virtual impaction stage at 1000 l min^{-1}.

The second concentration stage consists of one slit-nozzle virtual impactor having a design identical to those of the first stage, operating at an intake flow rate of 1000 l min^{-1}. The design and operating parameters of these impactors are described in detail elsewhere (Sioutas et al., 1995a,b). The concentrated flow of this stage is drawn through a human body exposure chamber at an inlet flow rate of 250 l min^{-1} and under a slightly negative pressure (i.e., 0.98 atm).

Studies of nitrate mass distribution in the past (Wang and John, 1988; Kleeman and Cass, 1998; Hering et al., 1997) have shown that almost all of the nitrate mass is associated with particles above 0.1 μm. We therefore expected that almost particulate nitrate would be contained in the minor (concentrated) flow of the concentrator since the cutpoint of the virtual impactor is about 0.1 μm.

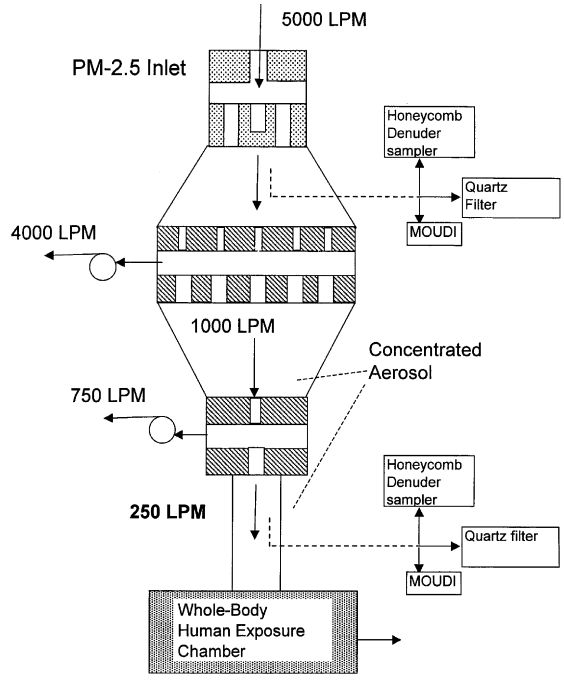

Fig. 1. Schematic diagram of the fine particle concentrator at the USC Rancho Los Amigos Medical Center and the set-up used for its characterization.

2.2. Study description

Performance evaluation of the concentrator was conducted at Rancho Los Amigos Medical Center, Downey, CA, using outdoor air as the test aerosols. Two sets of Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP Corporation, Minneapolis, MN), Honeycomb denuder/filter pack system (Koutrakis et al., 1993) and undenuded filter samplers were used as shown in Fig. 1. One set was connected to the plenum after the $PM_{2.5}$ selective inlet and upstream of the first concentration stage in order to sample the ambient aerosols. Another set was placed immediately downstream of the second stage and upstream of the exposure chamber. The MOUDIs (Marple et al., 1991) were used to determine the enrichment factor and its dependence on particle aerodynamic diameter and chemical composition. The MOUDIs sampled at 30 l min^{-1} and classified particles in the following aerodynamic diameter intervals:) 0.1, 0.1–0.18, 0.18–0.32, 0.32–0.56, 0.56–1.0, 1.0–1.8, 1.8–3.2, 3.2–5.6, and 5.6–10.0 μm. Thirty-seven millimeter Teflon filters (2 μm, PTFE, Gelman, Ann Arbor, MI) were placed at the back up stage to collect less than 0.1 μm particles and 47 mm Teflon filters at all other stages. The

Honeycomb denuder/filter pack system removed coarse particles (d_p* 2.5 μm) with an impactor inlet, followed by two honeycomb denuders coated with sodium carbonate and citric acid to remove acidic gases and ammonia, respectively, at a flow rate of 10 l min^{-1}. The two-stage filter pack had a 47 mm Teflon filter to collect fine particles and a 47 mm sodium carbonate-coated glass fiber filter (2 μm, Gelman, Ann Arbor, MI) to collect particulate nitrate that volatized from the Teflon filter. The total ammonium nitrate collected in both Teflon and coated glass fiber filters yields the actual ammonium nitrate concentration in the particulate phase. The undenuded filter samplers were operated at 10 l min^{-1} and used the same 47 mm Teflon filters as the MOUDI and honeycomb samplers. This sampling strategy enabled us to compare the actual nitrate losses during filter sampling with losses predicted by Zhang and McMurry (1992) from the MOUDI as well as from denuded and undenuded filter samplers for both ambient and concentrated aerosols.

Prior to the characterization of the concentrator, the two MOUDIs sampled room air in collocation to confirm that they measure the same size distribution when sampling the same aerosols. Over the period of concentrator characterization, temperature and relative humidity were measured every 30 min in the ambient and concentrated air by a thermohygrometer HI-9161F (Hanna Instruments, Italy). No substantial differences in temperature and relative humidity were observed between ambient and concentrated air. Pressure drop through the concentrator stages was recorded every 30 min. The sampling time for each characterization test varied from 4 to 7 h, depending on the observed concentrations. Ambient temperature ranged from 13°C to 34°C, relative humidity ranged from 7 to 92% and ambient $PM_{2.5}$ levels varied from 8.9 to 122.6 μg/m^3.

The Teflon filters of all samplers were pre-weighed and post-weighed to determine fine particle mass concentration using a MT5 Microbalance (Mettler Toledo Inc, Highstown, NJ) in a room with controlled temperature of 21–24°C, and relative humidity of 40–50%. All Teflon filters and coated glass fiber filters were subsequently extracted with ultra-pure water and analyzed by means of ion chromatography to determine particulate sulfate and nitrate. Sampling flow rates of MOUDIs, honeycomb denuders, and filter samplers were measured with calibrated flowmeters (Matheson, VWR Brand, Catalogue d 61016-208). The nitrate limits of detection (LOD) were 0.72 and 0.24 μg/m^3 for the filter (denuded or undenuded) and the MOUDI samplers, respectively. The LOD were defined as three times the field blanks (Koutrakis et al., 1992) and correspond to a 7-h sampling period. The enrichment factor was determined on the basis of fine mass, nitrate and sulfate concentrations for each stage.

3. Results and discussion

3.1. Experimental data

Evaporation nitrate losses in different samplers were evaluated by comparing nitrate concentrations collected by the denuded Teflon filter, undenuded Teflon filter and MOUDI. The total nitrate was determined by the sum of the nitrate collected on both Teflon and glass fiber filters in the denuder. The results of the sampler comparison tests are summarized in Figs. 2–4 and in Tables 1 and 2 . Figs. 2a, 3a and 4a are plots of the nitrate concentrations determined by the MOUDI, denuded, and undenuded filters as a function of the total nitrate for ambient air, whereas Figs. 2b, 3b and 4b are plots of the MOUDI, denuded, and undenuded filter nitrate as a function of the total for concentrated air. The linear regression lines are also plotted in each figure. Paired *t*-test comparisons were conducted between the total nitrate concentrations and those determined with the MOUDI, denuded and undenuded filter samplers for ambient and concentrated air. The results of this comparison, along with the correlation coefficients and *p*-values are shown in Table 2.

As shown in Figs. 2a–4a, the nitrate concentrations determined by either sampler were in general considerably lower than the total nitrate concentrations. The average nitrate sampling efficiencies (defined as the ratio of the collected-to-total nitrate) for the MOUDI, denuded and undenuded filter samplers are 0.57 ($ 0.27), 0.39 ($ 0.31) and 0.41 ($ 0.32), respectively. The results shown in Figs. 2a–4a and in Table 1 also show that the nitrate concentrations determined by the MOUDI, denuded, and undenuded filter samplers were also highly correlated with the total nitrate concentrations, with correlation coefficients varying from 0.91 to 0.98. Furthermore, the *p*-values of the paired comparison between the total nitrate concentration and those measured with the MOUDI, denuded and undenuded filter samplers indicate that these differences are statistically significant.

The effect of concentration enrichment in reducing nitrate losses from the MOUDI and the filter samplers is best illustrated in Figs. 2b–4b. Excellent agreement between the total nitrate concentration and that determined with the MOUDI, denuded, and undenuded filter samplers is obtained.

The average nitrate sampling efficiencies for the MOUDI, denuded, and undenuded filter samplers collecting concentrated particles are 0.99 ($ 0.17), 0.81 ($ 0.19) and 0.93 ($ 0.11), respectively. Similar to the data corresponding to ambient air samples, the total nitrate concentration and those measured with MOUDI and the filter samplers are highly correlated, with correlation coefficients varying from 0.96 to 0.99 (Table 2). Furthermore, there is no statistical difference between the total nitrate concentration and those determined with the

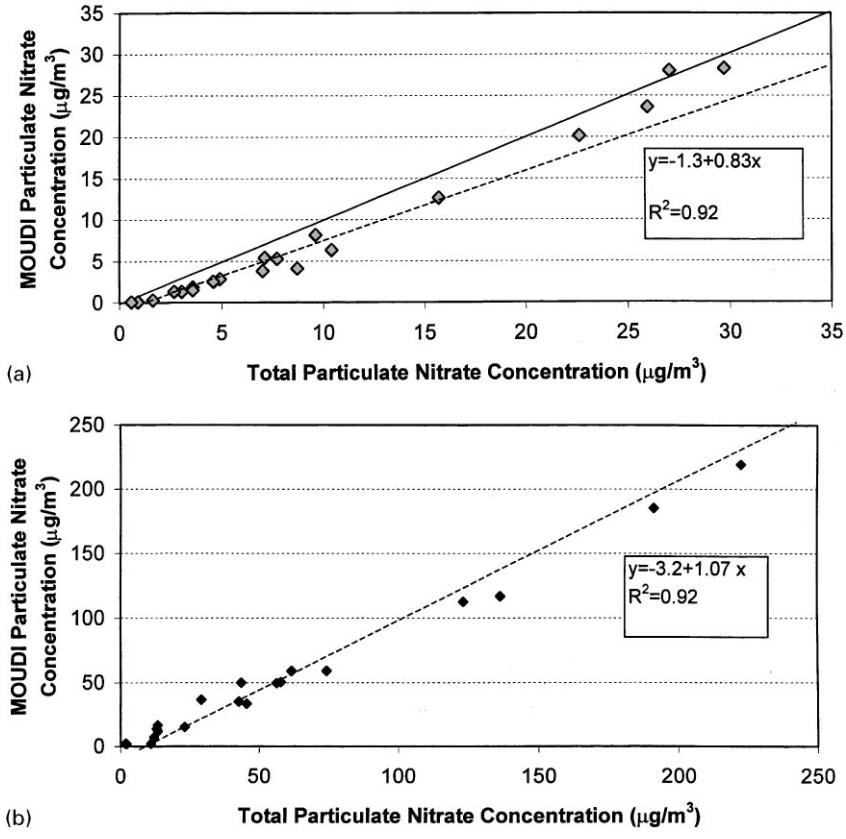

Fig. 2. (a) Plot of MOUDI vs. total particulate nitrate concentrations for ambient air, (b) plot of MOUDI vs. total particulate nitrate concentrations for concentrated air.

MOUDI, as the p-value shown in Table 2 is higher than 0.05. The p-value obtained by comparing the total to denuded and undenuded filter nitrate concentrations indicate statistical differences (the corresponding p-values are 0.03 and 0.001, respectively). Nevertheless, the actual difference between the undenuded filter and total nitrate concentrations (hence nitrate loss) is rather small, as the average sampling efficiency value for undenuded Teflon filters sampling concentrated air is 0.93. The higher loss observed for the denuded filter is due to the vapor depletion upstream of the filter because the denuder removes all of the nitric acid, a condition that enhances volatilization.

3.2. Comparison of the experimental data with theoretical predictions on volatilization losses

The sampling efficiency for a given species, g_s, of any sampler can be expressed as follows:

$$g_s = 1 - \frac{M_e}{M_d}, \tag{1}$$

where M_d is the particulate species mass delivered to the sampler, and M_e is the mass evaporating from the deposited particles. The mass delivered to the sampler is expressed by the following equation:

$$M_d = QC_m t g, \tag{2}$$

where C_m is the actual aerosol mass concentration upstream of the sampler, and g is the collection efficiency of the sampler. The rate of evaporative mass transfer from a deposit surface to the gas in a flowing air stream can be expressed as follows:

$$M = KA\Delta o, \tag{3}$$

where K is a mass transfer coefficient, A is the surface area of the deposit, and Δo is the difference in vapor concentration just above the surface of the deposit and that of the free airstream.

Eqs. (1)–(3) indicate the importance of concentration enrichment in reducing sampling losses for particulate nitrate from any type of sampler. While the driving potential for evaporation (i.e., the difference in vapor

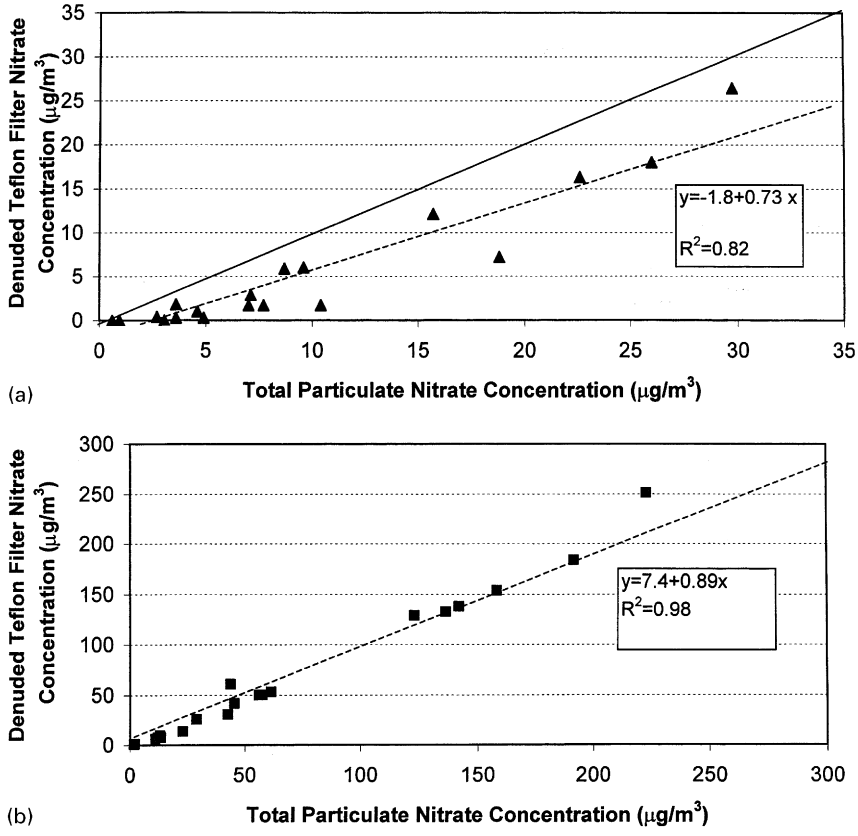

Fig. 3. (a) Plot of denuded teflon filter vs. total particulate nitrate concentration for ambient air, (b) plot of denuded teflon filter vs. total particulate nitrate concentration for concentrated air.

concentrations between the filter or impactor deposit and the free airstream) is the same for either ambient or concentrated air, more particulate mass is delivered to the sampler when the aerosol is concentrated, thereby increasing the sampling efficiency for nitrate.

According to the theory of Zhang and McMurry (1987), a lower limit for the sampling efficiency of filter and impactor samplers can be calculated by the following equations:

$$g_s'' \quad \frac{1}{1\# \quad m[S\# \quad (1! \quad S)/d]o_e/C_m}. \tag{4}$$

Here n_s is the sampling collection efficiency of the filter or impactor sampler, m and d are dimensionless factors defined as $* P/(P_0! \quad * P)$ and $* P/hP_0$, respectively, in which h is 1 for filters. P_0 is the inlet pressure and $* P$ is the pressure drop across the filter. o_e/C_m is the ratio of the equilibrium gas-phase concentration averaged over the sampling period to the measured particle concentration. S is the average saturation ratio at the sampler inlet, which is zero for a denuded filter. For the undenuded filters, the gases are usually assumed to be at equilibrium concentrations, therefore S'' 1. The total pressure drop through both the denuded and undenuded filters was equal to 10 in of water (equivalently, 2.45 kPa) therefore mwas equal to 0.0245.

For impactors, due to different mass transfer mechanisms, mshould be calculated by the following equation (Zhang and McMurry, 1987):

$$m_i'' \quad Sc^{-0.64}Re^{-1/2}\frac{* P}{g(P_0! \quad * P)}\left(1\# \frac{o_a; \frac{2}{0}}{4* P}\right)$$

$$\# \quad 2.42\left(\frac{r_e}{R}\right)^{1.14} ! \quad 1. \tag{5}$$

Here Sc is Schmidt number, defined as the ratio of the air kinematic viscosity (l) to the diffusivity of evaporating species (D), Re is Reynolds number based on jet diameter, g is collection efficiency for non-volatile species, o_a is air density, ; $_0$ is impactor jet velocity, r_e is radius of impactor deposit, and R is impactor jet radius. For the purposes of our theoretical calculations, Sc was taken equal to 1.1. The ratio of r_e/R was assumed to be equal to 1.3.

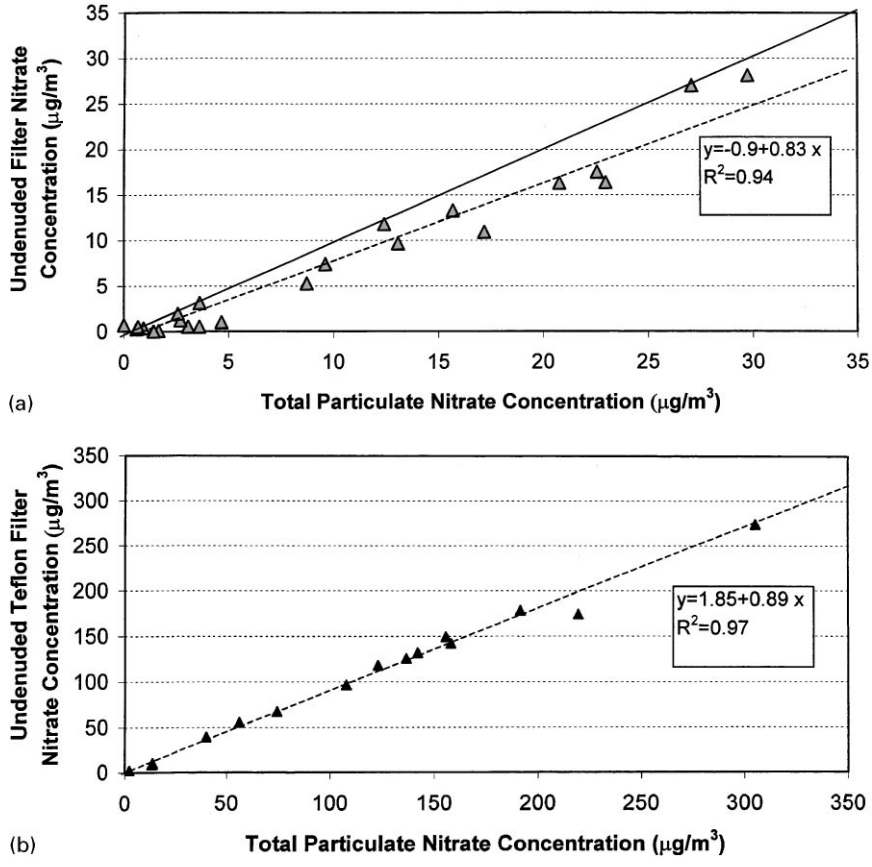

Fig. 4. (a) Plot of undenuded teflon filter vs. total particulate nitrate concentration for ambient air, (b) plot of undenuded teflon filter vs. total particulate nitrate concentration for concentrated air.

Table 1
Sampling efficiencies for particulate nitrate of the MOUDI, undenuded and denuded filter samplers for ambient and concentrated air

Sampler type	Ambient air	Concentrated air
MOUDI	0.57 (\$ 0.27)	0.99 (\$ 0.17)
Denuded filter	0.39 (\$ 0.31)	0.81 (\$ 0.19)
Undenuded filter	0.41 (\$ 0.32)	0.93 (\$ 0.11)

The calculations of the m values for each MOUDI stage were not particularly sensitive to the r_e/R ratio for values in the range of 1.2–1.7. The assumption that the radius of the particle deposit is about 1.3 times that of the radius of the acceleration jet of the impactor has been based on previous studies on impaction patterns (Sethi and John, 1993). Estimated m values for each MOUDI stage are shown in Table 3.

For either concentrated or ambient air, the original particulate nitrate size distribution (i.e., prior to volatilization) is unknown. We assumed that PM-2.5 nitrate mass is evenly distributed in the last five MOUDI stages. Our actual field data showed that there was no measurable nitrate in the after-filter of either MOUDI (collecting particles smaller than 0.09 μm) and the mass median diameter of nitrate varied from 0.4 to 0.6 μm. The same assumption of even nitrate mass distribution within the stages of a cascade impactor was also made by Zhang and McMurry (1992) when they compared predicted and experimental nitrate losses in impactors and filters. Zhang and McMurry argued that the uncertainty introduced by this assumption is small in comparison to the range of gas/particle distributions (which, in this field study ranged from 0.02 to about 30).

The effect of the parameters m on volatilization losses from impactor substrates can be best illustrated in Fig. 5, in which the concentration enrichment based on mass, sulfate and nitrate is plotted as a function of MOUDI aerodynamic particle diameter range. The values of m corresponding to each MOUDI stage are also plotted.

Fig. 5 shows that the concentration enrichment achieved by the two-stage concentrator based on either

Table 2
Summary of the statistical paired comparisons between total particulate nitrate and MOUDI, denuded and undenuded filter particulate nitrate concentrations

	Mean ($ S.D.) nitrate concentration (μg/m^3)	*p*-value[a]	Correlation coefficient[b]
Ambient air			
Total	11.5 ($ 10.7)		
MOUDI	9.2 ($ 11.1)	0.0013	0.97
Denuded filter	7.2 ($ 10.3)	5] 10^{-6}	0.90
Undenuded filter	8.9 ($ 10.8)	0.00013	0.97
Concentrated air			
Total	97.6 ($ 68.3)		
MOUDI	93.4 ($ 64.1)	0.60	0.96
Denuded filter	90.2 ($ 68.3)	0.14	0.99
Undenuded filter	86.9 ($ 73.8)	0.03	0.99

[a] *p*-value of paired *t*-test between nitrate concentrations measured by sampler and total nitrate concentration.
[b] Correlation coefficient between nitrate concentrations measured by sampler and total nitrate concentration.

Table 3
Estimation of m for each MOUDI stage

MOUDI cutpoint (μm)	* $P/(P_0$! $P)$[a]	Re[b]	; $_0$[b] (cm/s)	m[c]
3.2	0	1680	1043	0
1.8	0	1510	1696	0
1.0	0.01	1440	3070	0.000672
0.56	0.02	1340	4974	0.001359
0.32	0.021	350	3609	0.002938
0.18	0.067	580	8733	0.006978
0.1	0.17	500	10 600	0.019837

[a] Ratio of pressure drop across the stage (* P) to the pressure upstream of the impaction stage.
[b] Reynolds numbers (Re) and average jet velocity (; $_0$). From Marple et al. (1991).
[c] Calculated from Eq. (5).

fine mass or particulate sulfate varies from approximately 6.5 to 9.5 for particles in the size range of 0.3–3.2 μm. The maximum enrichment factor is achieved for the 1–1.8 μm particles, as expected, since the separation and concentration process by means of virtual impaction is based on particle inertia. The enrichment decreases considerably for particles below 0.25 μm. For any aerodynamic particle diameter range, there is no real difference in the concentration enrichment between fine mass and particulate sulfate. The enrichment also decreases for particles smaller than 0.25 μm since these particles are comparable in size to the 50% cutpoint of the virtual impactors.

The concentration enrichment based on nitrate is very similar to that based on fine mass and sulfate for particles in the range of 0.5–3.2 μm. The enrichment based on nitrate, however, is considerably higher than those based on mass or sulfate for particles smaller than 0.5 μm, with the disparity between the enrichment factors becoming more pronounced as particle size decreases. As the process of particle concentration is based on particle inertia, the concentration enrichment should not be dependent on particle chemical composition. The increased enrichment observed at lower stages can only be due to sampling artifacts of the MOUDI sampling the ambient aerosol. The lower MOUDI stages, collecting smaller particles, are also operating at a lower pressure (hence higher pressure drop across the stage), higher jet velocity (; $_0$) and lower Reynolds numbers (Re), all of which lead to higher values of the parameter m (Table 2). Increased values of m lead to lower values of the sampling efficiency (g_s), as indicated by Eq. (1). The discrepancy in the concentration enrichment factors between mass, sulfate and nitrate data can be therefore attributed to the higher nitrate losses at the lower MOUDI stages.

The mechanism of ammonium nitrate dissociation is described by the following equation:

$$NH_4NO_{3(s)} \% NH_{3(g)} \# \quad HNO_{3(g)}. \tag{6}$$

The concentrations of nitric acid and ammonia can be either measured by means of diffusion denuders, or estimated from the dissociation constant of ammonium nitrate, K. Due to the large number of our field tests, we conducted only limited measurements of nitric acid concentrations and estimated the rest from the dissociation constant.

At temperature ¹ (in K), the dissociation constant (in ppb²) is given by the following equation (Mozurkewich, 1993):

$$\ln(K)'' \quad 118.87! \quad \frac{24084}{1}! \quad 6.025 \ln(1\ ). \tag{7}$$

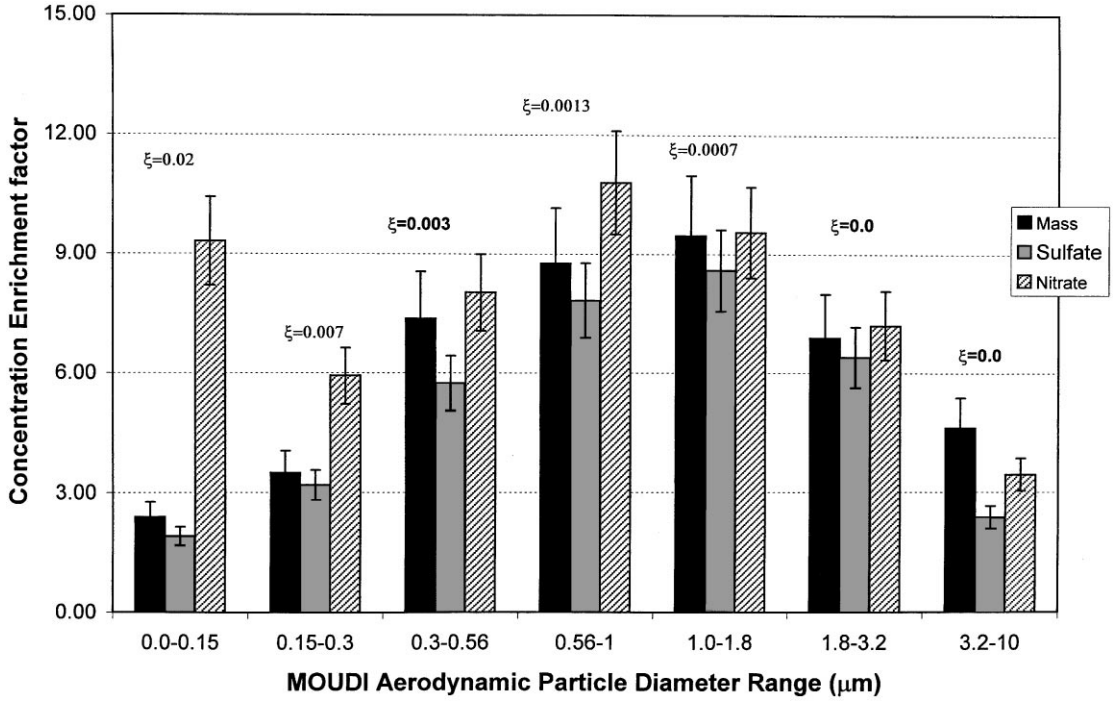

Fig. 5. Enrichment factor for the two-stage concentrator.

K is also dependent on relative humidity. When the relative humidity (a_W) is higher than the deliquescence point of ammonium nitrate, K should be replaced by KH(Mozurkewich, 1993):

$$KH' \quad [P_1! \quad P_2(1! \quad a_W)\# \quad P_3(1! \quad a_W)^2](1! \quad a_W)^{1.75}K, \tag{8}$$

where

$$\ln(P_1)'' \quad ! \quad 135.94\# \quad \frac{8763}{1}\# \quad 19.12\ \ln(^1\ ), \tag{9}$$

$$\ln(P_2)'' \quad ! \quad 122.65\# \quad \frac{9969}{1}\# \quad 16.22\ \ln(^1\ ) \tag{10}$$

and

$$\ln(P_3)'' \quad ! \quad 182.61\# \quad \frac{13875}{1}\# \quad 24.46\ \ln(^1\ ). \tag{11}$$

As the dissociation constant applies to a pure solid or saturated solution, the determined gas-phase nitric acid and ammonia concentrations represent an upper limit. However, numerous studies conducted in Southern California have found that measured nitric acid and ammonia concentrations agree with those predicted at equilibrium with pure ammonium nitrate via use of the dissociation constant at a given RH/^{1} to within 15% (Solomon et al., 1988; Lawson, 1990; Hering and Cass, 1999) at those times when ammonium nitrate is present in the particle phase. Agreement to within 20% was also found in our limited tests conducted at the environment of Rancho Los Amigos Medical Center, in which the gas-phase nitric acid concentrations determined with the honeycomb denuders were measured and compared to those predicted by the dissociation constant theory.

When sampling is conducted over a prolonged time period t, the time-average equilibrium gas-phase concentration can be expressed as follows:

$$\overline{o_e}'' \quad \frac{:\!\!\!\!\!\!\int o_e(t)\mathrm{d}t}{t}. \tag{12}$$

The logarithmic dependence of the dissociation constant on temperature and humidity implies that temperature and relative humidity need to be measured in short time intervals in order to accurately estimate the ammonium nitrate dissociation constant. Temperature and relative humidity were measured and recorded every 30 min in our experiments. As the time scales required for a substantial change in either temperature or relative humidity are typically higher than 30 min, this sampling scheme allowed us to obtain (at least in theory) reasonably accurate estimates of the equilibrium nitric acid concentrations over sampling periods as long as 7 h.

Figs. 6–8 show the sampling efficiencies of ambient and concentrated particulate nitrate in denuded and undenuded filters and MOUDI samplers. In Fig. 6 (denuded

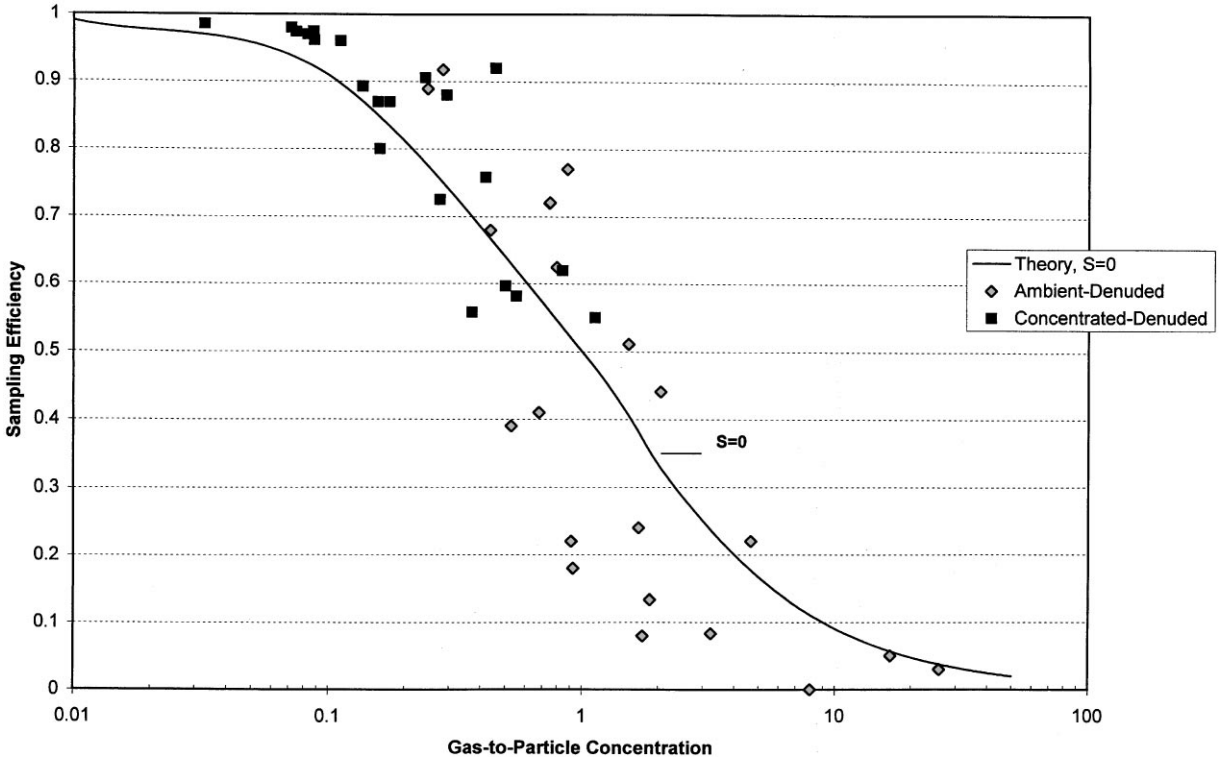

Fig. 6. Particulate nitrate sampling efficiency for denuded teflon filters.

filters), very good agreement between the theory and field sampling data was observed. When the gas-to-particle concentration ratio is less than 0.1, nitrate collection efficiency is as high as 90%. As the gas-to-particle concentration ratio decreases, nitrate collection efficiency decreases sharply to 50% when gas-to-particle ratio is 1, and further to less than 25% when the ratio increases to about 3. The majority of the concentrated nitrate data correspond to sampling efficiencies higher than 70%. Considering that all of nitric acid has been removed by the diffusion denuder upstream of the Teflon filter (a condition that should enhance volatilization), the obtained sampling efficiencies are remarkably high. Furthermore, the theoretically predicted sampling efficiencies and those obtained experimentally are highly correlated (the correlation coefficient R'' 0.86).

Fig. 7 shows the nitrate collection efficiency of the MOUDI sampling ambient and concentrated air. Along with the curve corresponding to S'' 1, the curve corresponding to S'' 0 is included in Fig. 7 in order to show a theoretical lower limit for sampling efficiencies associated with evaporative losses during sampling. All of the experimental data points fall within the S'' 0 and curves. Fig. 7 indicates that the theory of Zhang and McMurry (1987) which assumes pure volatilization loss, overestimates the nitrate sampling efficiencies for both concentrated and ambient air. Such discrepancies between theoretical predictions in nitrate collection efficiencies and experimental data were also observed by Zhang and McMurry (1992) and Tsai and Perng (1998). In both studies, the theoretically predicted sampling efficiencies of impactor and filter sampler were found to be higher than those determined experimentally.

In addition to volatilization, nitrate can also be lost due to chemical reactions between collected ammonium nitrate particles and species such as particulate sulfuric acid or gaseous hydrochloric acid (Appel and Tokiwa, 1983; Koutrakis et al., 1992). An additional explanation for the differences between theoretical and experimental sampling efficiencies may be related to possible losses of nitric acid in the inlet of the sampler as well as on the surface of the aluminum isokinetic sampling probes used to sample ambient and concentrated aerosols. John et al. (1988) showed that the aluminum inlet of dichotomous samplers, when clean, could be an effective denuder for nitric acid. It is thus possible that some nitric acid is lost in the aluminum sampling probes. A plot of the theoretical curve corresponding to S'' 0.85 (i.e., assuming a nitric acid loss of 15%) shows that both ambient and concentrated MOUDI data can be well fitted by this curve (the

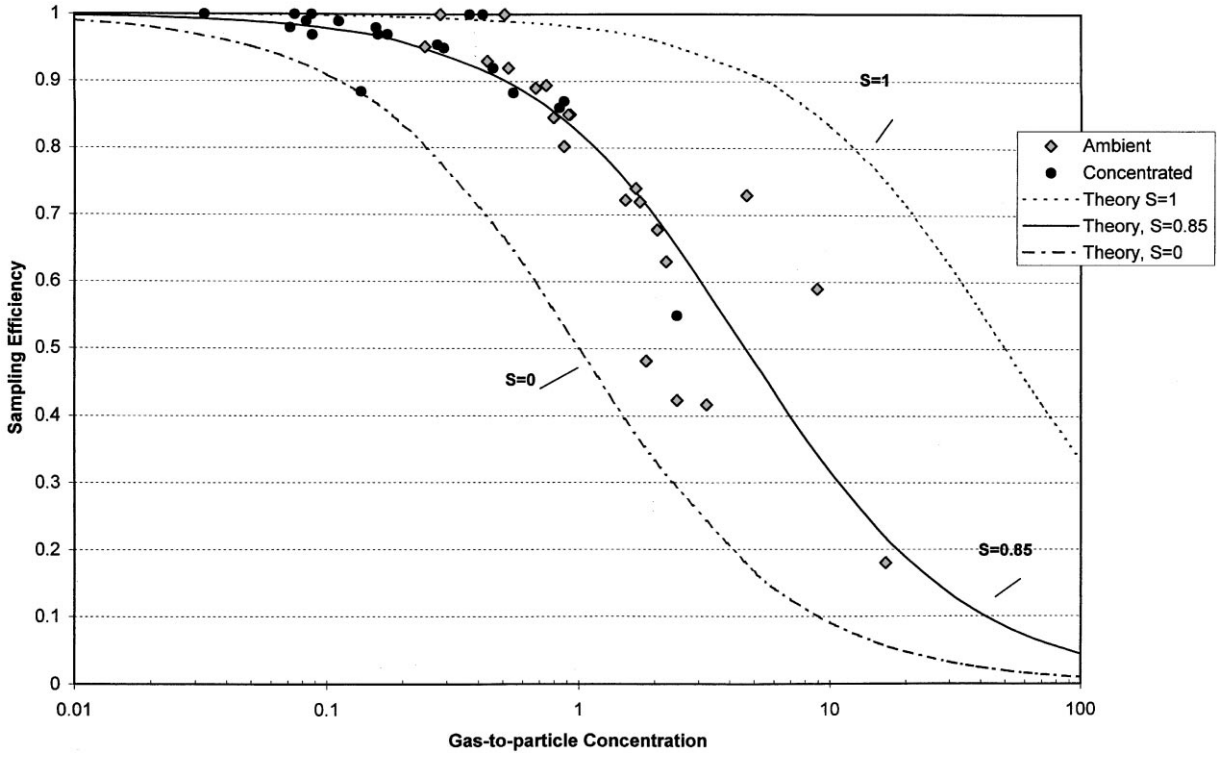

Fig. 7. Nitrate sampling efficiency for MOUDI.

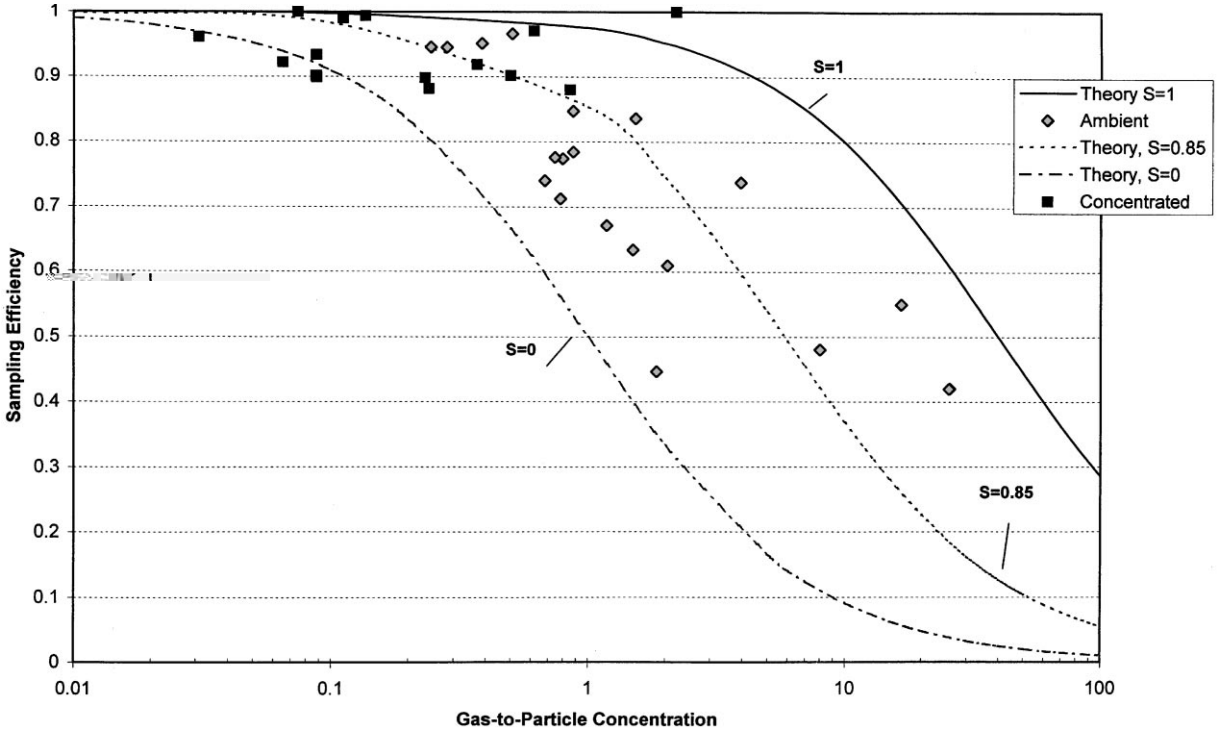

Fig. 8. Nitrate sampling efficiency for undenuded teflon filters.