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A Fabric Denuder for Sampling Semi-Volatile Species

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ABSTRACT

A new style of diffusion denuder has been evaluated specifically for sampling HNO_3. A coated fabric is used as the denuder substrate, which can be loaded directly into a standard filter holder. This approach allows direct denuder sampling with no additional capital costs over filter sampling and simplifies the coating and extraction process.

Potential denuder materials and coatings were evaluated in the laboratory to test the removal efficiency. NaCl coatings were used to assess more than 20 materials for HNO_3 collection efficiency. Particle retention, which would cause a denuder to have a positive bias for gas concentration measurements, was evaluated by ambient air sampling using particulate sulfate as the reference aerosol. Particle retention varied from 0 to 15%, depending on the denuder material tested. The best performing material showed an average particle retention of less than 3%.

Denuder efficiency of four fabric materials was tested under ambient conditions to determine removal efficiency. The fabric denuder method was compared with a long path-length Fourier transform infrared (FTIR) spectrometer, a tunable diode laser absorption spectrometer (TDLAS), and a denuder difference sampler to independently measure HNO_3. HNO_3 collection efficiency was typically 90% for the denuders, whether coated with NaCl or not. For 10-L/min sampling rates with the fabric denuder, the square of the correlation coefficient with the FTIR spectrometer was 0.73, compared to 0.24 with the TDLAS.

IMPLICATIONS

A simple fabric material used as a diffusion denuder has been shown to be an effective and inexpensive method to measure species such as HNO_3 and NH_3 which partition into both gaseous and particulate phases. The low cost of this approach compared with other types of denuders may encourage more measurements of these air pollutants. With a larger database available, the environmental and health effects of these species may be better assessed.

INTRODUCTION

Background

HNO_3 in the atmosphere may pose a significant health risk and environmental hazard. In the atmosphere, HNO_3 and NH_3 are in equilibrium with NH_4NO_3 particulate matter. These particles are primarily in the $PM_{2.5}$ size range, a particulate range for which a new federal ambient air quality standard has been promulgated.[1]

Particulate NH_4NO_3 exists in a temperature-dependent equilibrium between the gas and solid phases.[2,3] At ambient temperatures, NH_4NO_3 is in equilibrium with a substantial amount of NH_3 and HNO_3. Higher temperatures shift the equilibrium to the gas phase, while lower temperatures shift the equilibrium to the particulate phase. At a given temperature, in situ spectroscopic measurements have shown the equilibrium constant to be quite variable in ambient air, although regression plots against the inverse of absolute temperature yielded free energy and enthalpy changes consistent with laboratory studies.[4] The variability may be due to humidity and whether the aerosol is internally or externally mixed.[5-7]

After NH_4NO_3 is collected on a filter, it is subject to these equilibrium shifts, which can increase or decrease the amount of NH_4NO_3 retained on the filter.[8] Both NH_3 and HNO_3 gases are also subject to acid-base reactions with previously collected particulate matter, resulting in ion formation and, therefore, transformation to the particulate phase. In order to accurately sample HNO_3, NH_3, NO_3^-, and NH_4^+ in the phases as they exist in the atmosphere, diffusion denuding techniques have been developed.[9-13] Diffusion denuders are devices that remove gaseous components while allowing particles to pass through them. This is physically possible due to the much higher diffusion rate of gases compared with typical ion-containing atmospheric particulate matter. Denuders are thus used to remove gaseous HNO_3 and NH_3. While the removal of these species will result in their replacement by volatilizing NH_4NO_3, this does not occur during the short period of time that the particles are passing through the denuder.[10] The remaining NH_4^+ and NO_3^- can then be collected on specially treated filters, which prevent further volatilization.

While denuder technology can result in the accurate measurements of these species, its application to routine sampling is difficult due to the cost and complexity of sampling equipment. Two approaches have been used in the past: direct denuder and denuder difference. In the denuder difference approach,[9,10,14] the denuders are not extracted after sampling; two sampling lines are used, one with a denuder and one without. These denuders are designed for high adsorptive capacity so they can be used for many sample collection periods before requiring reactivation or replacement. Both lines then collect samples on specially coated filters, which prevent further volatilization. The filter used on the line without the denuder also retains the corresponding gas-phase component. Both filters are extracted, and the ion of interest is quantified. The concentration on the filter with the denuder is a measure of the particulate concentration, while that of the filter without the denuder is the total concentration for gas and particulate phases. The difference in concentration between the two filters is, therefore, a measure of the gaseous concentration.

While this approach requires considerably less labor and capital investment than the direct denuder method, the difference technique is subject to greater measurement uncertainty for the gas-phase species. In addition, denuder surfaces must be occasionally renewed. This applies to the denuders for HNO_3, which used anodized aluminum denuder surfaces. While they were thought to have infinite capacity for removing HNO_3,[14] we have recently found that breakthrough is possible under both laboratory and ambient air conditions.[15]

In the direct denuder approach,[11,13,16,17] the adsorbent layer of the denuder is extracted and analyzed for either NO_3^- or NH_4^+. (Separate denuders are used for HNO_3 and NH_3 because different sorbent coatings are required.) This method requires the denuder to be recoated after each sampling period, usually a labor-intensive laboratory procedure. Normally, annular denuders are used, which are relatively expensive precision sampling devices. This approach, in which the gas of interest is adsorbed on a denuder coating and quantified, is generally favored over the denuder difference method due to its greater sensitivity.

Several types of denuders have been developed along with specialized size-selective inlets to minimize HNO_3 adsorption. These designs include annular,[11] tubular,[13] coiled tubing,[18] and honeycomb[19] denuders. While these denuders offer several advantages over the denuder difference approach, a significant capital investment in denuder hardware is needed for routine field measurement programs.

Another limitation with conventional denuders is that it is necessary to remove large particles (usually greater than 2 μm-aerodynamic diameter) containing the species to be measured, since they may deposit in the long, narrow channels typically necessary to allow gases to diffuse to the treated surface. This would result in a positive interference. Size-selective inlets, however, present another surface to which HNO_3 and NH_3 may deposit, which could result in measurements with a negative bias. At the same time, NH_4NO_3 might volatilize from particles collected in the inlet, resulting in a positive bias.

We report herein a new approach with the potential to offer measurement sensitivity of the direct denuder approach with lower capital and operating costs. This denuder is based on diffusion research for devices used to remove very fine particles. These devices, known as diffusion batteries, are used to size-resolve submicron particles in situ. Originally constructed using a single long channel, they were then made more compact, but more difficult to fabricate, by using tubing bundles. These evolved to honeycomb structures and finally to wire screens.[20] This development is analogous to the development of diffusion denuders for sampling semi-volatile species, which started with tubing bundles,[9] progressed to annular geometry,[11] and then to honeycomb structures.[19]

Our approach uses a fabric as the denuder substrate, analogous to wire screen denuders that collect very fine particles in diffusion batteries. The finer the mesh, the greater the deposition by either particles or gases. In the case of particles, the wire of the mesh is typically 10 μm in diameter with a spacing of 20–50 μm. Typically, more than 100 such screens are necessary to remove submicron-sized particles. Since the diffusion coefficient for gases is several orders of magnitude higher than for particulate matter, a single screen, which need not be as fine, could be used. An open-weave fabric, with a typical thread size of 100 μm spaced on centers of 250 μm, leaving an open grid of 150 μm (typical dimensions for fabric with a loose weave), would be sufficient. In addition, an adsorbent material would allow the fabric to be coated with a variety of chemicals for selectively removing target gases. The denuders, therefore, could be soaked in solutions of $C_6H_8O_7$ or H_3PO_4, NaCl, triethanolamine, and K_2CO_3, which would selectively adsorb NH_3, HNO_3, NO_2, and SO_2, respectively.

Theoretical Basis

The feasibility of the concept was first evaluated by using the theory developed for wire diffusion screens.[21] The equation to describe the fractional penetration of a particle (P) is given by

$$P = \exp(-AnPe^{-2/3}) \qquad (1)$$

where

$$A = \frac{2\beta a h}{\pi(1-a)r}$$

where β is 2.7; a is the solid surface fraction (volume solid/total volume ≈ 0.3 by geometry); r is the fiber radius, cm; h is the screen thickness, cm; and n is the number of screens.

$$P_e = \text{Peclet number} = 2r\,U_{0/D}$$

where U_0 is the undisturbed flow velocity, cm sec^{-1} and D is the diffusion coefficient, $cm^2\ sec^{-1}$.

Assuming a denuder is treated with a chemical that quantitatively removes a target gas upon contact with the denuder surface, we can calculate the theoretical denuder efficiency. To apply this equation to HNO_3, for example, for a 4.0-cm-diameter screen sampling at 10 L/min, we use the dimensions of the fabric grid cell (100 µm spaced on centers of 250 µm), and the diffusion constant for HNO_3 at room temperature, 0.12 cm^2/sec.[22] This results in a penetration of 0.02, or 2%. However, using the diffusion coefficient of a 0.1-µm particle (6×10^{-6} cm^2/sec) results in a penetration of greater than 99%.[21]

Since fabric substrates have not previously been used as gaseous diffusion denuders, laboratory testing was needed to optimize the denuder geometry and coating material. Additional testing was needed to determine whether the laboratory performance could be maintained under actual field sampling conditions. Field testing was also conducted to evaluate the penetration of particulate matter through the denuder.

EXPERIMENTAL

Denuder Substrates

A variety of fabric materials was obtained at a local store. The materials were chosen for open weave (those with greater porosity), to allow maximum particle penetration. The store could provide little information as to the composition of the fabrics other than whether they were all cotton or contained synthetic components (determined by a char test using a match in cases where fabric was not labeled). The bolts contained no information other than the manufacturer name, and sometimes this information was not present. Fabrics were cut into 47-mm circles with a custom-made arch punch and installed into open-face perfluoro alkoxy (PFA) Teflon filter holders (Savillex Corp.). Fabrics of a variety of weave patterns and materials were evaluated. Table 1 summarizes the materials used.

Denuder Coatings

Denuders were coated by dissolving the coating material in a 50/50 (v/v) solution of methanol/water, which also contained 2% glycerol, by volume. The concentration of the denuder coating solution was expressed as the mass percentage of the coating agent in solution. Denuders were dipped in this solution and allowed to drain and air dry, after which they were immediately sealed in polyethylene bags and stored in a refrigerator at 4 °C.

The following denuder coating materials were evaluated:

- NaCl (2 and 9%)—NaCl denuder coatings have been shown to be more selective at removing HNO_3 than any other coating material reported in the literature.[23]
- $NaCO_3$ (2%)—Coated on a filter, this base has been shown to be effective in removing HNO_3, HNO_2, carboxylic acids, and SO_2.[12,16,24]

Overview of Testing Methods

Laboratory Evaluation. Denuders were evaluated in the laboratory by passing known concentrations (10–40 ppbv) of HNO_3. Figure 1 is a schematic drawing of the equipment used to expose the denuders to HNO_3 for penetration efficiency testing. Air was generated with an Aadco model 727 pure air generator. Air was humidified by splitting the flow, bubbling one fraction through deionized water, and then recombining the dry air with the water-saturated air. All plumbing components consisted of PFA Teflon tubing, fittings, and filter holders, while the permeation tube holder, trap, and humidifier were constructed of borosilicate glass. All airflows were measured with rotameters and a mass flow meter, and controlled with needle valves. The rotameters and the mass flow meter were calibrated against a certified dry gas meter.

Concentration measurements, used to determine penetration, were made before and after the denuder by sampling with a commercial chemiluminescent NO-NO_x

Table 1. Fabric denuder materials evaluated in the laboratory.

Material	Material Type	Material	Material Type
1	35/65 cotton-synthetic blend	11	Polyester
2	Cotton-polyester blend	12	Silk
3	Rayon-polyester	13	Silk
4	Rayon-acetate	14	Nylon
5	Cotton	15	Nylon
6	Cotton	16	Polyester
7	Cotton	17	Cotton
8	Cotton	18	50/50 cotton-polyester blend
9	Nylon	19	Cotton
10	Polyester		

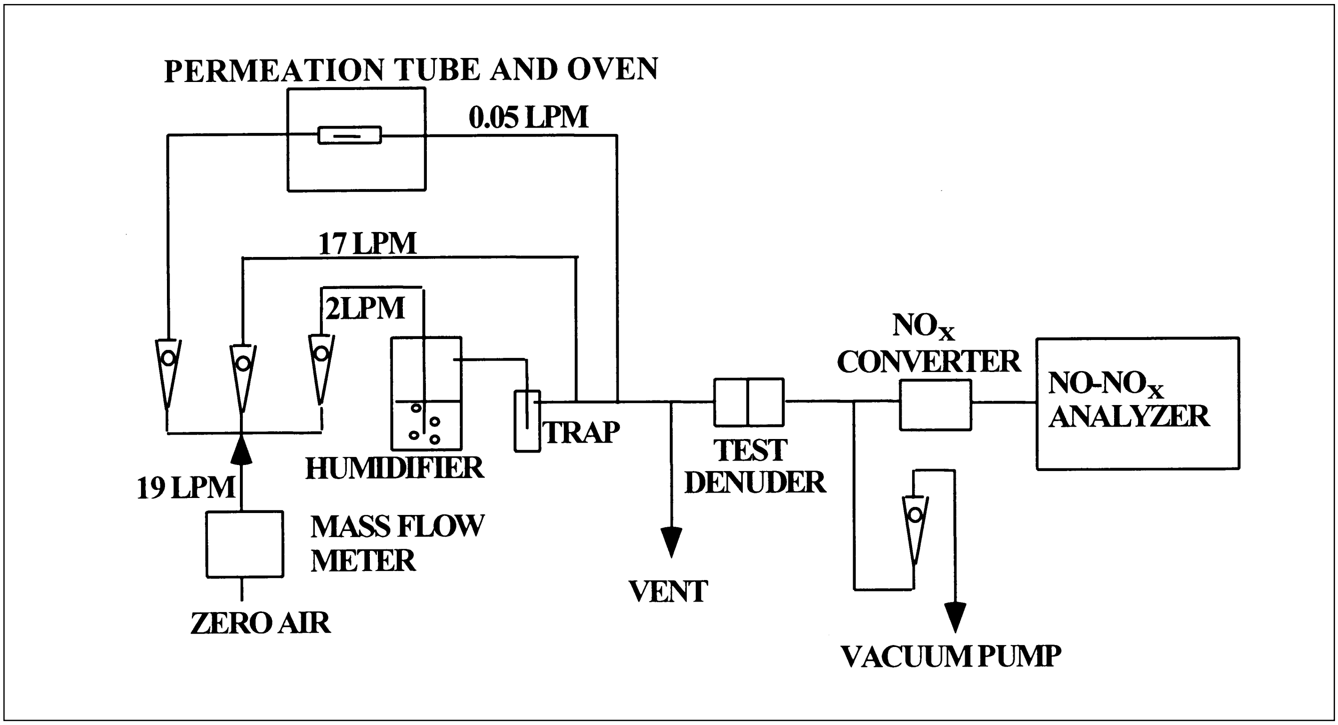

Figure 1. Denuder test schematic for HNO_3.

analyzer (Thermo Environmental Corp. model 42C) through Teflon "T" tube fittings. To reduce HNO_3 losses, the NO_x converter was removed from the instrument's cabinet and placed within 10 cm of the HNO_3 source. The analyzer approach allowed greater time resolution and a nearly immediate feedback of results. This allowed us to rapidly evaluate denuder collection efficiency as a function of flow rate so an optimum range could be determined.

Ambient Measurements. An ambient air study to determine particulate penetration through the denuder and to compare HNO_3 measurements with other methods was conducted in Claremont, CA, from August 28 to September 26, 1995. The other methods included a denuder difference sampler, a long path-length Fourier transform infrared (FTIR) spectrometer, and a tunable diode laser absorption spectrometer (TDLAS). A detailed comparison of HNO_3 measurements between all of these methods is described elsewhere.[25]

SO_4^{2-} measurements were used to determine the amount of particulate NO_3^- that the denuder could possibly collect. Since SO_4^{2-} is a non-volatile particulate species, the amount of SO_4^{2-} collected by each denuder compared to the sulfate on the Teflon front filter (or the sum of the SO_4^{2-} on the back Teflon filter plus all of the preceding denuders) provides a measure of the penetration of fine particulate matter through the denuder. This approach also assumes that NO_3^- and SO_4^{2-} have a similar size distribution. Many studies have shown that this is the case, especially in Southern California,[26,27] but others have noted a large size mode greater than 2.5 µm aerodynamic diameter.[28] Presumably, this large size mode originates with sea salt and therefore is normally found where a marine influence is common. The use of SO_4^{2-} as a NO_3^- particle surrogate also assumes that the NaCl-coated denuders do not collect gaseous SO_2 as SO_4^{2-}. This has been verified previously[28] and was again during this laboratory evaluation.

For this study, a number of fabric denuder configurations were tested in order to determine denuder efficiency and particulate penetration at 2 and 10 L/min for various gaseous pollutants, to determine the feasibility of the method for both short- and long-term collection periods. The 2-L/min samples were collected for 7 days while 10-L/min samples were collected for nominal periods of 8 hr during the daytime and 16 hr overnight. Collocated sampling was used to determine precision.

During the Claremont evaluation, denuders with four types of material and two flow rates were evaluated. Each denuder pack contained a Teflon filter either before or after it in order to estimate variability and particulate penetration (as determined by SO_4^{2-} concentrations). The following describes the sampling lines by number:

- sampler line 1 (2 L/min) and sampler line 4 (10 L/min): three uncoated denuders followed by a Teflon filter, which measures the adsorptive characteristic of the uncoated denuder and particulate penetration.
- sampler line 2 (2 L/min) and sampler line 5 (10 L/min): three NaCl-coated denuders followed by

a Teflon filter, which measures the penetration of HNO_3 and particulate matter.
- sampler line 3 (2 L/min) and sampler line 6 (10 L/min): These contained a Teflon filter prior to the denuders as a reference for particulate penetration. The first denuder was uncoated, allowing for a second determination of gas retention. The second and third denuders provided a second measurement of HNO_3 penetration through a NaCl-coated denuder at 2 L/min.

The 2-L/min samplers were operated for 1-week intervals, while the 10-L/min samplers were operated during nominal intervals of 1100–1700 hr PDT. Samplers collected at 2 L/min all used the same material (#5); the 10-L/min sampling substrates were rotated between materials 1, 5, 7, and 8. We obtained substrate (both filter and denuder) blanks by loading them into denuder cassettes and immediately unloading them into petri dishes. The handling was, therefore, identical to the substrates used for sampling, except that they did not encounter any sample flow. Denuder substrates were extracted in carbonate buffer used for ion chromatographic analysis (2.97 mM Na_2CO_3/0.33 mM $NaHCO_3$) and analyzed for SO_4^{2-} and NO_3^-. All values were corrected by subtracting the mean blank concentration.

Samples were collected with this arrangement for 28 consecutive days. All samples collected for 1-week intervals were chemically analyzed, while eight selected sets of the daily samples were analyzed. The criteria for analysis days included the availability and quality of spectroscopic data, in addition to evaluating each denuder material at least twice. The analysis days tended to be those of highest HNO_3 concentration, the species of most interest in this study. The first set of four was chosen based on days of high HNO_3 as determined by the TDLAS. The second set of four was chosen based on the availability of FTIR spectrometer data.

The denuder difference sampler[29] was developed by the South Coast Air Quality Management District (SCAQMD). The $PM_{2.5}$ component was set up at the Claremont site and operated on the same twice-per-day schedule as the fabric denuder test samplers. This component consisted of a PFA Teflon-coated cyclone (nominal flow of 27 L/min) to remove particles larger than 2.5 µm aerodynamic diameter. The air was then divided using PFA-coated metal plumbing components. Each stream was sampled at a nominal 9 L/min. In one stream, HNO_3 was removed by a denuder consisting of plates of anodized aluminum and followed by quartz and nylon filters in series to collect particles and volatilized NO_3^-. In another, a quartz filter was used to remove particulate matter, and a nylon filter removed HNO_3 and volatilized NO_3^-. The detection limit for 8-hr sample intervals was estimated to be 0.1 µg/m^3.

Real-time spectroscopic measurements of HNO_3 were made using both a TDLAS and a long path-length FTIR spectrometer. The TDLAS has greater sensitivity than the FTIR spectrometer (sub-ppbv compared with approximately 5 ppbv) and was able to provide around-the-clock measurements. Unlike the FTIR spectrometer, the TDLAS was potentially subject to more sampling artifacts since it needed to sample ambient air through a Teflon filter into a cell at 20-Torr pressure. The FTIR spectrometer, which measured HNO_3 directly in the air, was therefore considered the ultimate reference method for HNO_3. Since the FTIR spectrometer could only measure relatively high concentrations of HNO_3, a nominal sampling interval for collection-based measurements was from 1100 to 1700 hr PDT, when HNO_3 was typically above the FTIR spectrometer detection limit.

The km path-length infrared spectroscopic system consisted of a Mattson Instruments Sirius 100 FTIR spectrometer interfaced, via a set of transfer optics, to a 25-m base path, open multiple reflection, and a gold-coated mirror system of the Horn-Pimentel-White design.[30,31] The instrumental system was similar to that previously reported,[32,33] but with an upgraded moving mirror for the interferometer, a new PC-based data system, and a current Mattson software package.

A Unisearch Associates model TAMS-150 TDLAS was used to measure HNO_3 in situ. This approach has been previously described[34] and found to compare favorably with other methods of HNO_3 measurement.[35,36] The residence time in the cell is approximately 4 sec. Calibrations were performed by introducing HNO_3 generated by a permeation tube maintained at constant temperature. The output rate of the permeation tube was measured by bubbling the effluent from the tube through a buffered aqueous solution and titrating with a standard solution of KOH, monitoring the change in pH with an electrode.

RESULTS

Laboratory Evaluation of Fabric Denuders

Efficiency Definitions and Sources of Uncertainty. Denuder collection efficiencies were determined by the following expression:

$$E = (1 - (C_d - Z)/(C_u - Z))*100 \qquad (2)$$

where C_d is the analyzer response downstream of the denuder, C_u is the analyzer response upstream of the denuder, and Z is the analyzer response to zero air.

HNO_3 was used for the initial denuder testing and development. There were several aspects that contributed to measurement uncertainty:

- The pure air system did not provide a stable background source of NO_x at the sub-ppbv level. A fluctuation of ±1 ppbv was typical during a 24-hr period. The diurnal pattern appeared to reflect ambient pollutant concentrations rather than instrument drift.

- A small amount of zero drift in the NO-NO_x analyzer caused significant uncertainty in determining the penetration of HNO_3 at low penetrations, since the outlet concentrations would be near the zero of the instrument.
- Long lag times, typically several hours, to reach 95% of the final value, occurred after step changes in the HNO_3 concentrations. This occurrence was observed previously in this laboratory[15] and may have been due to adsorption/desorption processes on the PFA Teflon tubing (used to introduce the HNO_3 to the denuder and provide an inlet to the analyzer) or in the NO_x converter.
- Changes in NO_x response (0.5 ppbv) were observed for zero air when the humidity was increased from 0 to 50%, and larger changes were seen (up to 2 ppbv) when additional water was added to the humidifier. The latter were not reproducible, and the zero returned to its approximate initial value within several hours. (Since the zero would drift for other reasons, this response was difficult to quantify.)

The combination of these phenomena above made the measurement uncertainty difficult to estimate. For example, while waiting for the concentration to stabilize after a step change, several ppbv of drift could occur. This is especially critical when determining the collection efficiency, as 1 ppbv change at zero concentration causes an apparent 5% change in efficiency when 20 ppbv of HNO_3 is used for the exposure. The NO-NO_x analyzer data should therefore be thought of in most cases as qualitative at low levels of penetration. The one exception is when the denuder is removing most of the HNO_3 *and* the analyzer has not been exposed to HNO_3 for several hours. However, for these requirements, it must be assumed that the HNO_3 at the inlet of the denuder remains unchanged (since it cannot be measured without requiring several hours to reach the final concentration, depending on the relative humidity, and several more hours to reach a stable zero). In the course of obtaining such a measurement, zero drift of the instrument may have occurred, although it would not be quantifiable.

Initial Testing with HNO_3. Denuders coated with NaCl and $NaCO_3$ were used for the initial laboratory evaluation of denuder performance. This study was conducted in two phases, the first to validate the approach and the second to optimize it for HNO_3. All exposures were conducted at room temperature (20 ± 1 °C) at a nominal relative humidity of 10% and with HNO_3 concentration in the 10–40-ppbv range. The HNO_3 concentration and relative humidities were chosen to provide the most difficult ambient conditions for a coated substrate to collect this species.

NaCl was the first coating mixture evaluated. With the 2% NaCl coating on material 1, the collection efficiency was never better than 89%, even at a flow rate as low as 0.6 L/min, and would not stabilize. The experiments were repeated with a $NaCO_3$ coating on material 1. HNO_3 was collected nearly quantitatively at flow rates up to 5 L/min, although the efficiency dropped to 83% after 4 hr of sampling. Figure 2 shows the efficiency (after initial stabilization, 15–30 min) of removing 33 ppbv of HNO_3 in dry air for a variety of flow rates. At 10 L/min the efficiency was 93%, which is in good agreement with the theoretical value of 98%. We expected the measured efficiency to be lower than the theoretical value, according to the theory that each HNO_3 molecule contacting the fiber was removed, which may not be the case. Two such denuders in series at 19 L/min were found to be as quantitative in retaining HNO_3 as a Nylasorb filter sampling at 15 L/min (a higher flow rate could not be obtained due to the pressure drop through the Nylasorb filter).

The fabrics shown in Table 1 were coated with NaCl and tested for HNO_3 removal. Increasing the coating solution to 9% improved the efficiency compared to 2%, but high concentrations and even supersaturated solutions did not cause further improvement. Cotton fabrics performed the best overall. Synthetic fabrics generally were initially efficient, but this efficiency rapidly dropped with continued sampling, possibly because the coating solution was not able to significantly adsorb into the individual fibers. Other materials tested briefly but not reported here were found to work poorly. These included uncoated nylon hosiery, aluminum window screen, bronze sieving, and fiberglass window screen coated with NaCl. Materials 1, 5, 7, and 8 showed over 80% initial

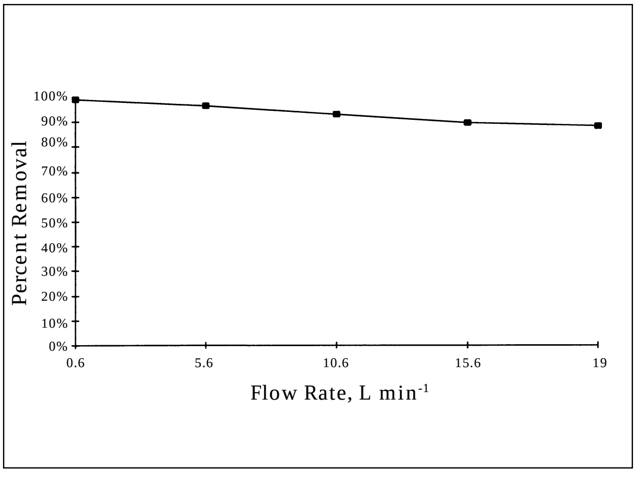

Figure 2. HNO_3 removal efficiency (35 ppb) with a $NaCO_3$-coated fabric denuder using material #1 (35-min average exposure at each step).

collection efficiency, although the efficiency invariably dropped with continued sampling. These materials were chosen for further ambient evaluations.

AMBIENT AIR EVALUATION OF FABRIC DENUDERS

Particulate Penetration

2-L/min Sampling Flow Rate. Figure 3 is a schematic diagram of the sampling system with these mean values of the four 1-week collection periods superimposed. Collocated sampling showed a relative standard deviation of 13%. Sampler 3 denuders should be considered the reference for particulate penetration, since the Teflon filter preceding the denuder removed all particulate SO_4^{2-} and therefore any SO_4^{2-} on the following denuders would be a result of the deposition of gas-phase sulfur-containing species (such as SO_2). The SO_4^{2-} on the denuders without a prefilter is low, near the expected blank variability and very similar to those in sampler 3. This is a good indication that fine particulate is not being significantly retained by the denuders. Comparing the SO_4^{2-} on the Teflon filter preceding the denuders to the SO_4^{2-} on the Teflon filters after the denuders indicated that 11% of the fine particles are lost when passing through three denuders in series. After subtracting the SO_4^{2-} found on sampler 3 denuders (0.02 μg/m^3 for uncoated and 0.16 μg/m^3 for NaCl-coated denuders) and dividing by the SO_4^{2-} expected to be passing through the denuder (5.29 μg/m^3 less the concentration from the previous stage), each denuder was calculated to remove 0–3% of the particulate SO_4^{2-}. The sum of the loss of SO_4^{2-} on individual denuders is, therefore, less than the overall SO_4^{2-} losses, indicating losses in the Teflon filter holder or the inability of the SO_4^{2-} to be quantitatively extracted from the denuder. This deposition may be enhanced by the electrostatic charge that Teflon surfaces tend to acquire.[15]

The conclusion is that while denuder measurements of gaseous HNO_3 will be affected very little by particulate deposition, approximately 10% of the fine particulate mass may be lost during passage through the sampling system of three fabric denuders. This loss, if not accounted for, would result in the underestimation of particulate concentrations. There also is no indication that a preseparator is needed to remove particles to reduce deposition in the denuder. Large particulate NO_3^-, presumably due to the reaction of HNO_3 with NaCl aerosol from sea salt, is one possible exception.[28]

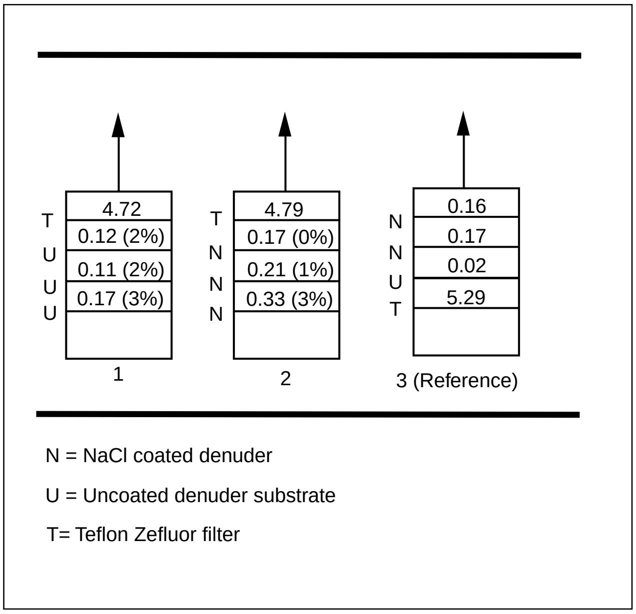

Figure 3. Summary of SO_4^{2-} data (μg/m^3) for the one-week samples using material #5 at 2 L min^{-1} (the percentages of SO_4^{2-} retained by the denuders before the Teflon filter are shown in parentheses).

10-L/min Sampling Flow Rate. Figure 4 summarizes the results of the SO_4^{2-} analyses from four high HNO_3 days, which have a representative of each denuder material. Collocated sampling showed a relative standard deviation of 24%. Comparison of SO_4^{2-} on the Teflon filter downstream of three denuders in series with the SO_4^{2-} on the front Teflon filter of sampler 6 shows the following overall losses through three denuders and holders: 20% for material 1, 18% for material 5, 20% for material 7, and 24% for material 8. To determine the losses for the individual denuders, the SO_4^{2-} from the equivalent denuders on the reference sample line (#6) are first subtracted. Note that the values for the reference sampler denuders are sometimes small negative numbers, indicating that they were slightly overcorrected by the denuder blank (the denuder that was inserted briefly into the substrate holder). This corrected value is then divided by the SO_4^{2-} expected to be passing through the denuder (the SO_4^{2-} found on the front Teflon filter of the reference sampler less the concentration from the previous stage) and multiplied by 100 to give the percentage of SO_4^{2-} removed. These values are shown in parentheses in Figure 4.

The sum of the loss of SO_4^{2-} on individual denuders was generally less than the overall SO_4^{2-} losses. The mean loss of SO_4^{2-} per denuder was 10% for material 1, 3% for material 5, 7% for material 7, and 9% for material 8. The sum of the loss of SO_4^{2-} on individual denuders is approximately equal to the overall SO_4^{2-} losses. We conclude that denuder material 5 allowed the highest particulate penetration of the four materials evaluated.

HNO_3 Measurements and Collection Efficiency

2-L/min Sampling Flow Rate. Figure 5 summarizes the results of NO_3^- analyses for the 2-L/min testing of denuder material 5 by showing the means over four collection periods. Collocated sampling showed a relative standard

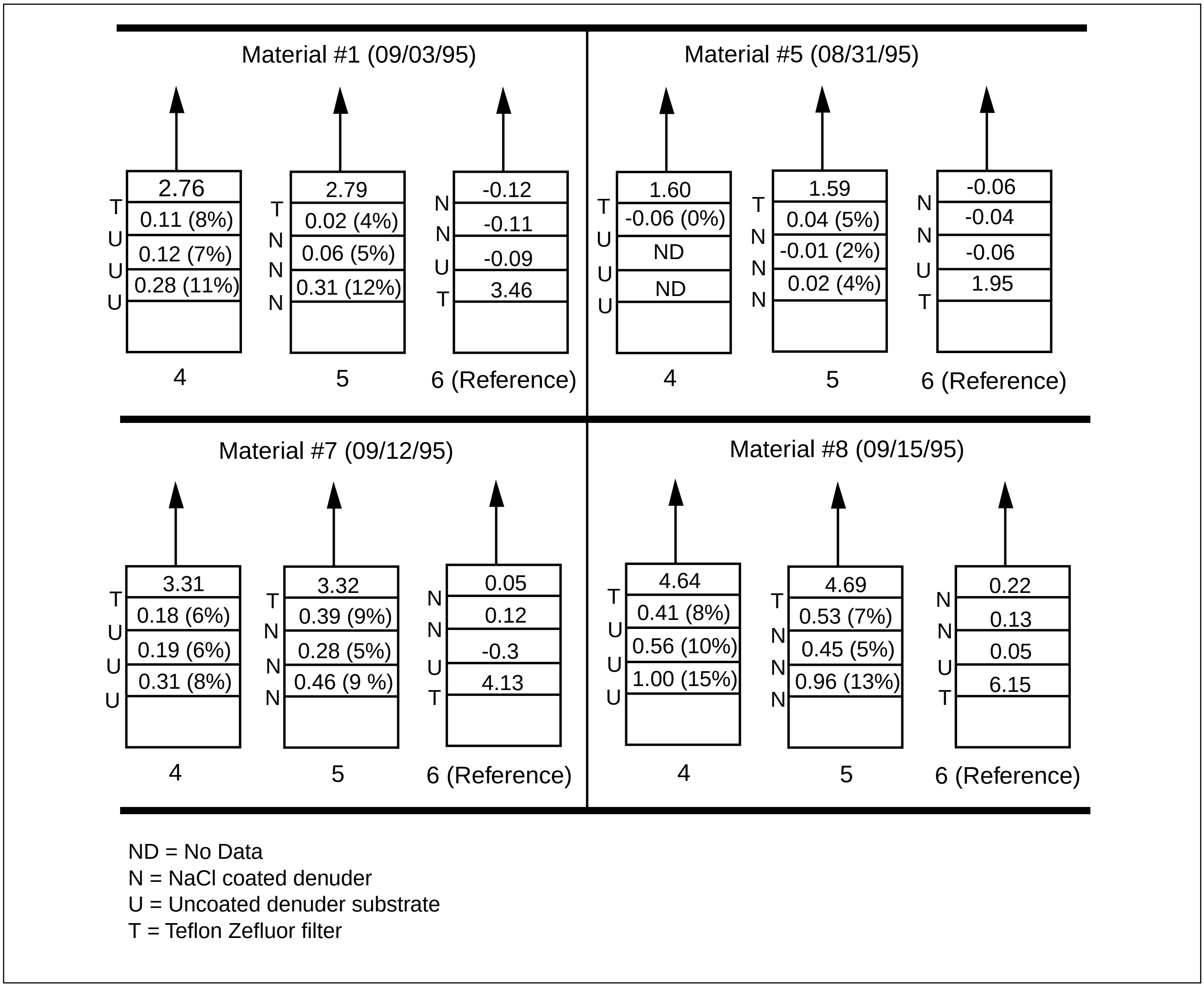

Figure 4. Summary of SO_4^{2-} measurements (µg/ m^3) for selected daytime collection at 10 L min^{-1} (the percentage of SO_4^{2-} retained by the denuders before the Teflon filters are shown in parentheses).

deviation of 8%. Also shown in Figure 5 are the denuder collection efficiencies based on the following equation:

$$E = (1 - L_2/L_1)*100 = \text{Percent Efficiency} \qquad (3)$$

where L_1 is the NO_3^- load measured on the first denuder in series and L_2 is the NO_3^- load measured on the second denuder in series. This expression assumes that the collection efficiency of each denuder is identical.

Since little particulate retention was observed for material 5, these data were not corrected for gains of particulate NO_3^-. The denuder efficiency calculated for the first denuder was expected to be much more accurate than that for the second because most of the HNO_3 was removed passing through the first denuder, thus increasing the uncertainty of the measurements for subsequent denuders. The collection efficiency for HNO_3 was nearly 90% for a single denuder whether the denuder was coated or not. This efficiency of the uncoated denuder was not expected since laboratory testing did not show efficient removal of HNO_3. It is possible that the denuders collected a basic material from the ambient air that aided in retention of HNO_3. Since the uncoated denuder efficiency was high whether the denuder preceded a Teflon filter or not, the basic material would therefore need to be gaseous, possibly NH_3. The conclusion is that the fabric denuders were approximately 90% efficient in removing HNO_3 and, therefore, two denuders are sufficient to quantify this species.

On sampler 3, the denuders, which were preceded by a Teflon filter, retained more NO_3^- than the samplers that did not have a Teflon prefilter, possibly due to the volatilization of particulate NO_3^- from the front filter. The NO_3^- on the sample lines with the Teflon filter after the denuders showed less NO_3^- than the Teflon prefilter. This was expected because the volatilization would be enhanced after HNO_3 is removed from the airstream. Basic material

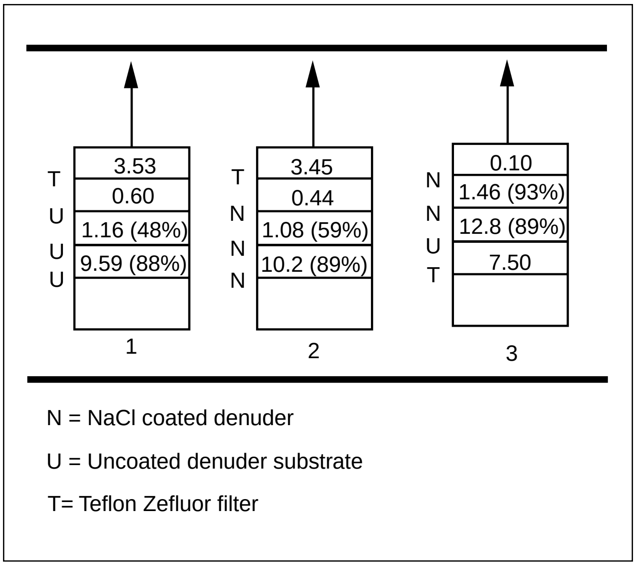

Figure 5. Mean NO_3^- concentrations (µg/m^3) of four 7-day samples (2 L min^{-1}) for material #5 (percent denuder efficiency in parentheses).

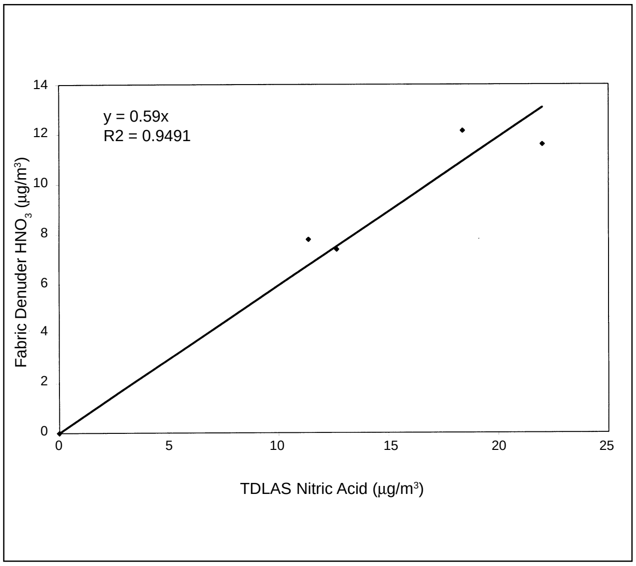

Figure 6. Comparison of HNO_3 measurements between 7-day, 2 L min^{-1} NaCl-coated fabric denuders (sample line #2) and the TDLAS.

deposited on the Teflon prefilter may also have contributed to HNO_3 retention.

To calculate HNO_3, the concentration of NO_3^- on the front NaCl-coated denuders was divided by the denuder efficiency. Figure 6 is a comparison of HNO_3 measured by the 1-week denuder sampling approach compared with that of the TDLAS. Some of the TDLAS data were missing for the weeklong sampling intervals. For short downtimes, less than several hours, the TDLAS HNO_3 data were interpolated in computing an average value for the period. This was not done for the two major downtimes (September 7 at 1900 hr to September 9 at 1345 hr, and September 13 at 0100 hr to September 15 at 0100 hr). Thus, the comparisons for the second- and third-week period of sampling were missing 25% of the TDLAS data.

The correlation is quite good, $r^2 = 0.95$. This correlation coefficient should be considered qualitative, as it is based on only four comparison points and some of the TDLAS data were missing. The mean of the HNO_3 measurement with the denuder was 9.7 µg/m^3, compared to 16.1 µg/m^3 for the TDLAS. The denuder values were, therefore, an average of 40% lower, in agreement with the slope of Figure 6.

10-L/min Sampling Flow Rate. Figure 7 summarizes the results of NO_3^- measurements for daytime samples of each material type by superimposing the concentrations on the samplers' schematic. Denuder efficiency is shown in parentheses. Collocated sampling showed a relative standard deviation of 4%. The uncoated denuder again removed significant HNO_3, with the efficiencies varying from 13 to 77%. Denuders from sampler 6 were expected to be more accurate than the other two since the Teflon prefilter would eliminate the effects of particulate NO_3^- collection on the denuder. The efficiency of the first denuder was also expected to be more accurate because the uncertainty of the calculation increases significantly for the second denuder, as the value of the third denuder (which is near the blank background after removing most of the HNO_3) must be used for the calculation. This spread in efficiency for the uncoated denuders may reflect day-to-day variation in the species responsible for enhancing the HNO_3 collection efficiency of the uncoated denuder (for the weeklong sampling intervals at 2 L/min, the collection efficiency of the uncoated denuder was consistently near 90%).

The overall HNO_3 removal efficiency for two NaCl-coated denuders sampling unfiltered air (calculated using eq 3 but combining the amounts collected by the first two denuders) was 95 ± 1%, regardless of the denuder material. These efficiencies may reflect the effect of particulate collection, which cannot be quantified. From these results, we conclude that the first two NaCl-coated denuders, regardless of material type, remove most of the HNO_3 at the 10-L/min flow rate.

Figure 8 compares the HNO_3 measured with the 10-L/min denuders to those of the TDLAS. The regression is forced through the origin, since nighttime HNO_3 concentrations are expected to be near zero, although we did not analyze nighttime denuder samples. There is a considerable amount of scatter ($r^2 = 0.24$). The mean of these HNO_3 measurements was 30.5 µg/m^3 for the denuder methods, compared with 43.6 µg/m^3 for the TDLAS. The denuder measurements were, therefore, an average of 30% lower than the TDLAS. This is consistent with the larger data set of denuder difference measurements using a denuder difference sampler.[25]

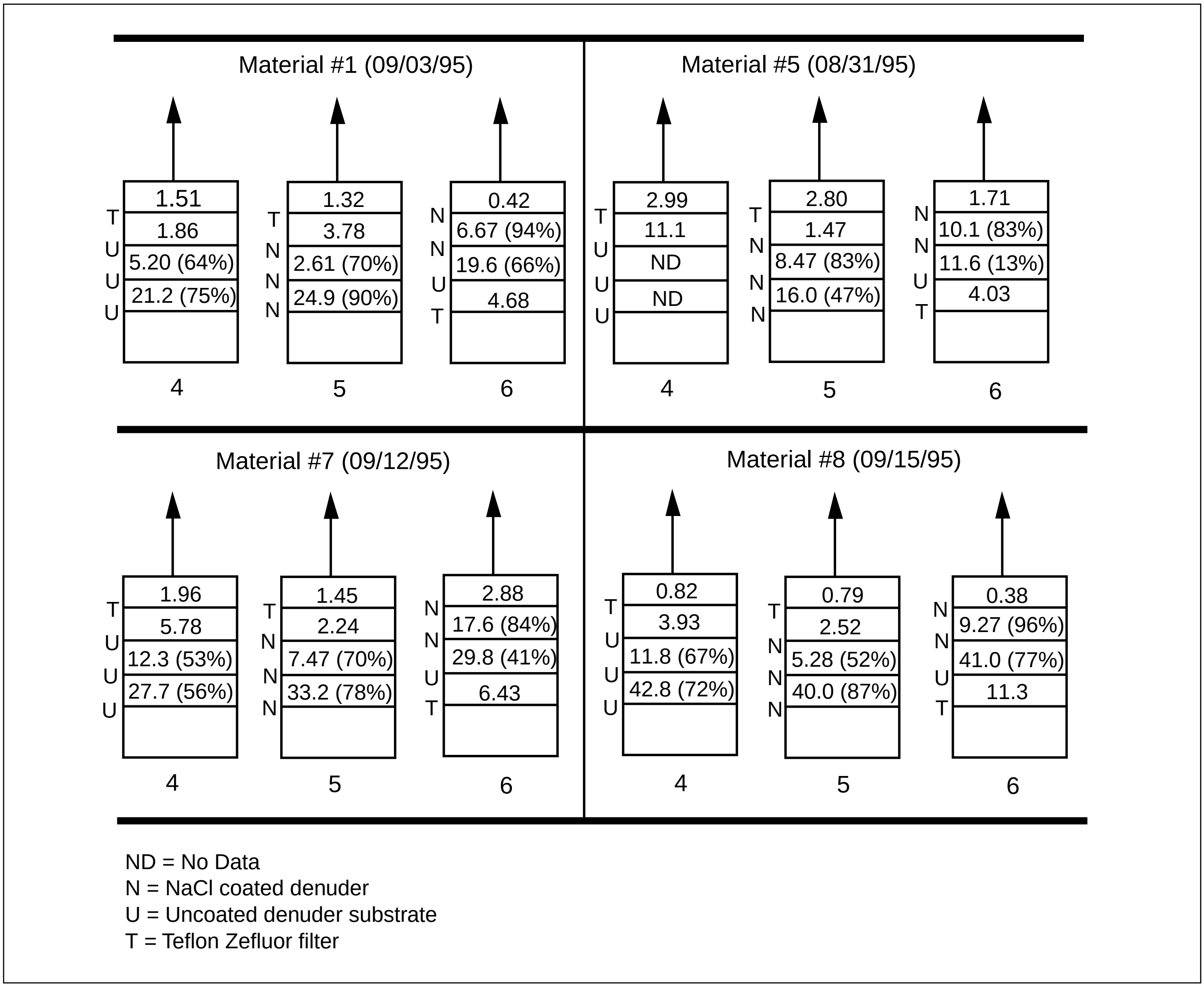

Figure 7. Summary of NO_3^- concentrations ($\mu g/m^3$) for 10 L min^{-1} sampling (corrected denuder efficiencies shown in parentheses).

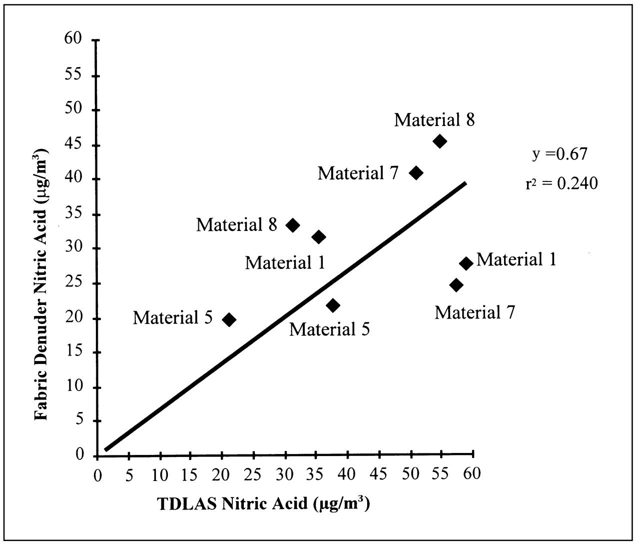

Figure 8. HNO_3 by TDLAS compared with the daily fabric denuder (sample line #5).

Figure 9 compares the HNO_3 measured with the 10-L/min fabric denuders to those of the FTIR spectrometer. The linear regression line again is forced through zero. The plot appears linear and well correlated ($r^2 = 0.73$). While the slope of 0.91 indicated the FTIR spectrometer values were lower, the means indicated that they were higher (35.5 compared with 32.0 $\mu g/m^3$). The application of the Wilcoxan two-tailed ranked sum test[37] showed that the data sets were equivalent at the 95% confidence level ($R_- = 3$, $R_+ = 18$, and $R_c = 2$). We conclude that the HNO_3 measurements obtained with any of the denuder materials are in good agreement with the FTIR spectrometer reference method.

Only five daytime samples were available to compare the fabric denuder with the denuder difference method. Due to the limited number of samples and because three different fabric denuder materials were used, a quantitative comparison was not possible. The qualitative agreement showed a small bias, with the HNO_3 measured by

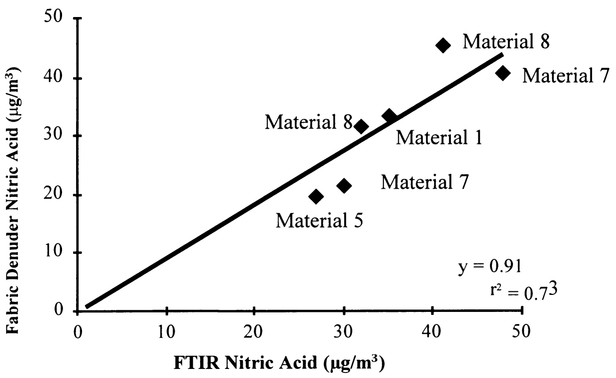

Figure 9. HNO_3 measured by FTIR compared with that measured by the daily fabric denuder (sample line #5).

the fabric denuders averaging 23.3 µg/m³ and the denuder difference sampler averaging 27.5 µg/m³.

CONCLUSIONS

We have shown that an inexpensive NaCl-coated fabric denuder is suitable for measuring HNO_3 in ambient air. For the recommended material (#5), two denuders in series are needed to ensure a collection of over 95% for flow rates up to 10 L/min. For two denuders of this material, the penetration of fine ambient particulate matter was less than 6% based on the amount of SO_4^{2-} collected. Particle losses in this range have been observed for all of the other types of denuders that have been reported. Although not supported by laboratory evaluations, uncoated denuders also showed efficiency in removing HNO_3 from ambient air. NaCl-coated denuders were more effective in removing HNO_3 in ambient air than indicated by laboratory testing. The fabric denuder HNO_3 measurements were in good agreement with those from the long path-length FTIR spectrometer used as the primary reference.

This paper presents the initial feasibility of using this type of diffusion denuder, and further testing is needed to confirm the viability of the approach. We would like to encourage others to use this denuder approach. Material 5 was found to be the overall best when sampling ambient air. It is identified as Imported Permanent Finish Organdy (Heberlein finish) by White Rose Fabric, and may be obtained from A.E. Nathan Co. Inc., 11 E. 36th St., New York, NY 10016.

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DISCLAIMER

This report is based on research sponsored, in whole or in part, by the California Air Resources Board under Contract 94-338. The statements and conclusions in this report are those of the authors and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products. The authors would also be pleased to provide samples of the material cut into 47-mm circles.

REFERENCES

1. National Ambient Air Quality Standards for Particulate Matter—Final Rule. *Fed. Regist.* **1997**, *62(138)*, 38651-38760.
2. Appel, B.R.; Wall, S.M.; Tokiwa, Y.; Haik, M. Simultaneous Nitric Acid, Particulate Nitrate and Acidity Measurements in Ambient Air; *Atmos. Environ.* **1980**, *14*, 549-554.
3. Spicer, C.W.; Howes, J.E., Jr.; Bishop, T.A.; Arnold, L.H.; Stevens, R.K. Nitric Acid Measurement Methods: An Intercomparison; *Atmos. Environ.* **1982**, *16*, 1487-1500.
4. Doyle, G.J.; Tuazon, E.C.; Graham, R.A.; Mischke, T.M.; Winer, A.M.; Pitts, J.N., Jr. Simultaneous Concentrations of Ammonia and Nitric Acid in a Polluted Atmosphere and Their Equilibrium Relationship to Particulate Ammonium Nitrate; *Environ. Sci. Technol.* **1979**, *13*, 1416-1419.
5. Stelson, A.W.; Seinfeld, J.H. Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant; *Atmos. Environ.* **1982**, *16*, 983-992.
6. Hildemann, L.M.; Russell, A.G.; Cass, G.R. Ammonia and Nitric Acid Concentrations in Equilibrium with Atmospheric Aerosols: Experiment vs. Theory; *Atmos. Environ.* **1984**, *9*, 1737-1750.
7. Jacob, D.J.; Waldman, J.M.; Munger, J.W.; Hoffmann, M.R. The H_2SO_4-HNO_3-NH_3 System at High Humidities and in Fogs 2. Comparison of Field Data with Thermodynamic Calculations; *J. Geophys. Res.* **1986**, *19*, 1089-1096.
8. Zhang, X.Q.; McMurry, P.H. Theoretical Analysis of Evaporative Losses from Impactor and Filter Deposits; *Atmos. Environ.* **1987**, *12*, 1779-1789.
9. Shaw, R.W., Jr.; Stevens, R.K.; Bowermaster, J.; Tesch, J.W.; Tew, E. Measurements of Atmospheric Nitrate and Nitric Acid: The Denuder Difference Experiment; *Atmos. Environ.* **1982**, *16*, 845-853.
10. Forrest, J.; Spandau, D.J.; Tanner, R.L.; Newman, L. Determination of Atmospheric Nitrate and Nitric Acid Employing a Diffusion Denuder with a Filter Pack; *Atmos. Environ.* **1982**, *16*, 1473-1485.
11. Possanzini, M.; Febo, A.; Liberti, A. New Design of a High-Performance Denuder for the Sampling of Atmospheric Pollutants; *Atmos. Environ.* **1983**, *17*, 2605-2610.
12. Ferm, M.; Sjodin, A. A Sodium Carbonate Coated Denuder for the Determination of Nitrous Acid in the Atmosphere; *Atmos. Environ.* **1985**, *19*, 979-983.
13. Ferm, M. A Na_2CO_3 Coated Denuder and Filter for Determination of Gaseous HNO_3 and Particulate NO_3^- in the Atmosphere; *Atmos. Environ.* **1986**, *20*, 1193-1201.
14. John, W.; Wall, S.M.; Ondo, J.L. A New Method for Nitric Acid and Nitrate Aerosol Measurement Using a Dichotomous Sampler; *Atmos. Environ.* **1988**, *22*, 1627-1635.
15. Fitz, D.R.; Hering, S.V. *Study to Evaluate the CADMP Sampler*; Final Report; Contract No. 93-333; California Air Resources Board: Sacramento, CA, 1996.

16. Allegrini, I.; De Santis, F.; Di Palo, V.; Febo, A.; Perrino, C.; Possanzini, M.; Liberti, A. Annular Denuder Method for Sampling Reactive Gases and Aerosols in the Atmosphere; *Sci. Total Environ.* **1987**, *67*, 1-16.
17. Vossler, T.L.; Stevens, R.K.; Paur, R.J.; Baumgarder, R.E..; Bell, J.P. Evaluation of Improved Inlet and Annular Denuder Systems to Measure Inorganic Air Pollutants; *Atmos. Environ.* **1988**, *22*, 1729-1736.
18. Pui, D.Y.H.; Lewis, C.W.; Tsai, C.J.; Liu, B.Y.H. A Compact Coiled Denuder for Atmospheric Sampling; *Environ. Sci. Technol.* **1990**, *24*, 307-312.
19. Koutrakis, P.; Sioutas, C.; Ferguson, S.T.; Wolfson, J.M.; Mulik, J.D.; Burton, R.M. Development and Evaluation of a Glass Honeycomb Denuder/Filterpack System to Collect Atmospheric Gases and Particles; *Environ. Sci. Technol.* **1993**, *27*, 2437-2501.
20. Sinclair, D. Measurement of Nanometer Aerosols; *Aerosol Sci. Technol.* **1986**, *5*, 187-204.
21. Cheng, Y.Y.; Yeh, H.C. Theory of a Screen-Type Diffusion Battery; *Atmos. Environ*. **1980**, *11*, 313-320.
22. Durham, J.L.; Stockburger, L. Nitric Acid-Air Diffusion Coefficient: Experimental Determination; *Atmos. Environ.* **1986**, *20*, 559-563.
23. Perrino, C.; DeSantis, F.; Febo, A. Criteria for the Choice of a Denuder Sampling Technique Devoted to the Measurement of Atmospheric Nitrous and Nitric Acids; *Atmos. Environ.* **1990**, *24*, 617-626.
24. Grosjean, D.; Parmar, S.S. Interferences from Aldehydes and Peroxyacetyl Nitrate When Sampling Urban Air Organic Acids on Alkaline Traps; *Environ. Sci. Technol.* **1990**, *24*, 1021-1026.
25. Fitz, D.R.; Tuazon, E.C.; Pisano, J. Comparison of Methods for Measuring Nitric Acid in Southern California; *Atmos. Environ.*, submitted for publication, 1999.
26. Lawson, D.R. The Southern California Air Quality Study; *J. Air Pollut. Control Assoc.* **1990**, *40*, 156-165.
27. Kim, B.M.; Lester, J.; Zeldin, M.D. Characterization of Particulate Matter in the South Coast Air Basin. Presented at the 89th Annual Meeting & Exhibition of A&WMA, Nashville, TN, June 23-28, 1996; Paper 96-MP3.04.
28. Wall, S.M,; John, W.; Ondo, J.L. Measurement of Aerosol Size Distributions for Nitrate and Major Ionic Species; *Atmos. Environ.* **1988**, *22*, 1649-1656.
29. Teffera, S.; Barbosa, S.; Bope, W. Design, Testing, and Implementation of a Multi-Channel Sampler for Use in an Enhanced Fine Particulate Monitoring Program at the South Coast Air Basin. Presented at the 89th Annual Meeting & Exhibition of A&WMA, Nashville, TN, June 23-28, 1996; Paper 96-TP50.01.
30. White, J.U. Long Optical Paths of Large Aperture; *J. Opt. Soc. Am.* **1942**, *32*, 285-288.
31. Horn, D.; Pimentel, G.C. 2.5 km Low-Temperature Multiple-Reflection Cell; *Appl. Opt.* **1971**, *10*, 1892-1898.
32. Winer, A.M.; Tuazon, E.C.; Biermann, H.W.; Wallington, T.J. *Absolute Measurements of Nitric Acid by Kilometer Pathlength FT-IR Spectroscopy and Their Intercomparison with Other Measurement Methods*; Final Report; Contract No. A5-051-32; California Air Resources Board: Sacramento, CA, May 1986.
33. Biermann, H.W.; Tuazon, E.C.; Winer, A.M.; Wallington, T.J.; Pitts, J.N., Jr. Simultaneous Absolute Measurements of Gaseous Nitrogen Species in Urban Air by Long Pathlength Infrared and Ultraviolet-Visible Spectroscopy; *Atmos. Environ.* **1988**, *22*, 1545-1554.
34. Hastie, D.R.; Mackay, G.I.; Iguchi, T.; Ridley, B.A.; Schiff, H.I. Tunable Diode Laser Systems for Measuring Trace Gases in Tropospheric Air; *Environ. Sci. Technol.* **1983,** *17*, 352A-364A.
35. Anlauf, K.G.; MacTavish, D.C.; Wiebe, H.A.; Schiff, H.I.; Mackay, G.I. Measurement of Atmospheric Nitric Acid by the Filter Method and Comparisons with the Tunable Diode Laser and Other Methods; *Atmos. Environ.* **1988**, *22*, 1579-1586.
36. Anlauf, K.G.; Wiebe, H.A.; Tuazon, E.C.; Winer, A.M.; Mackay, G.I.; Schiff, H.I.; Ellestad, T.G.; Knapp, K.T. Intercomparison of Atmospheric Nitric Acid Measurements at Elevated Concentrations; *Atmos. Environ.* **1991**, *25A*, 393-399.
37. Mendenhall, W. *Introduction to Probability and Statistics*; Duxbury Press: Belmont, CA, 1971.

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