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A Counter-Current Parallel-Plate Membrane Denuder for the Non-Specific Removal of Trace Gases

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In this paper we present a counter-current parallel-plate membrane diffusion denuder for the non-specific removal of trace gases from an air flow. In this design, gaseous pollutants are removed by diffusing from a sample channel to two purge channels by crossing microporous membranes. In the laboratory, at a sample flow rate of 5 L/min and purge flow rates of 5 L/min each, gas removal efficiencies ranged from 84% for CO to 72% for SF_6. Removal efficiencies increased with lower sample flow rate, a higher sample to purge flow rate ratio, a longer channel length, and using molecules with higher diffusion coefficient. Removal efficiencies were, however, not affected by the sample channel height. In addition, gas penetration was exponentially associated with the product of channel length, diffusion coefficient, and the inverse of sample flow rate. Particle losses were significant (10−25% losses) only for particles smaller than 50 nm. In a field evaluation, the denuder's performance was tested with an aerosol produced in a photochemical chamber. The denuder's performance was similar to that observed in the laboratory and was stable over time. Finally, the denuder was tested with a semivolatile organic aerosol. Particle mass losses due to volatilization were about 30%.

Introduction

To study the effects of ambient air particles, many applications require the removal of gas components. For instance, when studying particle toxicity, the presence of gaseous copollutants may mislead the interpretation of observed effects. Gases are usually removed from an air stream using diffusion denuders. These denuders use special coatings to trap specific gases (*1*−*5*). For example, basic coatings have been used to trap acid gases, such as nitric acid (HNO_3), similarly, charcoal coatings have been used to trap organic compounds (*5*). Several geometries have been used to increase gas removal efficiencies. Initial denuders were simple hollow tubes (*1*). Later, more efficient annular (*2*, *3*) and honeycomb (*4*) denuder designs were introduced. Also, parallel-plate liquid denuders have been used to determine the concentrations of soluble gases continuously (*6*−*9*). This design utilizes a membrane to separate a sample channel from a liquid flow that is passed in a counter-current fashion. The liquid specifically traps certain gas pollutants and it is subsequently analyzed to determine gas concentrations.

The use of these denuders, however, is limited when relatively more inert gases need to be removed. For instance, there are no appropriate coatings to remove nitric oxide (NO) and carbon monoxide (CO). These gases can be toxic, and a large fraction of them may need to be removed from an aerosol when studying particle toxicity. In this paper we present the design and development of a new counter-current parallel-plate membrane diffusion denuder that removes gases nonselectively. In this new design (Figure 1), gaseous pollutants are removed by diffusing from an inner, sample channel to two purge channels where clean air is passed in a counter-flow fashion. Microporous Teflon membranes are used to separate the channels while allowing the diffusion of gases. Particles, which diffuse much more slowly than gases, are less likely to reach the walls of the sample channel, and thus pass through with relatively small losses.

The main objective of this study was to demonstrate that the proposed method is able to remove a significant amount of trace gases from an air stream while having minimal particle losses. Additionally, we examined the effect of changing experimental parameters on the gas removal efficiency. Finally, we tested the denuder's performance and stability in a field setting using real-life aerosols produced in reaction chambers.

Materials and Methods

Denuder Dimensions, Materials and Operation. The denuder parts, assembly, and operations are presented schematically in Figure 1. The denuder consists of three sections made of stainless steel: a sample and two purge sections. The sample section had a center channel of 90 cm length, 10 cm width, and 1 cm height through which the aerosol was passed. At each end of this section, 6.4 mm o.d. tube connections were used as inlet and outlet ports. Purge sections had center channels of dimensions similar to those of the sample section but a height of 2 cm, with two 6.4 mm o.d. tube connections at each end to supply and take out the purge air. Some tests, using CO, were performed with a sample section made of polycarbonate plastic. This plastic does not react with this inert gas.

Two types of Teflon PTFE membranes were used to separate the sample and the purge-channels: (1) Mupor PM23JSH membrane (Porex Corporation, Fairburn, GA) with a thickness of 0.254 mm and a pore size of 1.5 μm (as measured by Hg intrusion); and (2) Tetratex 1301 membrane (Donaldson Co. Inc., Ivyland, PA), with a thickness of 0.089 mm and a pore size of 0.23 μm (as reported by the manufacturer). The membranes were supported on a 20 mesh stainless steel screen to prevent physical distortion and thus maintain a uniform height of the central channel.

All sections were assembled, with supporting screens and microporous membranes placed between channels, using bolts and screws. To minimize leaks, a rubber O-ring gasket was set in a machined groove along the edges of the denuder. Leak tests were done after every denuder assembly. Leaks were measured by passing a 5 L/min flow through the sample channel and measuring flow recovery downstream, while keeping the remaining ports closed and pressurizing the denuder by 1240 Pa above atmospheric pressure (a much higher pressurization than at normal operations). The denuder was considered leak-free if at least 97% of the flow was recovered. If the denuder failed the leak test, it was reassembled.

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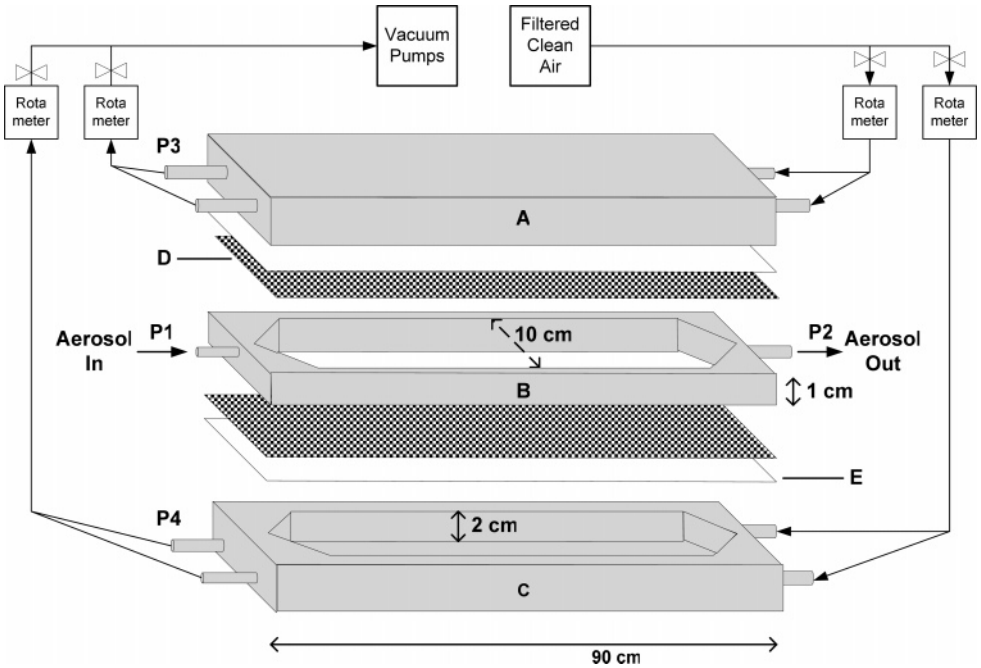

FIGURE 1. Diagram of the parallel-plate membrane denuder: Parts assembly. The denuder consists of an upper (A) and lower (C) purge channels section, a sample channel section (B), two stainless steel screens (D), and two microporous Teflon membranes (E). Sampling ports (P1−P4) are indicated.

Convective flow between the channels was avoided. If convective flow from the purge channel to the sample channel had taken place, the pollutant concentrations in the sample channel would be diluted and the sample channel flow rate would increase. The opposite is expected if the flow went in the opposite direction. Consequently, the flows of air both supplied and removed from the purge channels were carefully balanced using calibrated rotameters and valves. For both the sample and purge channels, the flow regime was laminar at all flows tested (maximum Reynolds number was 215 at a flow rate of 20 L/min).

Laboratory Performance Evaluation. The denuder performance was evaluated in the laboratory using artificial gas and particle atmospheres. The ability of the denuder to remove gases by the principles presented above was evaluated with experiments that included both inert and more reactive gases. The effect of experimental parameters on performance was tested. Because the construction of a denuder is very labor intensive, we only studied the effects of varying sample flow rate (Q_s), purge flow rate (Q_p), sample channel length (L), sample channel height (H_s), and diffusion coefficient (D). Particle losses were measured using an artificial aerosol.

Determination of Gas Removal Efficiency (E) and Mass Balance (MB). To determine E and MB, gas mixtures were prepared using a dynamic gas dilution system (model 146C, Thermo Electron Corp., Franklin, MA). CO, NO, SO_2, and SF_6 were provided from standard gas cylinders. NO_2 was produced by titrating NO with ozone (O_3), which was generated within the dilution system. The system was used to control both the total flow rate (from 2 to 10 L/min) and the concentrations of the gas mixtures. Concentrations of CO, SO_2, NO, and NO_2 were measured continuously using the following Thermo Electron Corp. instruments (Franklin, MA): CO by infrared absorption (model 48C); SO_2 by pulsed fluorescence (model 43C), and $NO/NO_2/NO_x$ by chemiluminescence (model 42C). SF_6 was measured using a photoacoustic Multi-gas Monitor (model 1302, Brüel & Kjaer, Naerum, Denmark). Because the SF_6 monitor samples intermittently, samples were collected at each sampling port using a 5-L Tedlar bag, and analyzed subsequently. These samples were collected at least twice at each sampling port.

Gas concentrations were measured at four different sampling ports (Figure 1, P1−P4): upstream ($C_{s,up}$) and downstream ($C_{s,down}$) of sample channel, and downstream of the upper ($C_{P1,down}$) and lower ($C_{P2,down}$) purge channels. Efficiency, E, was calculated using eq 1.

$$E\ (\%) = 100\left(1 - \frac{C_{s,down}}{C_{s,up}}\right) \tag{1}$$

To demonstrate that gases were removed by diffusion only and not by wall reactions, mass balance (MB) was calculated as the ratio of gas being removed from the sample channel to the gas mass leaving the purge channels, as shown in eq 2,

$$\text{MB}\ (\%) = 100\frac{(C_{P1,Down}Q_{P1} + C_{P2,Down}Q_{P2}}{(C_{S,up} - C_{S,down})Q_S} \tag{2}$$

where Q_S, Q_{P1} ,and Q_{P2} are the flow rates of the sample and the two purge channels, respectively. A measured mass balance of less than 100% would indicate wall losses or similar processes.

E and MB were evaluated in a subset of initial experiments. For these experiments, sample flow rate was set to the overall target flow of 5 L/min, while purge flow rates were set to either 5 L/min or 10 L/min each. The inert gases CO and SF_6 were tested, along with the reactive gas SO_2.

In subsequent experiments, the effects of changing five different experimental parameters on removal efficiencies were examined: (1) sample flow rate (Q_s); (2) purge to sample flow rate ratio (Q_p/Q_s); (3) sample channel height (H_s); (4) channel length (L); and (5) diffusion coefficient (D). For the initial tests the Mupor membrane was used. Because of the difficulties in obtaining large supplies of the Mupor membrane, Tetratex membrane was used for the remaining experiments (for testing of the diffusion coefficient and in field tests). For a first set of experiments, the sample flow rate (Q_s) was varied from 3 to 10 L/min. These tests were done using CO and adjusting each of the purge flow rates to the same value as the sample channel ($Q_p/Q_s = 1$). This set

was used as reference for the other sets. For the next set, the effect of the purge to sample flow rates ratio was tested by repeating the conditions of the reference test but adjusting the purge flow rates to double the sample flow rates ($Q_p/Q_s = 2$). For the next set, the effect of channel length (L) was determined by covering half the length of the membrane (45 cm) with an impermeable sheet. Two extra sample flow rates, of 2 and 2.5 L/min, were tested to increase the overlapping in E values between the reference set and the half-length set. Another set examined the effect of the sample channel height (H_s) by using a taller (2 cm) sample channel section made of polycarbonate plastic.

A final set of laboratory experiments tested the effect of varying the diffusion coefficient (D), using air mixtures of different gases. These gases included nitric oxide (NO), carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and sulfur hexafluoride (SF_6). Because the availability of D values for these gases in the literature is limited, they were estimated from their molecular weights using Graham's law and the D value of CO (0.208 $cm^2\ s^{-1}$) at 20 °C as reference, as shown in eq 3,

$$\frac{D_T}{D_{CO}} = \sqrt{\frac{MW_{CO}}{MW_T}} \tag{3}$$

where D_T and D_{CO}, and MW_T and MW_{CO}, are the diffusion coefficients and molecular weights of target gas (T) and CO, respectively. Using this equation, the calculated D values for NO, NO_2, SO_2, and SF_6 were 0.201, 0.162, 0.138, and 0.091 $cm^2\ s^{-1}$, respectively. All experiments were done at a sample flow rate of 5 L/min, while the purge to sample flow rate ratio (Q_p/Q_s) was set to either 1 or 2.

Particle Losses. To test for particle losses, the denuder was challenged with an aerosol of artificial particles, with particle concentrations being measured upstream and downstream of the denuder. The aerosol was generated by nebulizing a sodium chloride solution using a constant output atomizer (model 3075, TSI, Shoreview, MN). The 3 L/min output of the atomizer was dried in a diffusion drier (TSI model 3062) and then diluted with particle-free air into a 5 L vessel to a total flow rate of 5 L/min. Particle charges were subsequently neutralized with a radioactive source (TSI model 3012), and the final 5 L/min test aerosol was passed through the denuder, with each purge flow rate set to 5 L/min.

Particle size distributions were determined both upstream and downstream of the sample channel using a Sequential Scanning Mobility Particle Sizer and Counter (model 5.5-900, GRIMM Technologies, Inc., Douglas, GA). The aerosol was sampled using a 1 m long flexible PVC plastic tube with an i.d. of about 6.4 mm. The same piece of tubing was used for upstream and downstream measurements. Scans were 3 min in duration, with particle number concentrations reported in particle size bins ranging from 20 to 700 nm. Due to the very low count of particles larger than 150 nm, only particles below that size were reported. Particle losses (%) were calculated for each size bin using eq 4,

$$Loss\ (\%) = 100\left(1 - \frac{C_{s,down}}{C_{s,up}}\right) \tag{4}$$

Five upstream and four downstream measurements were alternated for a total of 8 pairs of comparisons. Average losses and standard error were calculated from the 8 pairs.

Field Evaluation. For a field evaluation, the denuder's performance was tested with simulated real-life aerosols generated in reaction chambers as part of a toxicological study. In this study, the Toxicological Evaluation of Realistic Emissions of Source Aerosols (TERESA) (*12*), animals are exposed to the products of these chambers. To avoid misinterpretation of the toxicological results, it is necessary to remove a large fraction of gaseous co-pollutants before exposures.

The first part of the field evaluation examined performance using the steady-state output of a photochemical chamber. This chamber was used to form secondary sulfuric acid (H_2SO_4) particles from the diluted emissions from a coal-fired power plant. The ability of the denuder to remove gases while transmitting H_2SO_4 particles was tested. In the second part, the denuder's performance was tested with a semi-volatile organic aerosol formed in a different reaction chamber. For a semivolatile aerosol the particle phase components are in equilibrium with its gas-phase components (*10*, *11*), therefore, when trace gases are removed in the denuder, some net particle mass losses are expected. Here we tested the extent of such losses.

Evaluation Using the Exhaust of a Photochemical Chamber. Methods to produce secondary particles from diluted coal-fired power plant emissions are described in detail elsewhere (*12*). Briefly, the diluted emissions are mixed in a 600 L well-mixed flow reactor with excess O_3 and H_2O vapor. In the chamber, the hydroxyl radical (OH) is produced by photolyzing O_3 with ultraviolet light. Then, OH oxidizes SO_2 and NO_2, forming sulfuric acid (H_2SO_4) and nitric acid (HNO_3), respectively. As a result, the chamber exhaust contains gas pollutants SO_2, O_3, HNO_3, and NO_2, and H_2SO_4 particles.

For the tests, a flow rate of 4.7 L/min of chamber exhaust was passed through the sample channel, while purge flow rates were set to 10 L/min each. Removal efficiency, E, and mass balance, MB, were determined as in the laboratory evaluations. To test the stability of E tests were repeated 3 times daily for 3 days. Particle losses were determined from sulfate collected on 47 mm Teflon membrane filters (R2PJ047, Pall Life Sciences, East Hills, NY). Samples were collected upstream and downstream of the denuder once a day and sulfate content of the filters was determined by IC analysis (*4*). Particle losses were calculated using eq 4.

Evaluation with a Semivolatile Aerosol. The method to produce semivolatile organic aerosol in a chamber was described in detail elsewhere (*12*, *13*). Briefly, secondary organic aerosol (SOA) was formed by reacting α-pinene with O_3 in a 100 L well-mixed flow reactor. Tests were done by passing 5 L/min of the steady-state output of the chamber through the sample channel, while purge flow rates were each set to 10 L/min. Particle losses were determined from particle size distributions measured with an SMPS (TSI model 3934) and an aerodynamic particle sizer (APS, TSI model 3310). The SMPS measured the equivalent diameter (d_e) for particle sizes between 13 and 700 nm. The APS measured the aerodynamic diameter (d_a) for particle sizes between 500 and 25 000 nm. Aerodynamic diameter (d_a) was converted to d_e as described by Peters el at. (*14*), assuming the density for SOA formed from α-pinene as 1.2 g cm^{-3} (as suggested by Bahreini et al. (*15*)). Mass concentrations for each particle size were calculated from particle number concentrations, particle density, and d_e. Each scan lasted 5 min. Four upstream measurements were alternated with three downstream measurements. Average mass concentrations and standard errors were calculated from these six pairs of observations.

Results and Discussion

Laboratory Evaluation. The purpose of the laboratory evaluations was to determine the gas removal efficiency (E) of the denuder as a function of the different experimental parameters. The reproducibility of the performance was evaluated more thoroughly in a subsequent field study.

Removal Efficiency (E) and Mass Balance (MB). Initial experiments were carried out using CO, SO_2, and SF_6 as test gases, a sample flow rate (Q_s) of 5 L/min, and purge flow

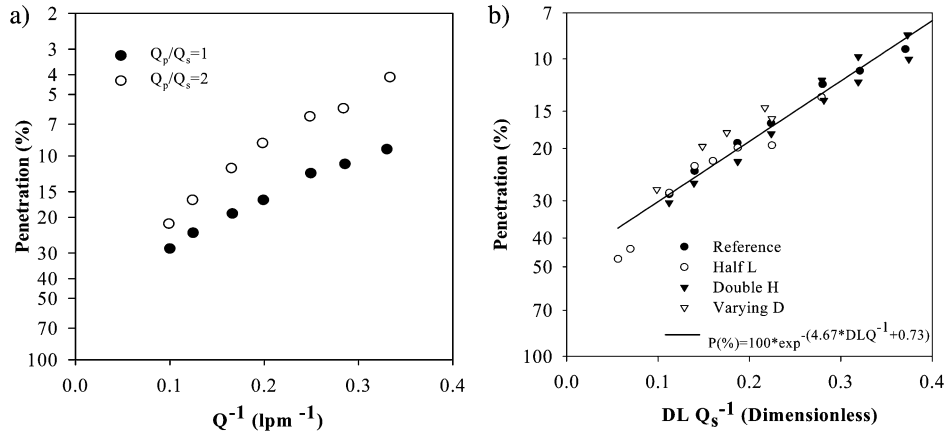

FIGURE 2. Effect of experimental parameters on penetration. (a) Effects of sample flow rate (Q_s) and purge to sample flow rate ratio (Q_p/Q_s). Experimental conditions: (closed circles) L = 90 cm, H_s = 1 cm, Q_s = 3−10 L/min, Q_p/Q_s = 1, Gas = CO; (open circles) L = 90 cm, H_s = 1 cm, Q_s = 3−10 L/min, Q_p/Q_s = 2, Gas = CO. (b) Effects of Q_s, sample channel length (L), sample channel height (H_s), and diffusion coefficient (D). Experimental conditions: (closed circles) L = 90 cm, H_s = 1 cm, Q_s = 3−10 L/min, Q_p/Q_s = 1, D = 0.2 cm^2 s^{-1}; (open circles) L = 45 cm, H_s = 1 cm, Q_s = 3−10 L/min, Q_p/Q_s = 1, Gas = CO; (closed triangles) L = 90 cm, H_s = 2 cm, Q_s = 3−10 L/min, Q_p/Q_s = 1, D = 0.2 cm^2 s^{-1}; (open triangles) L = 90 cm, H_s = 1 cm, Q_s = 5 and 10 L/min, Q_p/Q_s = 1, Gas = CO, NO, NO_2, SO_2, and SF_6.

rates (Q_p) of 5 and 10 L/min. Results for E and MB are shown in Table S1 of the Supporting Information. These trace gases were efficiently removed, with E between 70 and 90%. CO and SF_6 were removed by diffusion only as MB values were close to 100%. For SO_2 tested at a Q_p/Q_s ratio of 1, MB was 77%, indicating that about 23% of the SO_2 was removed by a mechanism other than diffusion, perhaps due to SO_2 deposition on wall surfaces.

Effect of Experimental Parameters on Removal Efficiency (E). The effects on E of changing the following parameters were investigated: (1) sample flow rate (Q_s), (2) purge to sample flow rate ratio (Q_p/Q_s), (3) channel length (L), and (4) channel height (H_s). Results are shown in Table S2 of the Supporting Information. Additionally, the effect of changing D values was tested, with results shown in Table S3.

When using a purge to sample flow rate ratio (Q_p/Q_s) of 1, we found higher removal efficiencies at lower sample flow rates (91% at 3 L/min) than at higher flow rates (72% at 10 L/min). As expected, a lower flow rate increases residence time in the denuder, hence increasing gas removal. When increasing the Q_p/Q_s ratio from 1 to 2, E increased for all sample flow rates examined, with E values ranging from 96% at 3 L/min to 79% at 10 L/min. This was expected as a higher Q_p/Q_s ratio increases the concentration gradient between the purge and the sample channel, thus increasing the diffusion rate between channels.

To examine the effect of channel length (L), half the membrane was covered with an impermeable sheet. With this shorter channel we found that E was always lower than in the full-length case, with E ranging from 80% at 3 L/min to 53% at 10 L/min. This reduction in E was expected as reducing channel length also reduces the time of gas exchange between the channels. To examine the effect of sample channel height (H_s), a taller (2 cm) sample channel section was used. The results from these experiments were no different than the results obtained using the normal sample channel section. These results were surprising and are discussed below.

To examine the effect of the diffusion coefficient (D), several molecules with different D values were tested. At a sample flow rate of 5 L/min and a Q_p/Q_s ratio of 1, we found that E was higher for molecules with higher D values (Table S3, Supporting Information), with E ranging from 85% for CO (D = 0.208 cm^2 s^{-1}) to 73% for SF_6 (D = 0.091 cm^2 s^{-1}). This was expected since molecules with higher D values diffuse faster. Experiments with a Q_p/Q_s ratio of 2 showed the same trend but with higher E, similarly to previous experiments. Since experiments testing the effects of varying D values were conducted using a different membrane than the others, it was important to determine whether the two membranes performed similarly. The results of tests using a sample flow rate of 5 L/min, with the same gas (CO), the difference in the value of E between the Mupor and the Tetratex membranes was only 0.7% at a Q_p/Q_s ratio of 1, and only 1.2% at a Q_p/Q_s ratio of 2.

We found an empirical relationship between penetration (P), which is 100 minus E, and the test parameters. P was exponentially associated with the inverse of the sample flow rate (Figure 2a) for experiments done at Q_p/Q_s ratios of 1 and 2. The slope of this association was higher at a Q_p/Q_s ratio of 2. Additionally, for the results of all experiments performed at a Q_p/Q_s ratio of 1, we found that there was an exponential relation between P and the factor DLQ_s^{-1} (Figure 2b). Equation 5 was derived by linear regression as follows:

$$P = 100 \cdot e^{-(4.67 \cdot DLQ_s^{-1} + 0.73)} \quad (5)$$

Previously, a theoretical equation to predict gas penetration in a parallel-plate denuder was developed by Gormley (*16*) (eq 6).

$$P = 100 \cdot \left(0.9099 \cdot e^{-7.54\frac{LWD}{QH}} + 0.531 e^{-85.7\frac{LWD}{QH}} + \ldots\right) \quad (6)$$

where H and W are the height and the width of the denuder channel, respectively. This equation has a mathematical relationship (logarithmical) similar to that of the empirical equation found by us. However, the Gormley equation predicts much higher removal efficiencies. For instance, with a denuder of length 90 cm, width 10 cm, and height 1 cm, operating at a flow rate of 10 L/min, eq 6 predicted E for CO of 99.97%, which is much higher than the 90% found for our membrane denuder. Additionally, the Gormley equation predicts that the performance is affected by the sample channel height, which was not observed in our experiments. The reasons for this discrepancy are probably because some assumptions of the Gormley equation do not hold in our case. First, it only considers the diffusion across one channel, while in our configuration we have diffusion across the purge and sample channels, and across the membrane. Second, it assumes that the walls act as perfect sinks; meaning that every molecule of the trace gas that reaches the wall is trapped, leading to null concentrations at the walls. In our case, the gas concentrations along the entire length of the

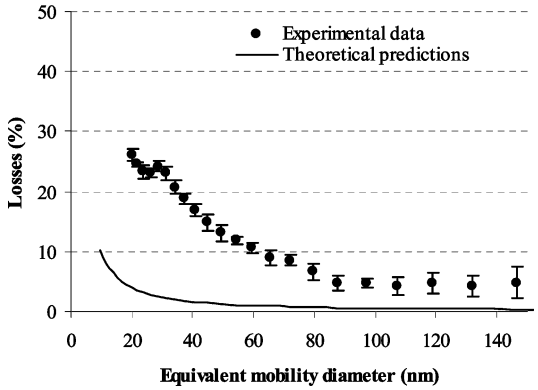

FIGURE 3. Laboratory evaluation of particle losses (%) in denuder as a function of particle size. Error bars show SD.

membrane and in the purge channel are not zero but rather a function of the amount of gas that has already crossed from the sample channel to the purge channel. A theoretical equation to describe the behavior of this new parallel-plate membrane denuder has not yet been developed, and is beyond the scope of this paper.

Evaluation of Particle Losses. To determine particle losses, the denuder's performance was tested using artificially generated NaCl particles. Figure 3 shows experimental losses (solid circles) and theoretical losses due to diffusion (shown as a solid line). Theoretical losses were calculated using eq 7 as suggested by Hinds (*17*):

$$Losses = 100(2.96\mu^{2/3} + 0.4\mu) \quad (7)$$

where μ is

$$\mu = \frac{DLW}{Qh} \quad (8)$$

Only small experimental losses (<5%) were observed for particles larger than 100 nm. For smaller particles, losses increased with particle size, with maximum losses of 25% observed for particles of about 30 nm in size. Experimental losses were much higher than expected theoretical losses. Similar loss levels of ultrafine particles have been observed for other diffusion denuders (*9*, *18*). In particular, the same level and pattern of particle losses as function of size was found for a wet parallel-plate membrane denuder (*9*). These authors demonstrated that the mechanism for particle removal was both diffusion and electrical mobility. The membranes used are nonconductive and they can build up charges. As a neutralized aerosol contains a fraction of charged particles, which follows the Boltzmann distribution, some of them can be attracted and removed by the membrane. In the future, the use of some type of conductive membrane may reduce these losses.

Field Evaluation. *Performance Using the Aerosol Produced in a Photochemical Chamber.* To evaluate the performance in a simulated real-life situation, the denuder's performance was tested with a sulfuric acid aerosol produced in a photochemical chamber. Table 1 shows the results of gas penetration and mass balance for SO_2 and O_3 for 3 days of experiments. NO_2 and HNO_3 measurements were not reported because the constant degassing of HNO_3 from the sampling tubes distorted NO_x measurements. The *E* value for SO_2 was 85% overall for the 3 days, with little variation both between and within days. This same value was observed in laboratory evaluations using the same conditions. MB for SO_2 was over 90% for all days indicating that most of the SO_2 was removed by diffusion from the sample channel to the purge channel. *E* for O_3 was 91%, with little variation both within days and between days. MB was around 60%,

TABLE 1. Field Evaluation Using Sulfuric Acid Aerosol Produced in a Photochemical Chamber[a]

	removal efficiency *E* (%)		mass balance MB (%)		sulfate losses (%)
	SO_2	O_3	SO_2	O_3	
day 1	82.7 ± 0.3	91.1 ± 0.6	96.4 ± 0.1	55.4 ± 1.2	4.9
day 2	84.6 ± 1.2	91.5 ± 1.3	91.0 ± 3.2	58.8 ± 5.3	8.1
day 3	86.2 ± 2.6	91.3 ± 1.4	92.2 ± 13.4	67.2 ± 0.9	5.2
overall	84.5 ± 1.8	91.3 ± 0.2	93.2 ± 2.9	60.4 ± 6.1	6.1 ± 1.7

[a] Experimental conditions: $L = 90$ cm, $H_s = 1$ cm, $Q_s = 4.7$ L/min, $Q_p = 10$ L/min, and Tetratex membrane. For *E* (%) and MB, average (± SD) was calculated from three daily measurements.

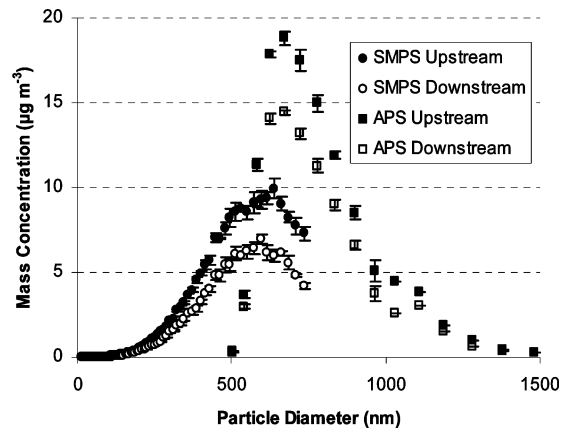

FIGURE 4. Size distribution of SOA upstream and downstream of the denuder. The APS reports aerodynamic diameter, while the SMPS reports electrical mobility diameter. Error bars represent the standard error of the mean.

indicating that, even though O_3 was removed by diffusion to the purge channel, there was a large fraction of O_3 that was lost to the denuder walls.

Particle losses were evaluated from daily filter measurements. Sulfate losses were determined to be 6.1% on average, with little variation between days. Overall, these results show that in a simulated real-life situation, the denuder can effectively remove pollutant gases with minimal losses of nonvolatile particles.

Performance using a Semivolatile Aerosol. The volatilization of a semivolatile aerosol was determined by studying the denuder's performance with a secondary organic aerosol (SOA). SOA was produced in a chamber and size distributions were measured semicontinuously upstream and downstream of the denuder (Figure 4). Total mass concentrations upstream of the denuder were 219 $\mu g\ m^{-3}$ for SMPS and 108 $\mu g\ m^{-3}$ for APS. Overall, particle mass concentrations were reduced by 32% as measured by the SMPS and by 24% as measured by the APS. Note that for size ranges measured by both instruments, the reported concentrations were higher for the APS. This apparent discrepancy is likely a consequence of the low sensitivity of both instruments in this size range (*19*). For future work, the extent of mass losses as function of varying SOA concentrations should be investigated. Partition theory (*10*, *11*) predicts that at smaller SOA concentrations a larger fraction of the semivolatile compounds are in the gas phase. Hence, higher mass losses are expected at lower mass concentrations. These results point out that mass losses for a semivolatile aerosol may be significant. Researchers using semivolatile aerosols should assess whether the use of this denuder is adequate for their particular application.

Applications and Future Work. This denuder can be used to remove gases and also to adjust the sample channel concentrations to the concentrations used in the purge

channel. This feature may be used, for example, to set the RH of an aerosol or to change the gas phase of a semivolatile aerosol. For future designs, removal efficiency could be improved by changing the denuder design and operation. Theoretically, increasing surface area and using a membrane that allows higher diffusion rates should also improve performance. Finally, the development of a theoretical equation would greatly help the design and development of new denuders based on the principles described here. The results presented in this paper can be used to validate such a model.

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Supporting Information Available

Table S1, removal efficiency (E) and mass balance (MB) values for experiments using different test gases and purge to sample flow rate ratios (Q_p/Q_s); Table S2, effect of different experimental parameters on removal efficiencies; Table S3, effect of diffusion coefficient (D) on removal efficiencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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