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A Diffusion Scrubber for the Collection of Gaseous Nitric Acid

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Abstract

A diffusion denuder with a thin anion exchanger membrane tube as the collecting element and with a scrubber solution flowing in a narrow annular gap outside the membrane is described. The use of this device with a dilute sulfate-sulfamic acid solution as scrubber has been exploited for collecting nitric acid. The method is essentially free from interference due to NO_2, and response characteristics are described for a continuous flow application. Direct UV detection, used to demonstrate response characteristics in the continuous monitoring mode, is not sufficiently sensitive for the measurement of low levels of ambient gaseous HNO_3.

INTRODUCTION

Atmospheric gases are commonly collected for analysis using bubblers/impingers, impregnated or otherwise reactive filters, and cartridges containing suitable adsorbents. These techniques are not readily compatible with automated continuous analysis. In a recent paper (*1*) the concept of a membrane-based sampling system for the collection of atmospheric gases was elucidated. A membrane tube is surrounded by a closely fitting outer jacket. A suitable scrubber liquid is made to flow through the annular space. Air is sampled through the membrane tube whereupon the contaminant gas of interest diffuses to the membrane wall. Under laminar flow conditions and assuming a linear configuration

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*To whom correspondence should be addressed and a cylindrical cross section, the efficiency of mass transfer of the species of interest to the wall is predictable by classical equations (*2*) as a function of flow rate, length of the tube, and the diffusion coefficient of the species of interest. If the membrane is solvophilic, resulting in a thin film of an efficient scrubber solution on the inner membrane wall, the "sticking coefficient" of the contaminant species is unity and transfer to the wall is synonymous with uptake at the membrane. For a solvophobic porous membrane (*3*), the sticking coefficient is, however, less than unity and collection is less efficient. The species collected at the membrane diffuses through the membrane into the flowing scrubber liquid. The collected analyte concentration in the scrubber effluent may be determined in a continuous flow analytical system utilizing appropriate chromogenic or fluorogenic reactions. Discrete samples may also be collected for manual analysis.

This device is named a "diffusion scrubber" because of its operational similarity with "diffusion denuders" routinely used in atmospheric analysis to remove specific gases (*4–9*). The diffusion denuder is a tube (or tubes in parallel), the inner walls of which have been coated with a suitable adsorbent to remove a specific gas of interest. The diffusion denuder is also used for the collection of a desired gas for subsequent analysis. Although thermal desorption is feasible in some cases (*10, 11*), more typically actual dissolution of the adsorbent coating is necessary for analysis.

If appropriately designed and operated (in a vertical configuration), a diffusion denuder can be used to discriminate effectively between gaseous and aerosol species when such a discrimination is impossible by chemical analysis once the gas is collected in the condensed phase. Notable examples, of considerable current interest in atmospheric analysis, include the differentiation of gaseous ammonia and particulate ammonium salts, and gaseous nitric acid and particulate nitrate salts. (Note that due to artificially induced equilibration, the simple expedient of using a filter to separate the gas and aerosol leads to large errors and is not acceptable; see, for example, Ref. *12*.) A diffusion denuder can perform such a separation (within a specified flow rate range) by collecting 99+% of the gas at the walls while the aerosol passes through virtually unaffected—a result of the large difference in the diffusion coefficients of the two phases.

Previously, the efficient collection of ammonia was reported using a perfluorosulfonate cation-exchange membrane surrounded by a glass jacket with dilute H_2SO_4 as the scrubbing liquid (*1*). A greater variety of atmospheric gases, e.g., CO_2, SO_2, HNO_3, HCl, etc., lead, however, to characteristic anions which cannot penetrate a cation-exchange membrane due to the Donnan barrier (*13*). In the present article the efficient collection for HNO_3 gas at concentrations down to 20 μg/m^3 is demonstrated using an anion exchanger membrane tube inside a flexible PTFE jacket, in a much improved physical design of the device. Dilute K_2SO_4 is used as the scrubber solution in which sulfamic acid is incorporated to remove NO_2 interference. The response of the device to an inlet pulse of HNO_3 vapor is demonstrated by coupling the diffusion scrubber in continuous flow mode to a UV-photometric detector.

EXPERIMENTAL

The anion-exchange membrane tubes utilized in this work were made at RAI Research Corp. (Hauppage, New York) by radiation grafting vinyl benzyl chloride on a thin walled PTFE tube by γ-radiation (1-1.2 Mrd from a Co-60 source) followed by quaternization with triethylamine in dichloromethane (*13*). Details of this radiation grafting technique have been described in more detail in the literature (*14*). The membrane tubes were 3 mm in internal diameter with ~100 μm wall thickness. The equivalent weight was determined to be ~2500 by previously described procedures (*13*). A 25-cm length of this tubing was utilized for device construction. A 21-cm length of flexible PTFE tubing (AWG 7, Scientific Specialties Service Inc., Randallstown, Maryland) of nominal internal diameter 3.8 mm and 200 μm wall thickness was flanged at both ends after inserting washers and male nuts for each end. A stainless steel flanging tip was machined to accommodate this size tubing; the male nuts were machined from high-density polypropylene and provided with ½-20 threads. The membrane tube was next inserted in the dry state in the PTFE tube and wetted thoroughly with water after insertion. The hydrophilic membrane tube expands significantly upon wetting, and gentle stretching ensured the protrusion of sufficient lengths of membrane tubing from both ends of the jacket. The nominal dry annular volume (between the membrane and the jacket) is 825 μL for the device, which is somewhat reduced during operation due to the expansion of the membrane upon wetting. Connecting tees, designed and threaded for this application as shown in Fig. 1, were next put in, allowing the membrane tube to just protrude from the tee ends. PTFE tubings 3.0 mm in outer diameter and 750 μm in wall thickness were next inserted into each end of the membrane tube to a depth of 1 cm. The inserted ends of these tubes were previously bored with a tapered bit to provide a gradually decreasing wall thickness at the end. This minimizes impedance mismatch as the sampled air flows into the membrane tube proper and

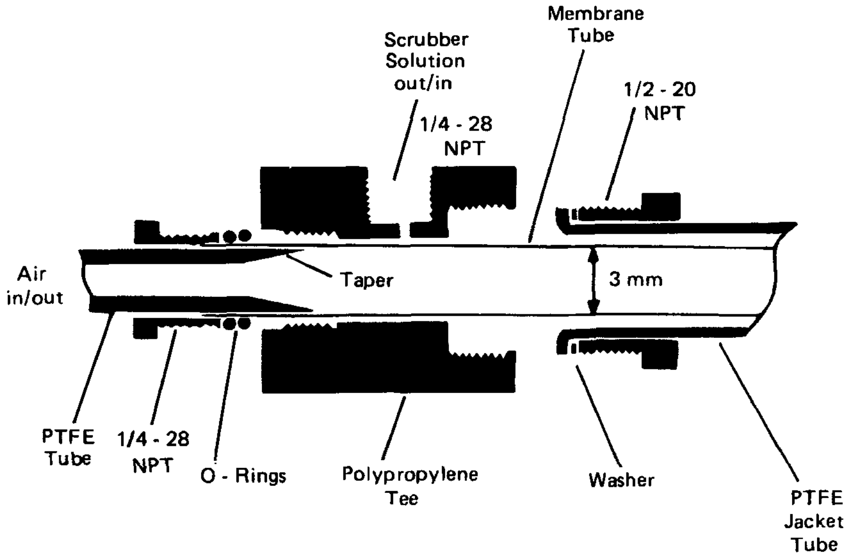

FIG. 1. Design of the diffusion scrubber.

maintains continuity of laminar flow. Without this precaution, significant particle deposition may occur. The inserted PTFE tubing provides the inlet/outlet for air flow, and O-rings with ¼-28 threaded male nuts provide the necessary sealing. The structural rigidity of the membrane tube is limited; after one end is sealed with O-rings and the tube wetted, the other end must be stretched taut before sealing to prevent any radial collapse during operation. The active length of the membrane tube is 23 cm.

The liquid end connections (liquid flow is countercurrent to air flow) are made with ¼-28 threaded male nuts and PTFE tubing 1.5 mm in outer diameter and 0.5 mm in inner diameter.

Nitric acid vapor was generated by passing metered house air through a large fritted (fine porosity) bubbler (500 mL) containing varied concentrations (0.02–1 *M*) of aqueous HNO_3. The nitric acid solution was prepared from a nitric acid stock obtained by distilling Ultrex (J. T. Baker) grade nitric acid in the dark and thereafter storing a diluted ~1 *M* solution of the same refrigerated in the dark. Unless such precautions are taken, large amounts of oxides of nitrogen are produced in the generation system, along with nitric acid gas.

The resultant air stream bearing the acid vapor was allowed to flow through a glass fiber filter to remove any entrained aerosol. This air stream was directed through the diffusion scrubber into a large bubbler (fine porosity frit) containing 50 mL water. Quantitative capture of HNO_3 vapor by a single bubbler was checked by placing a second bubbler in series. The flow of the scrubber liquid (*vide infra*) through the device was directed countercurrent to the air flow and was maintained at 2 mL/h by a Pharmacia P-1 peristaltic pump. The pressure drop in the liquid flow path in this device is quite small and allows gravity feed, if desired. Scrubber liquid samples were collected in screw-top culture tubes equipped with PTFE-lined caps. Sampling periods of 30 min–3 h, depending on the gaseous HNO_3 concentration, were used for collecting samples. At the end of sampling (airflow terminated), liquid flow was continued for an additional period at an enhanced flow rate. An additional ~4 mL (~5 scrubber volumes) of scrubber liquid was collected this way to collect the remaining analyte held up in the scrubber annular volume and the membrane. Replicate samples were collected for all air flow rates studied: 0.5, 1.0, 2.0, 2.5, and 3.0 L/min. In all cases, direct bubbler samples were also collected by omitting the diffusion scrubber from the flow circuit to determine the total HNO_3 output. At an airflow rate of 0.5 L/min, gas-phase nitric acid concentrations ranged from ~100 mg/m^3 at 30°C and ~15 mg/m^3 at 25°C for the 1 *M* generation solution to ~20 $\mu g/m^3$ for the 0.02 *M* generation solution at 15°C (for HNO_3, 2.6 $\mu g/m^3$ = 1 ppbv at 25°C). The nitrate in the scrubber effluent and the bubbler samples was measured by the chromotropic acid nitration procedure (*15*) by spectrophotometry at 400 nm with a Perkin-Elmer 559 instrument. For high concentrations of HNO_3 gas ($\geqslant 1$ mg/m^3), quantitative dilution of the scrubber effluent with blank scrubber solution was necessary. In all cases the nitrate concentrations were computed from a calibration plot obtained from standards prepared in the scrubber solution medium.

Three different scrubber solutions were used in these experiments: 0.1 *M* K_2SO_4, 0.1 *M* K_2SO_4 containing 1% (w/v) sulfamic acid, and 0.1 *M* K_2SO_4 containing 5% sulfamic acid. The sulfamic acid containing solutions were prepared fresh daily.

Gaseous NO_2 was generated from a permeation tube at a concentration of 5.1 mg/m^3 (2.7 ppmv) and standardized by gravimetry as well as the Saltzman procedure (*16*) employing the Griess reaction using a $NO_2(g) \rightarrow NO_2^-$ conversion efficiency of 72% (*17*) for calculating concentrations. The gravimetric results agreed within 5–10% with the colorimetric data.

For the continuous flow detection experiments, the scrubber outlet was directly connected to a HPLC-type variable wavelength detector (Model

770, Kratos Instruments, Ramsey, New Jersey) set at 210 nm. The molar absorptivity of nitrate at this wavelength was measured to be 8.0×10^3 using the slitwidth of this photometer whereas the background absorbance (against water) of a 0.1-*M* K_2SO_4 solution containing 5% sulfamic acid, when prepared fresh from recrystallized reagents, is $\leqslant$ 0.1 AU. Humidified clean air was drawn through the scrubber at 3 L/min with a vacuum pump. The scrubber liquid was contained in a pneumatically pressurized (1 psi) reservoir, and the scrubber liquid was continually withdrawn by suction at the detector outlet with a peristaltic pump at the rate of 16 mL/h. This direct detection method is significantly less sensitive than the chromotropic acid procedure. At the time indicated in Fig. 2, the air source was switched from the clean air source to the nitric acid generator, independently calibrated to be emitting 100 µg/m^3 HNO_3. The air source is switched back to clean air after a period of 5 min.

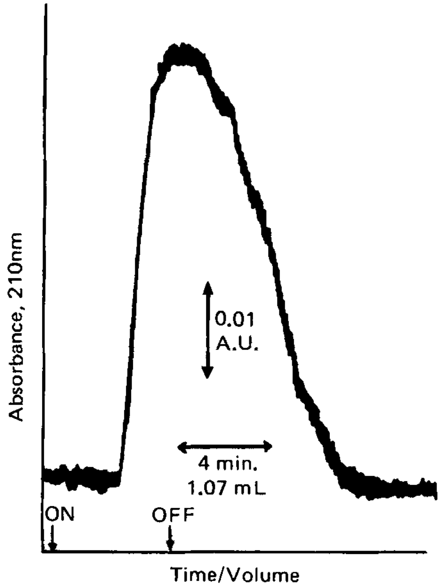

FIG. 2. Response of the device to an inlet pulse (5 min) of 100 µg/m^3 HNO_3, sampled at 3 L/min, liquid flow rate 16 mL/h, direct UV detection at 210 nm.

RESULTS AND DISCUSSION

Capture Efficiency

The fraction (f) of the total HNO_3 captured by the scrubber (defined as the ratio of the amount of NO_3^- found in the scrubber solution to the combined amount of NO_3^- found in the scrubber and the bubbler) is listed in Table 1 as a function of the sampling rate. According to the Gormley-Kennedy equation (*2*) (only the first term is used here; this approximation is valid for the present case), f is related to the volumetric sampling rate Q (in cm^3/s) as:

$$-\ln(1-f) = 0.200 + 3.657\pi DL/Q \qquad (1)$$

where D is the diffusion coefficient of the sampled gas in cm^2/s and L is the active length of the membrane tube in cm. The capture efficiency data are also shown in Table 1. A plot of $1/Q$ vs $\ln(1-f)$ is shown in Fig. 3. The intercept, 0.250, is close to the theoretically predicted value, and using $L = 23$ cm, we calculate from the slope of the best fit regression line that $D = 0.12\ cm^2/s$. This value of D is in good agreement with the values obtained by Braman et al. (*10*) and Durham and Stockburger (*18*) and does not provide any evidence for significant hydration of gas-phase HNO_3 (*19*).

TABLE 1
Capture Efficiency for Nitric Acid[a]

Sampling rate (L/min)	Fraction collected by scrubber, % (± SD)[b]
0.5	93.8 (0.3)
1.0	89.5 (1.0)
1.5	78.1 (2.1)
2.0	68.6 (2.2)
2.5	65.0 (1.8)
3.0	58.5 (2.5)

[a] 3 mm i.d. anion exchange membrane tube, 23 cm active length, 22°C.
[b] $N \geqslant 5$.

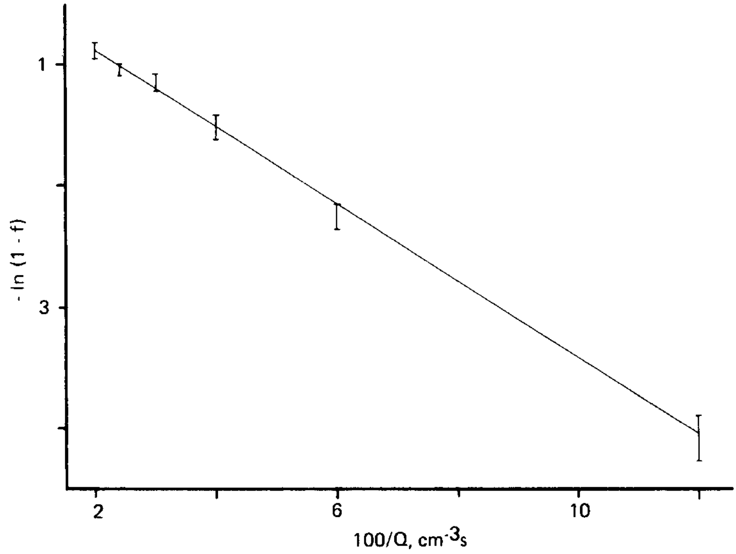

FIG. 3. Plot of the natural log of the fraction of analyte penetrating through the scrubber $(1 - f)$ vs the reciprocal of the sampling rate Q.

Interference from Nitrogen Dioxide

Initial work was carried out with 1 *M* NaOH as scrubber and the sampling of NO_2 indicated very large potential interference. Although NO_2^- rather than NO_3^- is generally produced from NO_2, most colorimetric methods, including the chromotropic acid procedure used in this work, do not discriminate between nitrite and nitrate unless specific measures are taken to destroy the former. Sulfamic acid and urea are commonly used for the removal of nitrite; sulfamic acid is regarded as the better reagent because essentially no nitrate is produced in the nitrite–sulfamic acid reaction (*20*). When 0.1 *M* K_2SO_4 was substituted for 1 *M* NaOH as the scrubber solution, the extent of NO_2 interference was reduced but remained variable and still substantial (34 ± 21% of the NO_2 appears as nitrate, see Table 2). Note that NO_2 is actually converted to nitrite. Since the analytical method does not differentiate between nitrate and nitrite and has a greater response for nitrite than nitrate, the actual fraction of NO_2 taken up by the scrubber is likely to be smaller than the data reported in Table 2, which is calculated in terms of nitrate. With the inclusion of 1% sulfamic acid in the K_2SO_4-based scrubber solution, the interference decreases to 10%, and with 5% sulfamic acid it is all but

TABLE 2
The Effect of Sulfamic Acid on NO_2 Interference[a]

Scrubber solution composition	Air flow rate (L/min)	Mol% NO_2 appearing as NO_3^- ($\pm$ SD)[b]
0.1 *M* K_2SO_4	0.85	34.2 (± 20.6)
0.1 *M* K_2SO_4, 1% NH_2SO_3H	0.85	10.1 (± 1.2)
0.1 *M* K_2SO_4, 5% NH_2SO_3H	0.5	1.4 (± 0.1)
0.1 *M* K_2SO_4, 5% NH_2SO_3H	0.85	0.6 (± 0.1)
0.1 *M* K_2SO_4, 5% NH_2SO_3H	1.75	0.5 (± 0.1)

[a] NO_2 concentration 5.1 mg/m^3 (2.7 ppmv), experimental temperature 22°C.
[b] As measured by the chromotropic acid method.

eliminated ($\leqslant$1%). Studies with a scrubber solution containing 0.1 *M* H_2SO_4 and 5% sulfamic acid indicate the same capture efficiency of HNO_3 and lack of interference from NO_2 as the K_2SO_4-sulfamic acid scrubber; further, this absorber decreases potential interference from other acidic gases which form UV-absorbing anions in solution (e.g., SO_2) and provides a somewhat lower background absorbance, thus improving detectability.

Response Characteristics

The response characteristics of the device in the continuous flow mode, with conditions as described in the Experimental section, were determined by following the response of the UV detector connected to the scrubber effluent and are shown in Fig. 2. The total amount of nitrate admitted to the sampler inlet is ~1.5 μg. Assuming a 59% capture efficiency at the sampling rate employed (see Table 1 and Fig. 3), ~900 ng HNO_3 is captured by the scrubber. The resulting peak is shown in Fig. 2. The area under the peak is ~0.11 AU · mL. For 900 ng HNO_3 captured and the optical path length being 1 cm, this translates to a molar absorptivity of 7700 for nitrate, in good agreement with the directly experimentally measured value of 8000.

The rise time for response is quite rapid, but a significant time is required for the system to return to baseline level. At smaller scrubber solution flow rates the rise time is delayed and the peak is higher. It was also noted that the volume of total scrubber flow necessary to affect complete clearance of the sample plug is not appreciably altered. This clearance volume (base width of the peak in time units multiplied by the liquid flow rate) may be calculated from Fig. 2 and amounts to ~2.5 mL, approximately equal to three times the holdup volume of the scrubber. These data suggest that the speed of the overall response is *not* being controlled by the transport rate through the membrane and that this transit time through the membrane is not prohibitively large for the present application. The transit time of the analyte through the membrane is governed by the relaxation time of the analyte in the membrane, given by t^2/D, where t is the thickness of the membrane and D is the diffusion coefficient of the analyte in the membrane matrix. Although no diffusion coefficient data are available for these membrane matrices, based on the data available on perfluorosulfonate cation-exchange membranes (*21*), we estimate that D for most ions of interest will fall in the range $5-10 \times 10^{-7}$ cm^2/s. Using $t = 0.01$ cm, a relaxation time of ~1-3 min is thus calculated. An overall faster response may therefore be expected, at the expense of attainable limit of detection, if the turnover rate of the scrubber liquid is increased further.

Operational Considerations

Although water serves as an excellent medium for collecting gaseous HNO_3 or HCl in a bubbler, it is not usable as a scrubber in the present device. Collection itself is not hampered, but desorption from the ion-exchange sites requires suitable displacing ions. The total ion-exchange capacity of the membrane in the present device is not insignificant and amounts to several mg of NO_3. Sulfate was chosen as the displacing ion because of its stability, high affinity for anion-exchange sites as a divalent anion, and lack of UV absorption.

If final analysis is manual, i.e., if the scrubber is operated in lieu of a bubbler, the device may be operated without the scrubber solution actually flowing through the device. In such cases the device design needs to incorporate a relatively larger annular volume (static scrubber volume). Otherwise, practical sampling periods may lead to complete or near-complete evaporative loss of the scrubber. A gravity-feed reservoir may also be connected to the scrubber.

In continuous flow applications, flow of the scrubber solution by suction at a constant rate at the detector outlet is preferable to pumping it by pressure (see Experimental section). This avoids any problems arising from mismatch of influent and effluent flow rates due to any evaporative loss of the scrubber solution. However, the scrubber solution reservoir should be kept at a slight positive pressure to avoid any bubble formation.

CONCLUSIONS

We have successfully demonstrated the utilization of an anion exchanger tubular membrane as the collecting element of a diffusion denuder, and elucidated its response characteristics in continuous flow applications. Although HNO_3 was chosen as the test gas because of considerable current interest in the role of HNO_3 in atmospheric acidity (*6, 10, 11, 21*), it is not our intention to claim that low response time, interference-free monitoring of low levels of ambient gaseous HNO_3 is immediately possible by this approach. While any interference due to the primary interferent, NO_2, has been virtually eliminated (note that at high levels NO_2 is believed to interfere in other existing methods (*19*)), extensive testing with other possible interferents will be necessary. Collection efficiencies for HNO_3 agree with theoretical predictions over a large concentration range down to 20 $\mu g/m^3$, and there is no reason to believe that the situation will be different at lower, typical ambient concentrations. The primary problem with the continuous detection approach used here is that direct UV detection for nitrate is relatively insensitive and quite nonspecific. Photometric methods that are sensitive for nitrate generally involve prior reduction to nitrite, and these cannot be practiced in the presence of large amounts of sulfamic acid. The chromotropic acid procedure used in this work for manual analysis and other similar methods involving nitration are of intermediate sensitivity and of acceptable specificity as long as nitrite is removed. The main problem with such methods, however, is the requirement of a concentrated H_2SO_4 medium. While the recently introduced pneumatically pressurized porous PTFE reactors (*22*) may be used to introduce such a highly corrosive reagent, the immediate potential of the present approach is likely greater for gases such as SO_2 which can be selectively detected with high sensitivity. In perspective, the existing approaches to nitric acid measurement are not sensitive enough to provide real time measurements and some are prone to artifact results as well (*23*).

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has not been subjected to review by the Environmental Protection Agency and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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