Collection Efficiencies of a Tandem Sampling System for Atmospheric Aerosol Particles and Gaseous Ammonia and Sulfur Dioxide

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The collection efficiencies of aerosol particles and gaseous NH₃ and SO₂ were tested for a tandem sampling system consisting of a cyclone separator followed by a 1.0 μm pore size 47-mm Millipore Teflon particle filter and four 47-mm Whatman 41 filters coated with oxalic acid and either K₂CO₃ or LiOH. The collection efficiency of the cyclone was compared with an 8.0 µm pore size Nuclepore filter using NaCl particles. Both the cyclone and the filter had a 50% collection efficiency at 0.9 μ m (50 standard L/min, 55 cm s⁻¹ filter face velocity). Known amounts of NH₃ and SO₂ were generated and collected on the coated filters. The collection efficiency of the system for NH₃ was found to be $103 \pm 30\%$. The SO_2 collection efficiency on K_2CO_3 - and LiOH-coated filters was 100 ± 21 and $88 \pm$ 9%, respectively, and was not affected by the presence of reduced sulfur gases or ozone in the sampled air stream.

Introduction

It is often desirable in atmospheric sampling to separate the gas and particulate phases to yield a better understanding of multiphase processes. A tandem sampling system consisting of a prefilter for the collection of particles followed by a series of treated paper filters for the collection of gaseous species is a simple approach to this problem. The particulate phase can be separated further on the basis of size by using a cyclone or two or more filters with different pore sizes in series. Size-segregated particle sampling is particularly important in the marine environment where the aerosol particle volume distribution is bimodal and often dominated by a large sea-salt component. Size-segregated/treated filter sampling systems have been used for the collection of NH_3 (1, 2) and SO_2 (3, 4) in remote marine atmospheres, yet laboratory and field collection efficiencies for these gases have never been reported.

This paper discusses the results of laboratory collection efficiency tests for particles and gaseous NH3 and SO2 using a tandem sampling system. This system (Figure 1) includes a cyclone followed by a 47-mm Millipore Teflon particle filter (1.0 μ m pore size) and four treated 47-mm Whatman 41 paper filters. The Whatman filters were coated with 0.01 M oxalic acid for the collection of NH3 and either 0.1 M potassium carbonate or 0.1 M LiOH for the collection of SO₂. The treated filters were deployed in series to evaluate the breakthrough properties of the system and to ensure collection of all of the gas in the air stream. The degree of breakthrough associated with the laboratory tests was compared to that which occurred during field sampling over the Pacific Ocean. The penetration efficiencies of the cyclone separator were compared with an 8.0 μ m pore size 47 mm Nuclepore filter used in other studies (3, 4).

Experimental Section

Calibration of the Cyclones and Membrane Filters.

The cyclones were machined from either polyethylene or acetal (drawings available from the authors) and were calibrated along with 8.0 μ m pore size, 47 mm diameter Nuclepore membrane filters in an air stream containing sea-salt particles. The aerosol was generated by sparging a 1% sea-salt solution with a 4 L min⁻¹ air flow through a fritted glass tube. The resulting air stream was diluted with humidified air at a flow rate of 400 L min⁻¹ to obtain a final relative humidity (RH) of 66% and a particle concentration of \sim 20 μ g m⁻³. Particle electrostatic charges were neutralized with a 85 Kr β source (TSI, Model 3077, St. Paul, MN). The aerosol particles were sized by an optical particle counter (Royco Corp., Menlo Park, CA), with and without the cyclone or filter, into 14 bins between 0.3- and 2.1- μ m particle diameter.

Preparation of Coated Whatman 41 Filters. The 47-mm Whatman 41 filters for NH₃ collection were washed with 4 L of 10% HCl followed by 4 L of distilled deionized water. After washing, they were vacuum dried and placed in an NH₃-free glovebox. The filters were then coated with 0.01 M oxalic acid in a 16/84 glycerol/methanol (Photrex reagent-grade methanol) solution and left to dry in the glovebox. Weighing of the filters before and after coating showed that $6.5 \pm 0.4~\mu \text{mol}$ of oxalic acid was deposited on each filter. Thus, each filter had a stoichiometric capacity for NH₃ of $13 \pm 0.8~\mu \text{mol}$.

The Whatman 41 filters for SO_2 collection were washed with 8 L of distilled deionized water, vacuum dried, and put in a SO_2 -free glovebox. The filters then were coated with either 0.1 M K_2CO_3 in a 20/70/10 water/methanol/glycerol solution or with 0.1 M LiOH in a 10/90 glycerol/methanol solution. Further details on making the LiOH solution can be found elsewhere (5). The filters were left to dry in the glovebox. Differential weighing showed that $46 \pm 2 \,\mu$ mol of K_2CO_3 and $52 \pm 3 \,\mu$ mol of LiOH were coated on each filter. Each K_2CO_3 and LiOH filter had a stoichiometric capacity for SO_2 of 92 ± 4 and $52 \pm 3 \,\mu$ mol, respectively.

Once the coated filters were dry, they were frozen in acid-washed sealed Petri dishes until use. The filters were coated no more than 24 h before use.

Preparation of the Tandem Sampling System. The 47-mm filter packs used to hold the Teflon and Whatman filters were made by Nuclepore Corp. (Pleasanton, CA). Both the cyclones and the filter packs were soaked for 2-4 h in 10% HCl and rinsed thoroughly with distilled deionized water prior to use.

Sampling of NH_3 and SO_2 Air Streams. SO_2 , NH_3 , OCS, $(CH_3)_2S$, H_2S , CH_3SH , and CS_2 standards were generated by using permeation tubes calibrated gravimetrically. The permeation tubes were kept at a constant 40 °C. O_3 was generated by a UV lamp (UV products, Inc., San Gabriel, CA), and its concentration was monitored with a chemiluminescent O_3 analyzer (Monitor Labs, San Diego, CA).

The system used for the generation of known amounts of the above gases is shown in Figure 1. Air, free of the gases to be sampled (zero air), was passed over the per-

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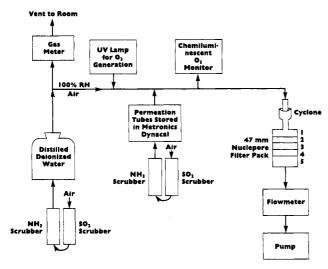


Figure 1. Apparatus used for testing the NH₃ and SO₂ collection efficiencies. For the filter pack, 1 is a 47 mm 1.0 μ m pore size Millipore Teflon particle filter and 2–5 are coated 47-mm Whatman 41 filters with either 0.01 M oxalic acid, 0.1 M K₂CO₃, or 0.1 M LiOH.

Table I. Concentrations of Standards as They Were Passed over the Coated Filters

std species	concn, nmol m ⁻³	std species	concn, nmol m ⁻³
$ \begin{array}{c} \text{NH}_3 \\ \text{SO}_2 \\ \text{OCS} \end{array} $	36 ± 4.5 160 ± 18 86 ± 4.3	$_{\mathrm{CH_3SH}}^{\mathrm{L2S}}$	200 ± 11 400 ± 20 44 ± 2.2
$(CH_3)_2S$	64 ± 3.2	CS_2	44 ± 2.2

meation tubes while a second stream of zero air was bubbled through a large volume of distilled deionized water. A portion of this air stream was vented to the room, and the remaining part was merged with the air from the permeation tubes. Another air stream containing O₃ joined the air flow upstream of the permeation tubes. The resulting sample air had a relative humidity near 75% and an ozone concentration of 15 ppbv (typical of low-latitude, marine boundary layer conditions). This air stream was pulled through the tandem sampling system at an average flow rate of 44 L min⁻¹. The concentrations of the standards as they passed over the coated filters are given in Table I. Sampling times ranged from 37 to 106 min. System blanks were run for both NH₃ and SO₂ by removing the permeation tubes from the sample air stream.

Analysis of Coated Whatman Filters for Ammonium and Sulfate. After sampling, the cyclone was removed from the tandem sampling system and the filter pack was transferred to an NH₃- and SO₂-free glovebox. Once in the glovebox, each oxalic acid coated filter was put into a centrifuge tube containing 10 mL of distilled deionized water. Likewise, each of the potassium carbonate and lithium hydroxide coated filters was placed into a centrifuge tube containing 10 mL of 0.1% H₂O₂. The filters were sonicated for 30 min for extraction of NH₄⁺ and SO₄²⁻ and then centrifuged for 10 min.

The NH₄⁺ samples were analyzed by the phenol hypochlorite colorimetric technique (6) with a Technicon Autoanalyzer II (Technicon Corp., Tarrytown, NY). The SO₄²⁻ samples were analyzed by a Dionex 2120i Ion Chromatograph (Dionex Corp., Sunnyvale, CA).

Results and Discussion

Size-Segregated Aerosol Particle Sampling. The particle number population was compared with and without the cyclone and filter and the difference was

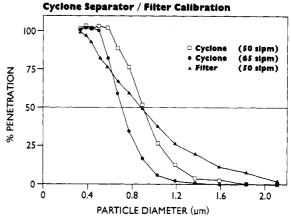


Figure 2. Particle penetration efficiency through the cyclone separator and an 8.0- μ m pore size Nuclepore membrane filter. The relative humidity of the air stream was 66%. The flow rates through the separator and filter are given in standard liters per minute. The face velocity on the Nuclepore filter at 50 slpm was 55 cm s⁻¹.

plotted as percent penetration for each size bin (Figure 2). At 50 standard L/min (slpm) (filter face velocity of 55 cm s⁻¹) and 66% RH, both the cyclone and filter passed essentially 100% of the particles less than 0.4- μ m diameter and had a 50% penetration efficiency (D_{50}) at 0.9 μ m. At 65 slpm the D_{50} was reduced to 0.7 μ m (Figure 2). John et al. (7), using 8.0 μ m pore size Nuclepore filters, predicted a D_{50} at 55 cm s⁻¹ of approximately 1.0 μ m for a particle of unit density. If this D_{50} is corrected for NaCl droplets with densities of 1.2 kg L⁻¹, the predicted D_{50} would be $(1.0/(1.2)^{1/2}) = 0.91~\mu$ m, in excellent agreement with our measured value.

At 50 slpm, both the cyclone and Nuclepore filter are effective at separating marine aerosol particles at the intermode minimum $(0.5-1.0 \cdot \mu \text{m})$ diameter) of their bimodal volume distribution (8, 9). The smaller particles are primarily ammoniated sulfuric acid, while the larger particles are dominated by sea salt (9, 10). During shipboard field experiments, the sulfate aerosol particles that passed the cyclone and were retained on the $1.0 \ \mu \text{m}$ pore size Teflon filter were at most 8% sea-salt sulfate. A salt correction using Na⁺ was still required, but by physically separating the two modes, it was possible to more accurately quantify the non-sea-salt sulfate, a key component of the atmospheric biogeochemical sulfur cycle.

Although the cyclone and Nuclepore filter have the same D_{50} , there are advantages of one over the other. The cyclone provides a sharper cut (Figure 2) and hence better resolution between the two size classes. The disadvantage of the cyclone is that the larger fraction is not retained for chemical analysis, whereas the large fraction on the Nuclepore filter is. Potential disadvantages of the filter include a change in collection efficiency with loading and changes in filter electrostatics. The collection efficiency can also be different for liquid and solid particles, and in the case of marine aerosol particles, basic sea salt collects on the Nuclepore filter, which can absorb acidic gases and aerosol particles. The separation technique of choice. therefore, depends upon the need to quantitatively analyze the larger fraction (>1 μ m diameter particles). It is also important to note that humidity plays an important role in collection efficiencies. At low humidities (dry laboratory air), the cyclone passed essentially all particles. This dependence on relative humidity indicates the need to determine the collection efficiency of a sampling system for each set of field conditions encountered. Also, as filter face velocities increase above 55 cm s⁻¹, an increasing fraction of the dense (1.8 kg L⁻¹) submicrometer sulfuric acid

Table II. Results of NH₃ Collection Efficiency Tests Using Oxalic Acid (C₂H₂O₄) Coated Filters and SO₂ Collection Efficiency Tests Using K₂CO₃- and LiOH-Coated Filters at 75% RH Except Where Noted^a

		loss rate, nmol min ⁻¹		colletn	
sample gases	tests, no.	measd	actual ^b	effic, %	$comments^c$
NH_3	3	1.7 ± 0.5	1.6 ± 0.2	103 ± 30	$0.01 \text{ M C}_2\text{H}_2\text{O}_4$
NH_3	12	0.54 ± 0.45	1.6 ± 0.2	33 ± 30	$0.01 \text{ M C}_2\text{H}_2\text{O}_4, \sim 40\% \text{ RH}$
SO_2	4	7.1 ± 1.5	7.1 ± 0.8	100 ± 21	0.1 M K ₂ CO ₃
SO_2	2	6.3 ± 0.6	7.1 ± 0.8	88 ± 9	0.1 M LiOH
SO_2 , O_3	2	7.2 ± 0.7	7.1 ± 0.8	101 ± 8	$0.1 \text{ M K}_2\text{CO}_3$
SO_2 , O_3	2	7.6 ± 0.8	7.1 ± 0.8	107 ± 10	0.1 M LiOH
SO_2 , OCS, $(CH_3)_2S$	1	8.0 ± 0.8	$7.1 \pm 0.8 \text{ (wrt SO}_2)$	113 ± 11	$0.1 \text{ M K}_2\text{CO}_3$
SO_2 , OCS, $(CH_3)_2S$, O_3	1	6.8 ± 0.7	$7.1 \pm 0.8 (\text{wrt SO}_2)$	96 ± 10	$0.1 \text{ M K}_2\text{CO}_3$
SO_2 , OCS, $(CH_3)_2S$, H_2S , CH_3SH ,	1	7.3 ± 0.7	$7.1 \pm 0.8 (\text{wrt SO}_2)$	103 ± 10	$0.1 \text{ M K}_2^{\circ} \text{CO}_3$
CS_2 , O_3					
OCS , $(CH_3)_2S$, CS_2 , O_3	1	0.86 ± 0.9	8.5 ± 0.1 (wrt OCS, (CH ₃) ₂ S, CS ₂)	10 ± 1	0.1 M K ₂ CO ₃
$(CH_3)_2S$, OCS	2	0.06 ± 0.01	$6.6 \pm 0.1 \text{ (wrt OCS, (CH3)2S)}$	0.9 ± 0.1	0.1 M LiOH
$(CH_3)_2S$, OCS, O_3	2	0.015 ± 0.001	$6.6 \pm 0.1 \text{ (wrt OCS, (CH_3)_2S)}$	0.2 ± 0.02	0.1 M LiOH

^a Errors are reported as the sample standard deviation for n > 2 and as the error associated with the sampling and analysis methods for n < 2. ^b wrt, with respect to. ^c Filter coating.

aerosol particles will be retained on the Nuclepore filters since the slope of the percent penetration curve (Figure 2) is more gradual than that of the cyclone.

Ammonia Collection Efficiencies. The results of the collection efficiency tests are summarized in Table II. Three tests using the system shown in Figure 1 predicted a mean loss rate from the NH₃ permeation tube of 1.7 nmol min⁻¹ with a sample standard deviation of ± 0.5 nmol min⁻¹. The actual loss rate as determined by measured weight loss was 1.6 ± 0.2 nmol min⁻¹, resulting in an NH₃ collection efficiency of $103 \pm 30\%$. The variability in the collection efficiency most likely was due to contamination during sampling and analysis.

A total of $92 \pm 5\%$ of the NH_3 was found to collect on the first oxalic acid filter stage, $6 \pm 3\%$ on the second, and $2 \pm 2\%$ on the third (Figure 3). NH_3 collection efficiencies with and without the cyclone in the tandem sampling system were not significantly different. Apparently, neither the polyethylene or acetal cyclones absorbed NH_3 from the sample stream.

The volume of water was removed from the system shown in Figure 1 to evaluate the effect of relative humidity on the NH₃ collection efficiency. The resulting relative humidity of the sample stream was approximately 40%, effectively that of room air. At this low relative humidity, the NH₃ collection efficiency was much lower and more variable, being $33 \pm 28\%$ based on the results of 12 tests. This difference indicates that a wetter filter results in a higher collection efficiency. It is also possible that the oxalic acid coating has a tendency to volatilize at low relative humidity, thereby decreasing the collection efficiency. The same effect on relative humidity on collection efficiencies may occur for SO₂ as well. This dependence indicates the need to perform collection efficiency tests for different sampling conditions, e.g., ground versus aircraft sampling.

Sulfur Dioxide Collection Efficiencies. Four tests involving the K_2CO_3 -coated filters predicted an SO_2 loss rate from the permeation tube of 7.1 ± 1.5 nmol min⁻¹. The actual loss rate was 7.1 ± 0.8 nmol min⁻¹, yielding an SO_2 collection efficiency for the K_2CO_3 -coated filters of 100 \pm 21% (Table II) with 100% of the sample collected on the first coated filter (Figure 3).

Based on two tests using LiOH-coated filters, the predicted SO_2 loss rate from the permeation tube was 6.3 ± 0.6 nmol min⁻¹, which corresponds to an $88 \pm 9\%$ collection efficiency. A total of 99% of the sample was collected on the first LiOH-coated filter and 1% was collected on the second (Figure 3).

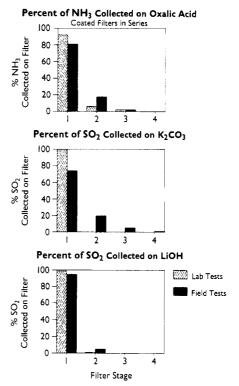


Figure 3. Distribution of sample gases collected on coated Whatman filters for laboratory and field tests.

In the marine atmosphere, SO_2 as well as O_3 and a variety of reduced sulfur gases including OCS, $(CH_3)_2S$, H_2S , CH_3SH , and CS_2 are present. The reduced sulfur species could potentially be oxidized to sulfate on the coated filter to produce artificially high sulfur dioxide concentrations. In addition, the presence of O_3 in the sample could enhance the oxidation of the sulfur compounds. To evaluate the effect of these other chemical species on the SO_2 collection efficiency, air streams were generated with known amounts of SO_2 , SO_2 and O_3 , SO_2 and reduced sulfur gases, and reduced sulfur gases and O_3 .

The addition of 15 ppbv of O_3 to the sample stream had no effect on the SO_2 collection efficiency of the K_2CO_3 -coated filters. However, it did result in an increase from 88 ± 9 to $107 \pm 10\%$ in the collection efficiency of the LiOH-coated filters. Although this increase is not statistically significant (as determined by a Student t test at the 95% confidence level), it does indicate a need for additional testing at O_3 levels that are typical of high-latitude,

midtropospheric values (40 ppbv).

 SO_2 collection efficiencies of the K_2CO_3 -coated filters of 113 ± 11, 96 ± 10, and 103 ± 10% were obtained for sample streams containing SO_2 , OCS, and $(CH_3)_2S$, SO_2 , OCS, $(CH_3)_2S$, and O_3 , and SO_2 , OCS, $(CH_3)_2S$, H_2S , CH_3SH , CS_2 , and O_3 , respectively (Table II). All of these collection efficiencies were within the range obtained from a sample stream containing only SO_2 .

The $\rm K_2\rm CO_3$ -coated filters also were exposed to a sample stream containing OCS, $\rm (CH_3)_2\rm S$, CS₂, and O₃ with no SO₂. The summed collection efficiency with respect to these gases was 10%. This collection efficiency is insignificant considering that the total concentration of all the reduced sulfur gases sampled was an order of magnitude higher than in the marine atmosphere. Similar tests were performed on the LiOH-coated filters. Upon exposure of the filters to $\rm (CH_3)_2\rm S/OCS$ and $\rm (CH_3)_2\rm S/OCS/O_3$, collection efficiencies with respect to these gases were 0.9 and 0.2%, respectively.

Results of Field Experiments. The percent of sample collected on each filter in the tandem sampling system was calculated for oxalic acid and potassium carbonate coated filters from samples collected on board the NOAA ship Oceanographer over the Pacific Ocean from 53° N to 14° S along 170° W during April of 1988. Similar statistics for LiOH-coated filters were calculated from marine air samples collected at the University of Washington research site on Cheeka Peak (48°18′ N, 124°37′ W; altitude, 480 m) during May of 1987.

For the oxalic acid coated filters, $81 \pm 21\%$ of the NH_3 collected was found on the first filter in the series; 17 ± 18 and 2 - 6% of the sample was collected on the second and third filters, respectively. No sample was collected on the last filter (Figure 3). The difference between the laboratory and field results could be the lower concentrations of NH_3 and, hence, longer sampling times encountered in the field experiments. The NH_3 concentrations over the Pacific Ocean were ~ 1 nmol m⁻³ while the NH_3 concentration sampled in the laboratory was 36 nmol m⁻³. Further laboratory tests are needed at lower NH_3 concentrations.

A total of $74 \pm 19\%$ of the SO_2 collected was found on the first potassium carbonate coated filter in series while 20 ± 12 , 5 ± 8 , and $1 \pm 4\%$ was found on the second, third, and fourth filters in series. For the LiOH-coated filters, $95 \pm 4\%$ of the SO_2 collected was found on the first filter in series and $5 \pm 4\%$ was found on the second (Figure 3). Again, the difference between laboratory and field results may be the lower concentrations of SO_2 in the field which led to longer sampling times. The average SO_2 concentration sampled in the field was 4 nmol m⁻³ while that in the laboratory was 160 nmol m⁻³. There may also be an unknown interferent in the marine atmosphere that is not

completely oxidized by the first filter in the series and so is collected as sulfate on subsequent filters.

Conclusion

Submicrometer aerosol particles in the marine atmosphere can be selectively collected by using either a cyclone or an 8.0- μ m Nuclepore filter (50 slpm, 55 cm s⁻¹ face velocity). NH₃ and SO₂ can be collected on oxalic acid and either potassium carbonate or lithium hydroxide coated filters at collection efficiencies near 100%. However, the NH₃ collection efficiency was found to decrease by a factor of 3 as the relative humidity was decreased from 75 to 33%. A series of four coated filters in the tandem sampling system maximizes the collection efficiency in field sampling. The first three filters collect essentially 100% of the sample while the fourth protects the sample from any back-diffusion of NH₃ or SO₂ into the filter pack.

Acknowledgments

We are deeply indebted to Dr. D. Covert for analytical assistance, helpful discussions, and review of the manuscript. We also thank Drs. D. Hegg and J. Johnson for reviewing the manuscript.

Registry No. NH₃, 7664-41-7; SO₂, 7446-09-5; $C_2H_2O_4$, 144-62-7; K_2CO_3 , 584-08-7; LiOH, 1310-65-2.

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Received for review July 22, 1988. Accepted January 24, 1989. This work was supported by Grant No. ATM8607377 from the NSF and by NOAA's National Acid Precipitation Assessment Program. Contribution no. 1052 from the NOAA Pacific Marine Environmental Laboratory.