

DETERMINATION OF ACIDITY IN AMBIENT AIR, PHASE II

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ABSTRACT

A laboratory and field study was conducted as part of a continuing assessment of methodologies for measurement of gaseous and particulate acids in the atmosphere. The acidic species included the gases nitric acid (HNO_3), nitrous acid (HONO), hydrochloric acid (HCl) and the particulate phase species, sulfuric acid. Nitric acid measurement by the automated tungstic acid technique (TAT) was evaluated for interferences due to NO, NO_2 and HONO. Loss of nitric acid in passage through various types of Teflon tubing as well as within a variety of cyclones was also studied. The annular denuder method (ADM) for HNO_3 was compared to the denuder difference method (DDM). An effort was made to assess NO_2 interference in HONO measurement with the ADM. Measurement of HCl by the DDM strategy used for HNO_3 was briefly investigated. A semi-continuous method for particulate S, permitting discrimination between H_2SO_4 and ammonium sulfates, was assembled and evaluated. The degree of interference in such H_2SO_4 measurements due to organo-sulfur species (hydroxymethane sulfonic acid (HMSA) and bis-hydroxymethyl sulfone) was assessed and a technique to improve the selectivity of the H_2SO_4 measurement was proposed and evaluated. Atmospheric sampling was done at a site chosen to provide elevated particulate S and low NH_3 levels to compare the semi-continuous particulate S monitor to filter collection techniques.

The TAT for HNO_3 was not subject to significant interference from HONO or NO_2 , alone, or in mixtures with NO in humidified air. Thus the cause of the large positive errors experienced in nighttime HNO_3 measurements with the TAT remains unknown. Loss of laboratory-generated HNO_3 was severe within PTFE Teflon tubing and within cyclones providing relatively long retention times.

With laboratory-generated HNO_3 , the ADM gave about 10% lower recovery than the DDM. However, when HNO_3 at very low concentrations in ambient air was sampled in parallel through equivalent inlets, the ADM results were notably higher than those by the DDM. Nitrous acid measurements with the ADM are subject to positive errors which may involve HONO formed within the inlet as well as a very low percentage retention of NO_2 . Hydrochloric acid can be measured with the DDM with at least an 80% accuracy.

In atmospheric sampling done in Torrance, CA, the semi-continuous monitor for sulfate salts and H_2SO_4 provided agreement within 20% with SO_4^{2-} measured by filter collection. However, no H_2SO_4 was detected. HMSA responded indistinguishably from H_2SO_4 , but NH_3 addition allowed discrimination of H_2SO_4 and the sulfone. Using aerosol mixtures, NH_4NO_3 , and $(\text{NH}_4)_2\text{SO}_4$ provided significant negative errors in H_2SO_4 measurement.

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I. SUMMARY AND CONCLUSIONS

A laboratory and field study was conducted as part of a continuing assessment of methods for measurement of gaseous and particulate acids in the atmosphere. The acidic species include the gases, nitric acid (HNO_3), nitrous acid (HONO), hydrochloric acid (HCl) and the particulate phase species, sulfuric acid. Nitric acid measurement by the automated tungstic acid technique (TAT) was evaluated for interferences due to NO , NO_2 and HONO. Loss of nitric acid during passage through various types of Teflon tubing as well as a variety of cyclones was assessed. The annular denuder method (ADM) was compared to the denuder difference method (DDM) for the measurement of HNO_3 . The DDM strategy was also briefly studied for measurement of HCl. An effort was made to assess NO_2 interference in HONO measurement with the ADM. A semi-continuous method for particulate S, permitting discrimination between H_2SO_4 and ammonium sulfates, was assembled and evaluated. The degree of interference in H_2SO_4 measurements due to two organosulfur species (hydroxymethane sulfonic acid (HMSA) and bis-hydroxymethyl sulfone) was measured, and a technique to improve the selectivity of the H_2SO_4 measurement was proposed and evaluated. Atmospheric sampling was done at a site chosen to provide elevated particulate S and low NH_3 levels to compare the semi-continuous particulate S monitor filter collection techniques.

The TAT, DDM, and ADM were evaluated in support of their use in the Nitrogen Species Methods Comparison Study (NSMCS). Although the NSMCS results with the TAT showed, on average, good agreement with the DDM for daytime HNO_3 concentrations, the nighttime TAT HNO_3 measurements were too high by about a factor of 6. The potential interferences in the TAT, HONO and NO_2 were assessed, the latter alone or in combination with NO at varying R.H. values. Significant interference was not observed, leaving the source of the error in nighttime HNO_3 measurement unknown. Our work with NO_2 suggests that partial conversion to HONO plus HNO_3 within the glass and Teflon sampler inlet system used in the NSMCS may have contributed to the nighttime error. This possibility will be addressed in the next phase of this continuing investigation.

The retention of HONO on Nylon filters under conditions used for the DDM, together with its removal on an alkali-coated denuder, and oxidation to NO_3^- , would cause a positive error in HNO_3 measurements. Retention of HONO with Gelman Nylasorb 47 mm Nylon filters at 20 Lpm, as used in the DDM, was $< 50\%$. Additional trials are needed to estimate such retention more precisely. Nylon filters from Gelman, Sartorius and Schleicher and Schuell showed $\leq 0.1\%$ NO_2 retention at about 80% R.H. Even if all retained NO_2 is converted to NO_3^- , this would be insignificant.

Loss of HNO_3 in transit through tubing at 1 Lpm was assessed by interposing a section of tubing between an HNO_3 source and the automated TAT. The degree of loss of HNO_3 in Teflon tubing ranged from negligible with perfluoroalkoxy (PFA) tubing to high with polytetrafluoroethylene (PTFE) tubing. Fluorinated ethylenepropylene (FEP) showed differing results with tubing from two sources. No effort was made in this preliminary evaluation to assess the generality of the observations. The variability in findings with FEP suggests that similar variability might be observed with the other types of Teflon as well.

Sampler inlets used for HNO_3 measurements at the NSMCS were, in general, cyclones made either of solid PTFE or of PFA-coated aluminum. Seven inlet devices, six cyclones and one impactor, were evaluated for transmission of HNO_3 at flow rates equal or similar to those used at the NSMCS. For this comparison, all units were pre-cleaned. The conditioning of the units for HNO_3 transmission reflect only that from passage of HNO_3 in purified air. The results showed HNO_3 loss to be directly proportional to residence time within each inlet. The smallest unit evaluated, an FEP-coated glass impactor, showed no loss of HNO_3 at 50% R.H. and < 20% loss at 80% R.H. The PFA-coated AIHL-design cyclone showed loss of 25-70%, the loss decreasing with conditioning within this range. Comparing the AIHL-design cyclones made from PFA-coated aluminum and solid PTFE, the latter provided substantially lower HNO_3 loss. The results obtained with solid PFA tubing are clearly not relevant to a PFA-coated aluminum cyclone.

The laboratory findings with the initially clean, PFA-coated aluminum cyclone are in marked contrast to those during and subsequent to the NSMCS. Comparison of DDM atmospheric HNO_3 concentrations, obtained with such cyclones at the NSMCS, to those by other techniques showed no evidence of significant HNO_3 loss. Furthermore, laboratory assessment of HNO_3 transmission by the still-dirty cyclone following the NSMCS showed < 5% loss. The inconsistency remains unresolved and will be addressed in the next phase of this study.

Nitric acid measurements by the DDM were compared to those by the ADM in laboratory and atmospheric trials at very low concentrations made in local (Emeryville) sampling. Laboratory sampling of HNO_3 in purified air was done under simulated daytime (50% R.H., 20°C) and nighttime (80% R.H., 13°C) conditions. For these trials, no inlet devices (e.g. cyclones) were used, avoiding losses in such devices as a source of difference between methods. With laboratory-generated HNO_3 , the DDM showed an accuracy of 99% compared to 89 to 93% for the ADM. However, with atmospheric trials, the ADM showed significantly higher results (mean 0.78 vs. 0.35 $\mu\text{g}/\text{m}^3$), suggesting interference from collection of other NO_x species and/or incomplete recovery of NO_3^- from Nylon filters at low dosage. The latter was previously found with spiked Nylon filters prepared for the NSMCS.

The partial retention of NO_2 on annular denuders coated with a carbonate salt causes a positive interference in HONO measurement. To overcome this, two annular denuders are used in tandem and the NO_2^- recovered from the second is subtracted from that on the first. In an effort to assess this correction strategy, 0.5 ppm NO_2 in purified air at 50 and 80% R.H. was sampled with ADM units consisting of two denuders in series. Results from preliminary experiments suggested that NO_2 was being partially converted to HONO (or other NO_2 species collectable with high efficiency on a CO_3 -coated denuder) ahead of the sampler. Using the NO_2^- recovered from the downstream denuder as an upper limit measure of NO_2 retention, < 0.2% NO_2 was retained. However, the correction strategy for HONO could not be directly assessed. Additional experiments are planned for the next phase of this continuing study in which any HONO (or other readily collected NO_2^-) is removed immediately before entry into devices being evaluated.

Data from the NSMCS suggested that the DDM was providing a measure of HCl as well as HNO_3 measurements. For quantitative measurements, HCl must be retained with very high efficiency and capacity on Nylon filters and

removed with high efficiency with an MgO-coated (or other alkali-coated) denuder. Furthermore, the Cl⁻ blank for the Nylon filters must be low relative to the atmospheric loadings. The retention of 100-200 µg dosages of HCl on Gelman Nylasorb Nylon filters was assessed. The results showed an efficiency of 82 ± 22% or 86 ± 2% depending on method of calculation. Although not evaluated, retention of HCl with high efficiency on the MgO denuder is very likely. Thus, the HCl measurements at the NSMCS are probably accurate within 20%.

A continuous monitor for particulate S was constructed, employing a denuder to remove S-containing gases and S compounds volatilized by heating after entry to the sampler. A flame photometric detector was used to detect particulate S, with its response enhanced by addition of SF₆ to the H₂ fuel. Speciation was based primarily on selective volatilization with a heater tube ahead of the S denuder, permitting, in the absence of interferents, measurement of H₂SO₄ discretely, but leaving the various ammonium sulfates unresolved. To discriminate between H₂SO₄ and organosulfur, particle phase materials, the unit was programmed to introduce NH₃ into the sample stream. Sulfuric acid was equated with a particulate S species volatilized at 125°C which reacts with NH₃ forming a S species not volatilized at that temperature. Interference effects were assessed for hydroxymethanesulfonic acid (HMSA) and its NH₄⁺ salt, and for bis-hydroxymethyl sulfone. HMSA is believed to form in the atmosphere by reaction of formaldehyde with SO₂. Interference effects were also assessed sampling two-component, external aerosol mixtures (i.e. those consisting of chemically different particles). These included NH₄Cl, NH₄NO₃, NH₄HSO₄, (NH₄)₂SO₄, NaCl and Na₂SO₄ in mixtures with H₂SO₄.

The potential interferent HMSA was found to behave indistinguishably from H₂SO₄ in the S monitor, and its NH₄⁺ salt, similar to (NH₄)₂SO₄. The non-acidic bis-hydroxymethyl sulfone could be distinguished from H₂SO₄ by NH₃ addition. We infer that this approach would also be useful with other non-acidic sulfur-containing compounds, as well.

Regarding interferents assessed in external aerosol mixtures, NH₄NO₃, and (NH₄)₂SO₄ both showed substantial negative interference. However, NH₄NO₃ did not interfere in a manner consistent with dissociation to NH₃ and HNO₃ at 125°C followed by H₂SO₄ neutralization.

Atmospheric sampling was done at El Camino College, Torrance, CA, in September 1986 during a period of generally light air pollution. No H₂SO₄ was measured with the continuous S monitor. However, the measured volatile particulate S (i.e. ammonium sulfates), correlated highly with filter SO₄⁼ measurements. On average, the continuous monitor values, expressed as SO₄⁼, were higher by 20%. Strong acid concentrations, obtained from pH values for extracts of Teflon filter samples, ranged from below detection to 46 nequiv/m³. Strong acid values were, on average, 75% of total acidity, as measured by titration to pH = 7.0.

Non-sulfate particulate S and, separately, particulate SO₃⁼ were also measured, the former by the difference between sulfate values before and after permanganate oxidation. Non-sulfate S was about 5% of the observed sulfate. Sulfite was present in trace levels, based on extraction of freshly collected samples with HCHO and IC analysis.

Ammonia was measured for 4 or 8-hour periods with a filter pack method and, with a denuder tube, for 12-hr periods. Denuder tube values

averaged 40% lower, similar to findings in previous studies. HNO_3 concentrations measured by the DDM were low, ranging from zero to $6 \mu\text{g}/\text{m}^3$ by the DDM. Efforts to measure HCl were hampered by high Cl^- blank values with Sartorius Nylon filters, and low ambient air concentrations. Reliable values could not be obtained.

Principal conclusions from this work are as follows:

- A. The cause of the large positive errors in nighttime nitric acid (HNO_3) readings with the automated tungstic acid technique (TAT) was not explained by interference from NO_2 , NO_2 plus NO , or HONO in laboratory simulations. Chemical conversion of NO_2 within the inlet system used at the NSMCS must be assessed.
- B. The annular denuder method (ADM) for HNO_3 gives results agreeing within about 10% from those by the denuder difference method (DDM) in laboratory trials.
- C. The ADM is subject to positive interference in the measurement of nitrous acid which may, in part, be related to the formation of an interferent within the sampler inlet.
- D. The ideal cyclone for use as an inlet in HNO_3 sampling should be made from solid Teflon or Teflon-coated glass and provide a sample residence time of ≤ 0.2 sec.
- E. Atmospheric hydrochloric acid can be measured within 20% by the DDM simultaneous with measuring HNO_3 , but Nylon filters with low Cl^- blank values (e.g. Gelman Nylasorb) must be used.
- F. Atmospheric sulfuric acid was below detectable levels, but the semi-continuous S monitor was at least useful to provide a measure of particulate sulfate.

II. INTRODUCTION

A. Objectives

The objectives of this study were:

1. Construct and evaluate a semi-real time sulfuric acid monitor.
2. Construct a semi-real time, automated nitric acid-ammonia analyzer specifically designed for field use.
3. Assess the extent of nitrous acid interference in nitric acid measurements with semi-real time and filter methods.
4. Evaluate a denuder method for HCl in laboratory and field trials.
5. Conduct atmospheric sampling trials of the semi-real time sulfuric acid monitor in parallel with integrated sampling techniques.
6. Assess the loss of HNO₃ on various types of Teflon.
7. Compare an annular denuder to the denuder difference method for HNO₃ in laboratory and ambient air trials.
8. Assess SO₂ and NO₂ retention on Nylon filters from different manufacturers.

B. Sulfuric Acid-Particulate Sulfate Measurement with a Continuous Monitor

Traditional methods for the measurement of atmospheric H₂SO₄ have employed collection of a filter sample followed by analyses providing varying degrees of specificity. This approach suffers from limited diurnal information and is subject to numerous sources of error resulting from interaction with other aerosol constituents (e.g. NH₄NO₃, NaCl) or gaseous pollutants (e.g. NH₃). Such sources of errors as well as evaluations of some of these methods have been reported in prior ARB-sponsored studies (1,2).

The present study extended this work to include a continuous method for particulate S with a least limited capability for speciation. The method relies primarily on the higher volatility of H₂SO₄ relative to that for NH₄HSO₄ and (NH₄)₂SO₄ which, in turn, are more volatile than metal sulfates. The principle of the method as well as a review of the principal contributors to its development are given in Appendix A. A unit employing this general design was constructed and given laboratory and field trials. The technique was modified to improve its selectivity. The major shortcoming of the technique was and remains its inability to distinguish NH₄HSO₄ from (NH₄)₂SO₄.

C. The Automated Tungstic Acid Technique (TAT)

In parallel with the current program, the TAT constructed for field application was employed for the ARB-sponsored 1985 Nitrogen Species Methods Comparison Study (NSMCS). The Final Report prepared

for that program (3) details the design of this unit as well as the results of atmospheric measurements. Accordingly, these are not included here. The present report includes an evaluation of interference effects with the TAT.

During the NSMCS, HNO_3 concentrations by the TAT were, on average, six times higher than those by the denuder difference method (DDM) during nighttime hours. This contrasted with good average agreement during daylight hours. During nighttime periods concentrations of NO_2 as well as relative humidities were higher than daytime levels. Thus, although prior interferences studies failed to reveal significant interference from NO_2 , supplement experiments were done. In addition to trials with NO_2 , alone, potential interference from $\text{NO}_2 + \text{NO}$ at low and high relative humidities was assessed to simulate more closely atmospheric conditions. Interference studies with HONO differed from those in the previous phase by employing a greatly improved, automated TAT as well as a different technique for generation and measurement of HONO.

D. Loss of HNO_3 on Surfaces

Previous studies with tubing of varying composition have demonstrated that gaseous HNO_3 is readily retained on reactive surfaces (4). This work suggested that glass and Teflon tubing are preferable for transmission of gaseous HNO_3 at low (e.g. < 100 ppb) concentration in air.

Studies with filter media (5,6) have shown relatively high capacity for HNO_3 retention for glass fiber and little or no retention of HNO_3 on polytetrafluoroethylene (PTFE) Teflon filters. The difference in results between glass tubing and glass fiber filters presumably parallels the available surface area which contains alkaline sites.

Results from the NSMCS as well as our previous laboratory findings suggested that PTFE Teflon could, in some cases, cause substantial removal of gaseous HNO_3 ; the low HNO_3 results obtained by Allegrini et al. (7) were thought to result, at least in part, from HNO_3 lost to the PTFE cyclone and manifold preceding an annular denuder system. Similarly, in our earlier studies, a PTFE ball valve was found to cause substantial loss of HNO_3 , a loss which was markedly reduced by glass lining the ball valve (8).

The above findings prompted the evaluation of the extent of loss of HNO_3 on tubing made from different types of Teflon as well as on cyclones of differing designs and wall compositions.

E. Annular Denuders

Diffusion denuders are devices designed to permit the removal of gaseous pollutants from a gas stream while allowing particulate phase materials to pass through with high efficiency. The technique is based on the high diffusion rate of gases relative to particle phase materials. Until recently most such denuders employed one or more tubes coated on their interiors with a material intended to remove the desired species with high efficiency. The behavior of such denuders is effectively approximated by the

Gormley-Kennedy equation (9). For example, a 30-cm, 4 mm I.D. tube coated on its interior with a strong acid can effectively remove NH_3 at flow rates of ca. 1 Lpm. Higher flow rates can be employed by sampling in parallel with an appropriate number of tubes. However, the recovery of the collected species becomes impractical in such cases.

A more efficient design was recently proposed in which the annulus between two concentric cylinders was coated and used as the collection medium (10). The efficiency of such annular denuders can be calculated with the equations:

$$\frac{c}{c_o} \approx 0.819 \exp (-14.6272 \Delta_a)$$

$$\Delta_a = \frac{DL}{\nu \text{Re} \delta}$$

where: c = average gas concentration leaving the denuder
 c_o = gas concentration entering the denuder
 D = diffusion coefficient of the gas (cm^2/sec)
 L = length of the coated annulus
 ν = kinematic viscosity of air ($0.152 \text{ cm}^2/\text{sec}$ at 20°C)
 Re = Reynolds number
 δ = equivalent diameter of the annulus

The equivalent diameter, $\delta = d_2 - d_1$ where d_1 and d_2 are the inside and outside diameters of the annulus, respectively.

Atmospheric nitric acid can readily be sampled with alkali-coated annular denuders followed by aqueous extraction of the denuder and analysis for NO_3^- . With elimination of coarse NO_3^- particles, the principal limitation of this strategy appears to be the partial retentions of NO_2 as NO_2^- , with subsequent slow conversion to NO_3^- , causing positive error in measurement of HNO_3 . Atmospheric HONO has also been estimated based on recovered NO_2^- but correction for NO_2 retention and/or conversion of NO_2 to HONO is essential. Section VII describes techniques and preliminary results from such NO_2 retention studies.

In this report, the ADM is compared to the DDM for both laboratory and atmospheric sampling of HNO_3 .

F. Retention of SO_2 and NO_x Species on Nylon Filters

The degree of retention of SO_2 on Nylon filters has been under increasing scrutiny recently. A 1984 publication reported that in sampling $70\text{-}235 \mu\text{g}/\text{m}^3$ SO_2 , $4.9 \pm 2.3\%$ conversion of SO_2 to SO_4^{2-} occurred on Ghia Nylon filters (Nylasorb) at relative humidities $> 55\%$ (11). More recently, Cadle (12) has reported retention of SO_2 on Membrana Nylon in the range 40 to 60% for SO_2 concentrations of $100\text{-}150 \mu\text{g}/\text{m}^3$, at relative humidities of 60 and 90%. Total dosages sampled ranged from 12 to $162 \mu\text{g}$. These high retentions were observed with post-1984 filters. The implied change in filter composition was not addressed. Chan et al., found widely varying

retention and conversion to $\text{SO}_4^{=}$. However with long term sampling of 1 to 8 $\mu\text{g}/\text{m}^3$ SO_2 , conversion ranged from 2 to 8% (32).

The practical effect of such SO_2 retention is to constrain the usefulness of Nylon filters for aerosol collection; sulfate results obtained on Nylon filters (without a prefilter) must be considered as upper limits to the levels of atmospheric particulate $\text{SO}_4^{=}$. Furthermore, sampling strategies relying on transmission of SO_2 through a Nylon filter to reach a base-impregnated filter for collection will provide only lower limit values for atmospheric SO_2 .

Since composition changes affecting SO_2 might influence retention of other acidic gases we investigated Nylon filters from alternative suppliers with respect to their retention of not only SO_2 but of NO_2 and HONO, as well.

Retention of NO_2 on Nylon filters followed by oxidation to NO_3^- could provide an error in estimation of atmospheric HNO_3 (e.g. in a simple filter pack method for HNO_3). With the denuder difference method, assuming no removal of NO_2 on the denuder, equal amounts of such NO_3^- would be expected. Thus HNO_3 results would be largely unaffected; fine particle NO_3^- values would be enhanced, however.

The rationale for evaluation of the retention of HONO on Nylon filters is similar to that for NO_2 . Both would initially be present as NO_2^- . Although the atmospheric concentration of HONO is about 10^2 lower than that for NO_2 , the efficiency of its retention on filters and other sampling media is likely to be much higher, raising the possibility of measurable NO_2^- from this source.

Collection of HONO on Nylon filters could cause error in HNO_3 measurement by the denuder difference method (DDM) if 1) conversion of NO_2^- to NO_3^- occurred on the filter during storage and/or analysis of the aqueous extract, and 2) if HONO were removed by the MgO denuder employed in the DDM (which is likely).

The evaluation of interference in TAT HNO_3 measurements by HONO continues the work reported in the preceding phase of this work (8). The earlier study employed a solution technique to generate HONO, and was hampered by rapidly changing HONO concentrations and experimental complexity. The present work employed a sublimation source of HONO based on reaction of vapor phase oxalic acid with solid NaNO_2 (14).

III. INTERFERENCE STUDIES FOR NITRIC ACID MEASUREMENTS

A. Interference in the TAT with NO₂ and NO

1. Experimental

Two sets of experiments were performed. In the first set, nitrogen dioxide in N₂ from a cylinder was diluted with synthetic or filtered room air. After dilution the calculated concentration was 3.8 ppm NO₂ (7135 μg/m³). The automated TAT draws a sample from a stream of diluted NO₂ making contamination from HNO₃ in the laboratory air an unlikely source of error.

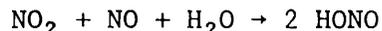
In the second set of experiments, NO₂ and NO from cylinders in N₂ were diluted with humidified, synthetic air and introduced into the automated TAT. In both sets of experiments, potential interferences were added immediately after preconditioning the TAT with a known dosage of HNO₃. The degree of interference was determined by comparing the observed response at the retention time for HNO₃ (after re-equilibration of the TAT) to that calculated for a molar equivalent dosage of HNO₃. In most cases the calculated HNO₃ response could not be verified since it exceeded the range of the TAT. Linearity of response above the calibration range was assumed to permit this calculation.

2. Results

The results for the first set of experiments are given in Table 1. Employing dosages of about 10⁴ ng (as NO₃), interference from NO₂ became measurable. Two peaks were observed on thermal desorption; one at 0.8 min and the second at about 1.05 min. The latter coincided with the peak for HNO₃ run under the same conditions. The significance of the first peak is unclear.

Based on the peak observed at 1.04-1.06 min. and the peak area observed for a known dosage of HNO₃, the efficiency of NO₂ interference is calculated to be 0.4 to 0.8%, with the latter value at lower R.H.

The results for the second set are given in Table 2. With NO₂, alone, at 20 and 80% R.H., interference was ≤ 0.5%. Addition of NO did not increase the observed interference, and, therefore, provided no support for interference involving the intermediate process:



These results are similar to those found by Roberts et al. (13) who observed < 1% interference by NO₂ in air at 50% R.H. During the September 1984 TAT sampling in Riverside (8), as well as at Claremont for the NSMCS (3), 4-hour average NO₂ or NO₂ + NO interference values remained ≤ 0.1 ppm, leading to an expected positive interference of ≤ ca. 1 μg/m³. Thus NO₂

Table 1. Interference of NO₂ with the Automated TAT (Data Set 1)

<u>Trial</u>	<u>Sample</u>	Dosage ng as <u>NO₃</u>	<u>Diluent</u>	Peak Area x 10 ⁻⁶		<u>Calculated</u> <u>Interference (%)</u>
				<u>Unknown</u> ^a	<u>HNO₃</u> ^b	
1 and 2	Blank	0	syn. air (ca. 0% R.H.)	0.075 ± 0.001	0.35 ± 0.04	-
3 and 4	3.8 ppm NO ₂	9616	syn. air (ca. 0% R.H.)	0.26 ± 0.01	1.18 ± 0.37	0.78
5 - 8	3.8 ppm NO ₂	9616	filtered room air (54% R.H.)	0.20 ± 0.03	0.89 ± 0.11	0.44
9	HNO ₃	96	filtered room air (54% R.H.)	0.11	1.30	-
10	HNO ₃	96	filtered room air (54% R.H.)	ca. 0	1.53	-

a. Refers to peak observed at 0.81 min. measured with an HP Model 3310 recorder-integrator.

b. Refers to peak observed at 1.04 - 1.06 min.

c. Expressed as a percent of that calculated for an equivalent amount of HNO₃.

Table 2. Interference of NO₂ with the Automated TAT (Data Set 2)

Dosage of NO _x (ng as NO ₃ ⁻)			R.H.	Response ^b	Calculated
HNO ₃	NO ₂	NO	%	(Area Units)	Interference, (%) ^c
384	-	-	ca.50	0.0794 ± 0.0047	-
-	7,500	-	85	0.00787 ± 0.0018	0.5
-	2,303	1,063	80	0.00338 ± 0.0005	0.14 ^a
-	39,080	-	20	0.0067	0.10
-	36,005	3,075	20	0.0036 ± .0004	0.05 ^a

- a. Determined relative to calculated response assuming HNO₃ equivalent to the total NO_x.
- b. Refers to peak observed at ca. 1.05 min. Values are in volt-min as provided by an ISAAC System 91A (Dynamic Solutions) and an APPLE IIe microcomputer.
- c. Expressed as a percent of that calculated for an equivalent amount of HNO₃.

could not explain the difference found between the TAT and denuder difference methods in atmospheric sampling in Riverside, and at Claremont.

B. Nitrite to Nitrate Conversion in Filter Sample Extracts

1. Introduction

The retention of nitrite species on filter samples followed by oxidation to NO_3^- could cause errors in atmospheric NO_3^- measurements. The present experiment sought to assess the significance of NO_2^- to NO_3^- conversion in alkaline extracts of atmospheric particulate samples spiked with varying levels of additional NO_2^- . On the assumption that the filter medium had a minor influence on conversions occurring in the filter extracts, experiments employed samples collected on quartz fiber filters. Samples extracts were reanalyzed at varying intervals of storage at 5°C or room temperature.

2. Experimental

The atmospheric particulate matter samples were collected at Claremont, 9/14-9/15/85 and 9/15-9/16/85 during the NSMCS employing a PM_{10} sampler and 8"x10" Whatman QMA "quartz" fiber filters. These samples were selected because they encompassed the highest HNO_3 concentrations observed, reflective of generally high pollution levels. From each filter sample, ten 47 mm discs were removed to provide equivalent samples for the experiment. A total of ten composite samples were used, each consisting of one 47 mm disc cut from each loaded filter sheet. Each sample was extracted by one hour mechanical shaking at room temperature in 10 mL IC eluent (0.003 M NaHCO_3 plus 0.0024 M Na_2CO_3) in screw cap plastic centrifuge tubes. The samples were transferred with washings to larger screw cap centrifuge tubes and diluted to 30 mL with additional eluent.

Aliquots of the filter extracts were spiked with NaNO_2 at levels ranging up to $6 \mu\text{g/mL}$. Three of the particulate samples receiving no spike plus those with 2, 4 and $6 \mu\text{g/mL}$ NO_2^- were stored at room temperature together with two blank filter samples spiked with $4 \mu\text{g/mL}$ NO_2^- . One unspiked, loaded sample was refrigerated at 5°C together with samples containing 2, 4 and $6 \mu\text{g/mL}$ NO_2^- .

3. Results

Experimental conditions and the results are shown in Table 3. Nitrite, whether in extracts from blank or loaded filter samples, decayed almost completely at room temperature over a one month period. The exception is the sample extract with $6 \mu\text{g/mL}$ added NO_2^- for which only about 56% decay was found. The most notable finding of this work is the absence of a corresponding increase in NO_3^- . In the absence of added NO_2^- ,

* These filters contain a small percentage glass fiber (according to the manufacturer).

Table 3. Recovery of NO_2^- and NO_3^- in Storage of NO_2^- Spiked Filter Sample Extracts ($\mu\text{g/mL}$)

Sample ID	Added NO_2^- ($\mu\text{g/mL}$)	Storage Temperature	Storage Times (Days) ^a							
			0 ^b		7		14		29	
			NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-
QMA-1A	0	r.t.	< 0.1	9.4	0.3	8.9	0.5	8.4	0.2	5.8
QMA-1B	0	r.t.	< 0.1	9.8	0.3	9.0	0.2	7.5	0.1	3.1
QMA-1C	0	r.t.	< 0.1	9.6	0.2	9.2	0.2	7.6	0.2	3.6
QMA-8	0	5°C	ca. 0.2	9.1	0.3	9.5	0.3	9.6	0.3	9.1
BQMA-1	4	r.t.	4.0	0.4	4.0	0.5	2.1	0.1	0.1	0.1
BQMA-2	4	r.t.	4.1	0.2	3.6	0.1	1.4	0.0	0.1	0.0
QMA-2	2	r.t.	2.1	9.4	2.1	9.4	1.3	8.3	0.3	4.8
QMA-5	2	5°C	2.2	9.4	2.2	9.5	2.2	9.4	2.0	9.4
QMA-3	4	r.t.	4.1	10.4	4.0	10.2	2.7	9.3	0.5	7.6
QMA-6	4	5°C	4.1	10.2	4.1	10.2	4.2	10.2	3.9	10.2
QMA-4	6	r.t.	6.3	10.0	6.1	10.0	4.9	9.5	2.8	8.1
QMA-7	6	5°C	6.3	10.0	6.3	10.1	6.4	10.2	5.9	10.2

a. Room temperature samples stored for the first seven days exposed to room light, next seven days near window and final 14 days in the dark. Refrigerated samples in the dark in all cases.

b. Analyzed within 24 hr of extraction.

NO₃⁻ also showed a decreasing concentration, averaging 56% after one month. With added NO₂⁻ the observed decrease in NO₃⁻ diminished with increasing NO₂⁻. Although partial conversion of NO₂⁻ to NO₃⁻ could, in principle, account for this, the absence of NO₃⁻ formation from the spiked blank quartz filters (BQMA-1 and BQMA-2) argues against such a process.

4. Conclusion

The loss of NO₂⁻ and NO₃⁻ from extracts of clean and loaded filter samples is probably the result of chemical reduction by bacteria, but the reduction of NO₃⁻ does not stop at nitrite. The apparent protective influence of added NO₂⁻ on NO₃⁻ may reflect the greater ease of reduction of the nitrite. Lighting levels at room temperature showed no substantial influence over decay rates. Whatever the actual mechanism, these results do not indicate a significant source of error in NO₃⁻ or HNO₃ measurements based upon oxidation in filter extracts of co-collected NO₂⁻ species.

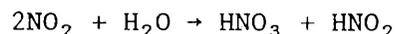
The present results with quartz fiber filter extracts stand in marked contrast to our earlier findings employing NaCl-impregnated Whatman 41 filter extracts (8). In the earlier work, loss of NO₂⁻ was accompanied by an increase in NO₃⁻. The NaCl concentration of the filter extracts (estimated at 0.005 g/mL) is probably insufficient to repress bacterial growth. The difference in solution pH (about 7 for the NaCl/W41 filters and 8.5 for eluent solutions) may be a factor. Considering the marked difference in results between these data sets, similar trials with Nylon filter extracts are warranted.

The instability observed for NO₃⁻ in the present study also contrasts with results obtained for water extracts of Teflon filter samples. Using 24-hr atmospheric particulate matter samples collected in Berkeley, no evidence of significant change in NO₃⁻ concentration other than that due to slight water evaporation, was observed in extracts stored at room temperature and re-analyzed after 7, 30, 43 and 90 days storage (33).

C. Retention of NO₂ on Nylon Filters

1. Experimental

Nylon filters from alternative manufacturers were assessed for NO₂ retention at 75%-85% relative humidity. High R.H. favors NO_x retention because of reactions such as:



The filters evaluated were Gelman Nylasorb, 1 μm pore size Nylon 6 filters (batch 871), as used in the NSMCS, Sartorius 0.65 μm pore size Nylon 6 filters, lot No. 311050675-8, and

Schleicher and Schuell 1.2 μm pore size Nylon 6,6 filters.* Six, 47 mm Nuclepore open face filter samplers sampled in parallel, each containing two Nylon filters (in direct contact with one another). Two holders were used for each filter type. The NO_2 concentration was 0.47 ppm, as measured with a TECO chemiluminescent analyzer calibrated against NO_2 of known concentration. For a 6 hour sampling trial the sampled NO_2 dosage was about 6300 μg .

The use of two filters in tandem was intended to permit discrimination between NO_3^- due to system contamination from that resulting from NO_2 retention plus oxidation. Contaminant NO_3^- , either as HNO_3 or NH_4NO_3 , would be efficiently retained on the Nylon prefilter. Nitrate formed after low percentage retention of NO_2 should be about equally distributed on tandem filters.

Following collection, samples were stored at -5°C until immediately before extraction. Samples were extracted in standard I.C. eluent with one hour mechanical shaking and analyzed by I.C.

2. Results and Conclusions

The results for filters from three suppliers are detailed in Table 4 and are corrected for the respective filter blank values. Similar levels of NO_3^- were determined on all of the prefilters but were nearly absent on the after-filters. This suggests that the material retained on the prefilters was initially NO_3^- rather than NO_3^- formed following NO_2 retention. Accordingly, the NO_3^- on the prefilter is considered to be due to system contamination, and is irrelevant to NO_2 retention measurements.

Only the Gelman filter showed NO_2 retention above the limit of detection. The recovered NO_2 of 4.4 to 7.0 μg corresponds to 0.07 to 0.11% retention. Assuming complete conversion to NO_3^- before analysis, sampling 0.5 ppm atmospheric NO_2 for four hours at 20 Lpm would produce a NO_3^- error of 1.3 $\mu\text{g}/\text{m}^3$. We consider this an insignificant source of error in HNO_3 and NO_3^- measurements at the NO_2 levels likely to be encountered.

D. Collection of Nitrous Acid on Nylon Filters and by the TAT

1. Experimental

To achieve a stable HONO output, the HONO generation source proposed by Braman (14) was evaluated. This consists of a tube filled, in sequence, with plugs of glass wool, crystalline oxalic acid, glass wool, crystalline NaNO_2 and glass wool. Our initial trials with this design employed a 6 mm

* Nylon 6 is prepared from the polymerization of caprolactam whereas Nylon 6,6 is prepared by reaction of hexamethylenediamine and adipic acid. The Sartorius Nylon 6 filter is said to be part of a batch left over following cessation of its manufacturer. Its pore size, 0.65 μm , is below that previously sold to Membrana and Gelman (ca. 1 μm) for sale as "Nylasorb".

Table 4. Retention of NO₂ on Nylon Filters^a

Supplier	Type	Recovered NO ₂ (μg)		Recovered NO ₃ (μg)	
		Prefilter	After-filter	Prefilter	After-filter
Gelman	Nylon 6	4.7	7.0	25.9	1.3 ± 0.3
		4.4	6.2	27.9	2.9 ± 0.3
Sartorius	Nylon 6	1.1	1.8	24.9	-1.2 ± 2.0
		1.1	2.2	27.9	-0.7 ± 2.0
S & S	Nylon 6,6	1.1 ^b	2.2	26.6	2.6 ± 0.2
		0.7 ^b	2.0	32.6	1.6 ± 0.2

a. Experimental conditions: 47 mm filters
 0.47 ppm NO₂ (872 μg/m³)
 20 ± 2°C
 75-80% R.H.
 6 hours at 20 Lpm

b. Results at the limit of detection.

I.D. tube packed with an estimated 1 g of each reagent. This provided $< 3 \mu\text{g}/\text{min NO}_2^-$ at room temperature. To achieve higher vapor concentrations, the present work used about 10 g of each reagent in a 1 cm I.D. plastic tube. HONO output was assessed using midget impingers. Collection media for these trials was 0.01M NaOH, a reagent with minimal Cl^- contaminant and, therefore, minimal interference in NO_2^- measurement by IC. The initial room temperature output observed with this tube was $20 \text{ ng}/\text{min NO}_2^-$ and a trace of NO_3^- in a flow of 0.9 Lpm synthetic air maintained at 40% R.H. This decreased to about $8 \text{ ng}/\text{min NO}_2^-$ within one week.

To assess filter collection efficiency, two Nylon filters (Gelman Nylasorb Batch 871) sampled in tandem at 20 Lpm total flow. This gas stream included 19 Lpm room air purified by passage through H_3PO_4 supported on glass wool, a glass fiber filter and a NaCl/Whatman 41 filter. Accordingly, the resulting air should be free of NH_3 , particulate matter and HNO_3 . The remaining 1 Lpm was provided by passing humidified synthetic air through the HONO generator, combining the two streams just ahead of the dual filters. Sampling times ranged from 16 to 23 hours. The present trials evaluated only the collection on initially clean filters.

Measurement of the response of the TAT system to HONO is complicated by the substantial memory effect of the system. To assess the response of the analyzer to HONO, the analyzer was preconditioned with HNO_3 and then switched to sample either purified air or HONO in air. The instrument response to HONO and air was compared over at least 7 instrument cycles as the response to previously sampled HNO_3 decayed.

Peaks at two retention times were typically observed, a small peak at ca. 0.8 min and a peak at 1.05-1.10 min. The latter coincided with the retention time for HNO_3 . Data included here are only for the latter peak as a measure of potential interference in HNO_3 measurement.

2. Results

For eight trials with added HONO, the NO_2^- and NO_3^- on the Nylon prefilter ranged from 21 to 29 μg and 3 to 6 μg , respectively. The after-filter showed similar levels, 18 to 24 μg and 3 to 6 μg , for NO_2^- and NO_3^- , respectively. These results compare with a total expected NO_2^- from the HONO source of about 30 μg .

Blank Nylon filter sorption trials with 20 Lpm purified room air yielded NO_2^- levels of about 15 μg on both the prefilter and after-filter, in 16 hour sampling. The measured levels on the prefilter corresponded to about $1 \mu\text{g}/\text{m}^3 \text{NO}_2^-$ based on the volume of room air sampled. The measured NO_3^- was insignificant.

We conclude that HONO was retained on 47 mm Nylon filters, with $< 50\%$ efficiency at 20 Lpm either as NO_2^- or NO_3^- . The observed NO_x species might result from the partially purified room air which should still contain some NO_x materials.

Table 5. Comparison of TAT Response on Change from HNO₃ to Dilute HONO or Synthetic Air^a

<u>Cycle</u>	<u>HONO</u> ^b	<u>Air</u> ^c	<u>HONO</u> ^d	<u>HONO</u> ^e	<u>Air</u> ^f
1	0.056	0.0414	0.0321	0.053	0.044
2	0.0198	0.0180	0.0143	0.020	0.0184
3	0.0171	0.0130	0.0052	0.0128	0.0144
4	0.01545	0.0105	0.0055	0.0103	0.0112
5	0.01318	0.0082	0.0054	0.0083	0.00999
6	0.01072	0.0070	0.0054	0.0069	0.00804
7	0.00822	0.0063	0.00417	0.0066	0.00666
8	0.00825		0.0033	0.0065	0.0056
9	0.00605		0.0029	0.0073	0.0050
10	0.00575			0.0088	0.0046
11	0.00468			0.0094	-
12	0.00459			0.0095	0.0038
13				-	0.0032
14				0.0082	0.0038
15				0.0074	0.0035
16				0.0068	0.0028
17				0.0066	0.0038

- a. Results are shown as peak areas (volt-min) for the peak at ca. 1.05 min. ascribed to HNO₃.
- b. Ten minute sample dosage 270 ng HONO as NO₃⁻. Trial date 4/22/86.
- c. Trial date 4/22/86.
- d. Trial date 4/1/86. Dosage 80 ng HONO as NO₃⁻.
- e. Trial date 4/10/86. Dosage 80 ng HONO as NO₃⁻. Cycles 1-7 in dry air. Cycles 8-17 at 69% R.H.
- f. Trial date 4/23/86.

Additionally trials are needed with cleaner diluent air to assess the possible low percentage retention of HONO on Nylon filters.

Regarding the response of the TAT to HONO, Table 5 compares the responses to HONO and air, following initial dosage with about 270 ng HNO₃. The HONO dosage was about 270 ng per cycle (calc. as NO₃⁻) on 4/22/86 and 80 ng per cycle (calc. as NO₃⁻) on 4/1 and 4/10/86. With both HONO and air, the response slowly decreased, requiring about 12 cycles to achieve < 2% of its response to 270 ng HNO₃. No significant difference was observed between the system response to HONO or synthetic air.

We conclude that HONO does not cause significant interference in HNO₃ measurements with the TAT.

E. Nitric Acid Retention on MgO-Coated Denuder Tubes

1. Introduction

Capacity of MgO Denuders for Nitric Acid

Although MgO-coated denuders have been in use for some years (5), data on their capacities for HNO₃ removal remained unavailable. The present study included a brief evaluation of such capacities relevant to denuders prepared from a thick slurry of MgO.

2. Experimental

Nitric acid in filtered ambient air at 1 Lpm was provided from a thermostated permeation tube with output of 253 ng/min. The HNO₃ source was attached directly to a single 30 cm long, 4 mm I.D. MgO-coated denuder tube. At varying time intervals, the output from the denuder was introduced into the automated TAT (freshly conditioned with HNO₃) to assess the degree of HNO₃ penetration by comparison to the TAT response without the denuder in line.

The flow rate through the denuder tube, 1 Lpm, compares to a total flow of 20 Lpm through 24 tubes in parallel in atmospheric sampling. Accordingly, residence time within the sampling tube in this experiment was 25% shorter than in atmospheric sampling. Accordingly, retention efficiencies for HNO₃ over time are lower limits to those expected in atmospheric sampling.

3. Results

The efficiency of the MgO tube for HNO₃ over time is shown in Table 6. The observed efficiency remained in the range 94 to 96%. The capacity of the tube is inferred to exceed 5.7 mg of HNO₃ (as NO₃⁻). Assuming the continuous sampling of 50 µg/m³ (the highest likely HNO₃ level to be encountered) with a 24-tube denuder at 20 Lpm, this corresponds to a minimum of 95 days capacity without increased penetration.

Table 6. Capacity of a MgO Denuder Tube for HNO₃^a

Date	Cumulative HNO ₃ ⁻ Dosage (μg as NO ₃ ⁻)	Equiv. No. Days at 50 μg/m ³	MgO Denuder Efficiency (%) ^b
7/1/86	0	0	95 ± 1
7/2/86	279	4.7	95 ± 1
7/8/86	3025	50	94.5
7/10/86	3600	60	95.3
7/16/86	5678	95	96.2 ± 1.3

- a. Sampling condition: 1.0 Lpm
4 mm I.D. tube coated for 30 cm
253 ± 9 μg/m³ HNO₃ (as NO₃⁻)
- b. Calculated for a 24-tube denuder sampling at 20 Lpm.

We estimate that variations in the technique for preparing MgO denuder tubes might cause up to 30% variation in such capacity. Even allowing for such variability the capacity remains extremely high. Testing of additional denuder tubes was judged to be unnecessary.

F. Retention of SO₂ on Nylon Filters

1. Experimental

The degree of retention of SO₂ was compared with Nylon filters identified as follows:

1. Gelman Nylasorb, 1 μm pore size, Batch 871, Nylon 6. This batch was employed by us in the NSMCS.
2. Sartorius, lot 311050675-8, 0.65 μm pore size, Nylon 6.
3. Schleicher and Schuell, 1.2 μm pore size, lot No. 03185, Nylon 6,6.

Two, 47 mm filters of each type sampled in parallel 0.1 ppm SO₂ for a single, 6-hr period at 80% R.H. and a flow rate of 20 Lpm. The SO₂ concentration was monitored throughout the run with a TECO pulsed fluorescence analyzer. In addition, a 6-hr average SO₂ concentration was measured by midget impinger sampling with 1% H₂O₂ solution followed by ion chromatographic analysis as SO₄.

2. Results

The results (Table 7) from SO₂ sampling as well as filter blank values are quite similar for Nylon 6 and 6,6 with the Nylon 6 filter exhibiting slightly greater SO₂ retention. However, in all cases the SO₂ retention under these conditions was < 2%. Blank values for the Gelman filter were notably lower than for the other filter types. Note, however, that expressing results by percentage retention may distort their significance. For example, assuming 24 hour sampling at 20 Lpm of SO₂ at 5 $\mu\text{g}/\text{m}^3$ provides a dosage of 216 μg as SO₄. It is likely (but not yet established) that up to saturation, SO₂ collection efficiency remains high. Assuming saturation at the levels observed in the present experiment, the artifact would represent 20-25% SO₂ retention. Further experiments are desirable to assess SO₂ retention at lower SO₂ dosages.

Table 7. Retention of SO₂ on Nylon Filters^a

<u>Supplier</u>	<u>Batch or Lot</u>	<u>Type</u>	<u>Artifact SO₄⁼ (μg)^b</u>	<u>SO₂ Retention (%)</u>
Gelman	871	Nylon 6	70.2 ± 2.1	1.8
Sartorius	311050675-8	Nylon 6	64.9 ± 0.71	1.7
S & S	03185	Nylon 6,6	55.9 ± 1.4	1.5

a. Experimental Conditions: 47 mm filters
 0.14 ppm (362 μg/m³) SO₂
 81 ± 1% R.H.
 20°C
 6 hr sampling at 20 Lpm
 Total dosages 2,600 μg SO₂

b. Results corrected for SO₄⁼ blank values. Filter blanks are as follows (μg/filter):

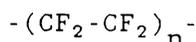
	<u>SO₄⁼</u>	<u>NO₃⁻</u>
Gelman	2.3 ± 0.2 (n=3)	1.1 ± 0.3 (n=3)
Sartorius	8.6 ± 0.1 (n=2)	4.1 ± 2.0 (n=2)
S & S	5.1 ± 0.6 (n=3)	2.4 ± 0.2 (n=3)

IV. LOSS OF HNO₃ IN TEFLON TUBING

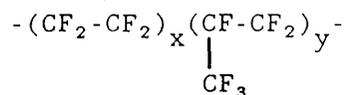
A. Introduction

1. Composition and Properties of Important Types of Teflon

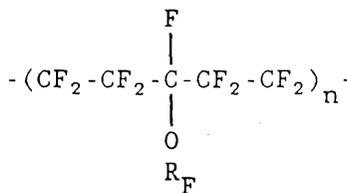
The three major forms of Teflon include polytetrafluoroethylene (PTFE), the first perfluorinated polymer produced, fluorinated ethylene-propylene copolymer (FEP), and perfluoroalkoxy copolymer (PFA). Structurally the three polymers are described as:



PTFE



FEP



PFA

The R_F in the structural formula for PFA indicated a fluorinated alkyl group.

Much of the impetus for developing FEP and PFA was to achieve a polymer which would permit fabrication of end use items (e.g., tubing) from the molten polymer, by extrusion, for example. The viscosity of molten PTFE is excessively high due to the crystallinity of this polymer. The incorporation of side chains, as in FEP and PFA, decreases both the melting point and melt viscosity. Accordingly, the manufacturing process for PTFE differs markedly from that for FEP and PFA.

PTFE is generally prepared (15) from a resin in the form of a dry powder compressed to 1500-6000 psi. The compressed material is heated above the melting point of the polymer for varying times depending on the thickness of the component being made. The compressed particles coalesce (or "sinter") giving the component its strength. The polymer is cooled at varying rates to achieve the desired degree of crystallinity.

An important variable, the void content of the finished product, depends on the pressure employed, sintering temperature, time, resin particle size, shape, porosity and molecular weight. An increase in void content is reported to cause up to a thousand-fold increase in the permeability of the finished product to CO₂ (15).

2. Identification of Teflon Polymers

PTFE is creamy white. It normally is made into products with thicker walls than those from the melt-extrudable FEP and PFA. PFA is the most transparent of the three forms. FEP, in the

thicknesses encountered for tubing, is translucent. The three polymers can also be distinguished by their infra-red spectra (Fig. 1, 2 and 3), and melting ranges. Melting ranges for PTFE, FEP and PFA are 342, 270-280, and 302-310°C, respectively.

The absence of CF_3 groups in PTFE accounts for the lack of an infra-red absorption band at around 1000 cm^{-1} , permitting easy discrimination of this form of Teflon. Comparing Figures 1 and 3 suggests about a 15 cm^{-1} difference in the ca. 1000 cm^{-1} absorption bands for FEP and PFA. This may, however, reflect the difference in resolution between the spectra.

B. Experimental

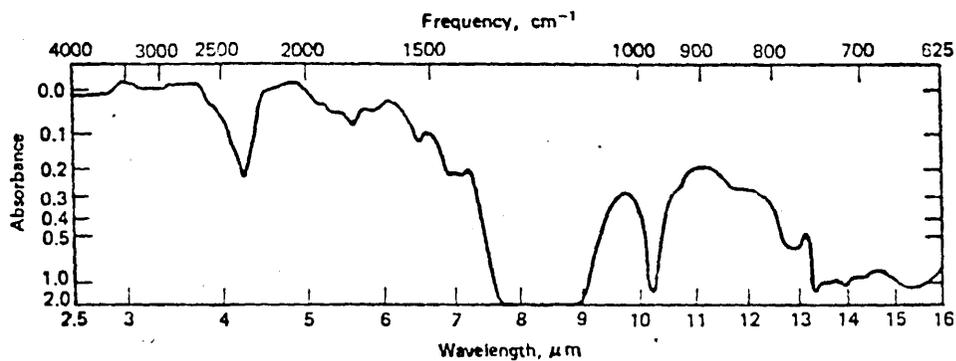
Samples of PFA and FEP tubing were provided by Unisearch Inc. These were supplemented by locally obtained, new FEP tubing and with previously used PTFE tubing. The latter was washed with hot water, distilled water and baked dry before testing.

In addition to tubing, HNO_3 loss was measured in a motor-driven ball valve constructed of PTFE*. A PTFE cyclone of the type used by Allegrini et al., with annular denuders at the NSMCS (7) was supplied by the Research Triangle Institute. As supplied, the cyclone was attached to a cylindrical PTFE section (I.D. 5 mm) which terminated in one half of a PTFE filter holder (Figure 4). To permit evaluation of HNO_3 loss, the usual cyclone inlets were sealed with tape and a tight fitting Teflon tube inserted in the cyclone base (with the collection cup removed). One half of a Nuclepore polycarbonate filter holder was attached to the other opening and then to the inlet of the automated TAT. Although the cyclone was intended for operation at about 15 Lpm, such a flow rate was incompatible with facilities then available. Accordingly HNO_3 loss was assessed at 1 Lpm, and the results are upper limits to those expected at 15 Lpm. Calculated average residence time in the PTFE portion was 3 sec. at 1 Lpm.

To assess HNO_3 loss, the permeation tube source was connected through a PTFE solenoid valve to the automated TAT. The valve and other components were conditioned until the HNO_3 response reached steady state. The tubing or component being evaluated was then connected between the solenoid valve and the TAT. Nitric acid entered the test section only during the 1.5 or 3 minute period in each cycle in which the TAT was sampling. During the remainder of each 12 minute cycle, HNO_3 was vented, bypassing the test section. In this way, the TAT provided a semi-continuous record of the degree of penetration of relatively small (380 or 760 ng) doses of HNO_3 .

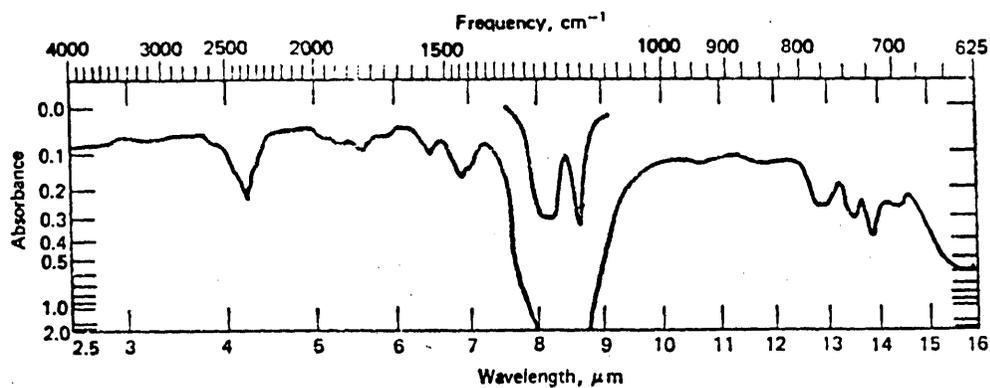
With Teflon test pieces showing substantial HNO_3 removal, it was frequently impractical to continue the experiment to achieve 100% penetration. Accordingly, the corresponding HNO_3 loss figures are generally shown as lower limits to the capacity of the test piece.

* According to the ball valve's manufacturer the Teflon is Grade 7 PTFE.



Infrared absorption spectrum of Teflon FEP.

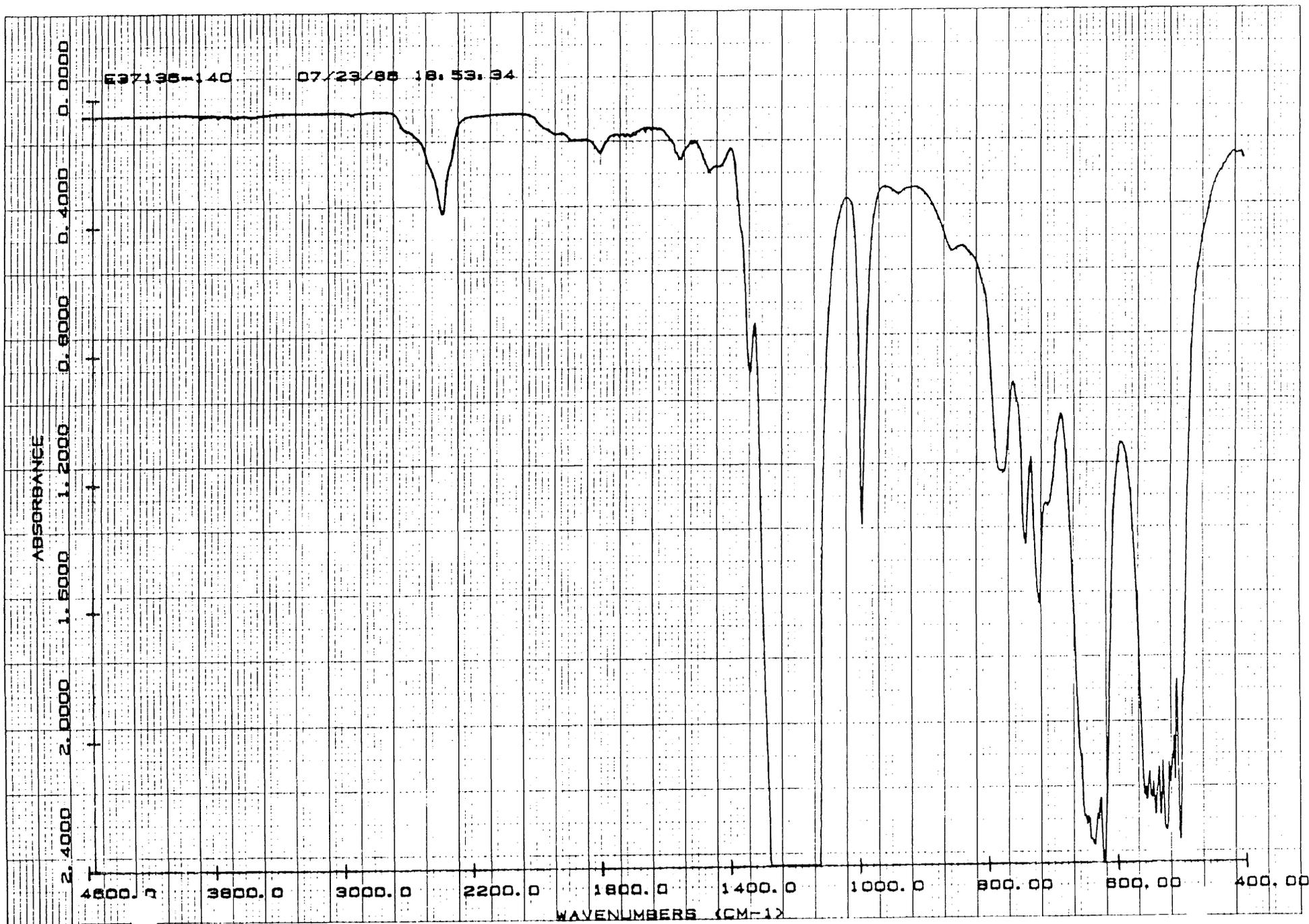
Fig. 1

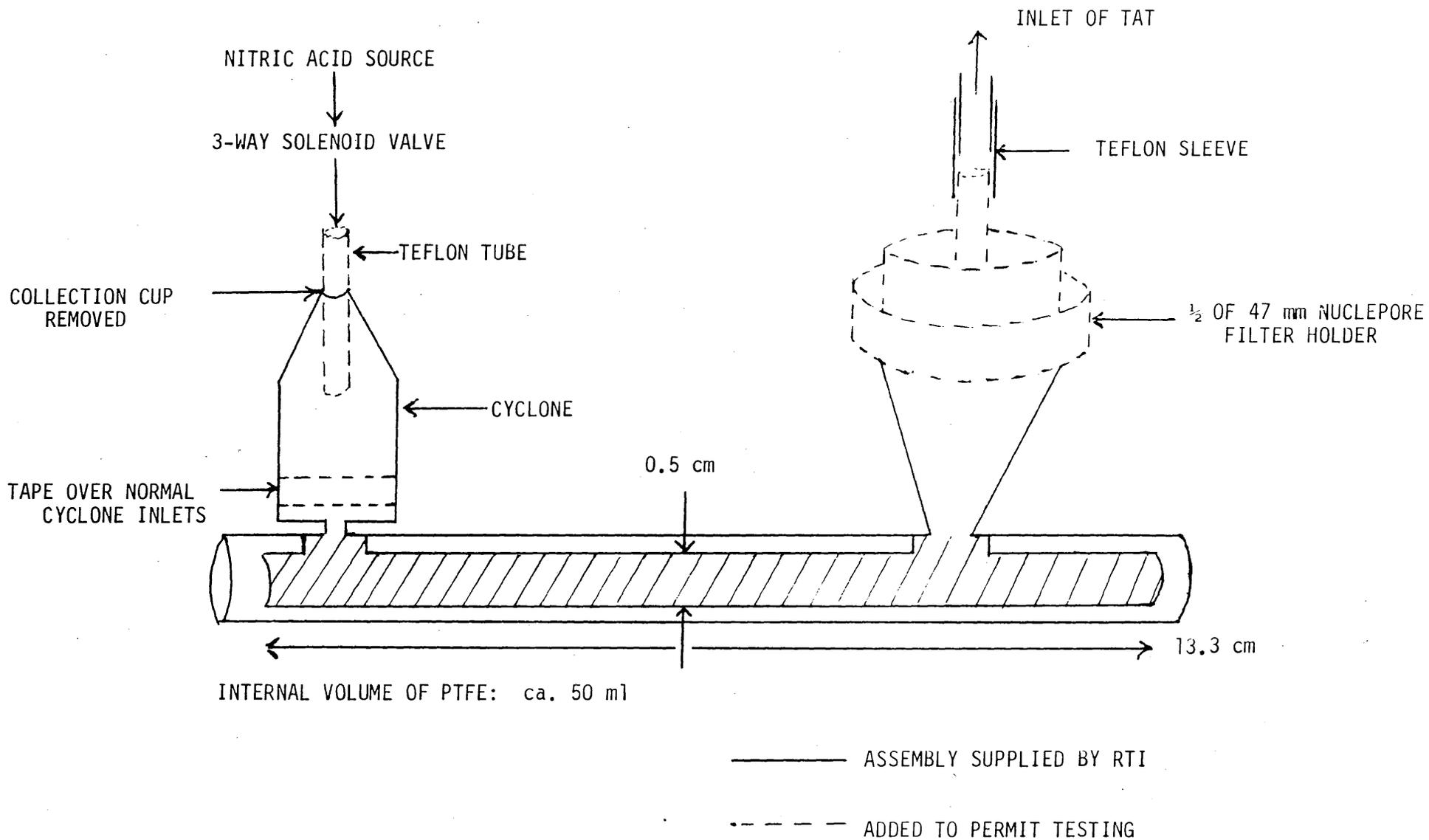


Infrared absorption spectrum of polytetrafluoroethylene.

Fig. 2

Figure 3. Infrared Absorption Spectrum of Teflon PFA





SCHEMATIC OF RTI CYCLONE AND ATTACHED COMPONENTS EVALUATED FOR NITRIC ACID RETENTION
(NOT TO SCALE)

Figure 4.

C. Results

The results for samples of tubing are given in Table 8. With the PFA tubing no loss of HNO_3 was measurable. Results for FEP were mixed. The sample supplied by Unisearch exhibited no HNO_3 loss, whereas the locally-obtained FEP showed marked loss. The difference in tube diameter and length altered residence times. The locally obtained material had a 6 sec residence time compared to 1 sec for the Unisearch sample. This probably contributed to the differences observed. It appears that the retained HNO_3 is at least partially lost between trials. The behavior in subsequent trials might be influenced by the time elapsed between trials as well as by storage conditions. PTFE showed the greatest efficiency for HNO_3 removal.

For trials dosing the PTFE motor-driven ball valve with either 380 or 769 ng per TAT cycle, the degree of HNO_3 loss remained relatively constant ($41.5 \pm 8.9\%$) over 18 cycles with an aggregate loss of > 3400 ng. The results with the RTI PTFE cyclone unit (Figure 4) showed $96.5 \pm 0.8\%$ HNO_3 loss, sampling $253 \mu\text{g}/\text{m}^3$ HNO_3 for 23 doses of 760 ng HNO_3 (as NO_3^-) each. The total dosage sampled was about $19 \mu\text{g}$ HNO_3 (as NO_3^-). Thus the results with the ball valve and long residence time sampling with a PTFE cyclone and associated components are qualitatively consistent with findings for PTFE tubing.

Table 8. Summary of Teflon Tubing HNO₃ Loss Study

Type	I.D.	Date	Length, cm	Internal Diameter, cm	Residence Time, sec	Loss
FEP	Unisearch	6/26/86	152	0.39	1.1	0.1 ± 4 (%)
PFA	Unisearch	6/27/86	300	0.48	3.8	ca. 0
FEP	AIHL #1	6/26/86	343	0.61	6.0	> 485 ng
		7/2/86				> 1205 ng
		7/9/86				> 2662 ng
		7/17/86				ca. 700 ng to saturate
PTFE	AIHL #2 ^a	7/2/86	78	0.29	0.3	> 1262 ng
		7/10/86				ca. 1200 ng to saturate
PTFE	AIHL #3 ^a	7/8/86	243	0.46	2.4	> 5357 ng
		7/19/86				5500 ng to saturate
		7/20/86				< 2000 ng to saturate

a. Tube washed with H₂O and dried in a stream of filtered room air at ambient temperature.

V. LOSS OF HNO₃ INLET DEVICES FOR ATMOSPHERIC SAMPLING

A. Introduction

Data from the NSMCS suggested that inconsistencies in results between certain methods could reflect primarily differences in the degree of loss of HNO₃ within sampler inlets. Except where filter packs were used, integrated sampling techniques used cyclones to remove coarse nitrate. We obtained for evaluation a number of inlet devices employed by various research groups to assess loss of laboratory-generated HNO₃ sampling at their normally employed flow rates. Of especial interest was a comparison of two cyclones of the AIHL design, with one fabricated of solid PTFE Teflon and the other, PFA-coated aluminum.

B. Experimental

The devices evaluated are listed in Table 9 together with their internal volumes. The AIHL PFA-coated cyclone was evaluated in two configurations:

1. With an attached 1-1/2" I.D. Pyrex glass "Y" to which was attached the downstream end of the cyclone, a vacuum source drawing 8 Lpm and a Nylon filter in a Nuclepore holder drawing 20 Lpm.
2. The cyclone with a Nylon filter attached directly to the downstream end, sampling at 20 Lpm.

Configuration (1) was employed at the NSMCS. The internal volume of the glass Y is substantially greater than that of the cyclone. Configuration (2) was evaluated to permit comparison of HNO₃ loss within the two AIHL-designed cyclones.

Nitric acid was generated with a Unisearch permeation tube maintained at 53°C. The acid was diluted to a total volume of 7 cfm. The seven units to be compared were attached to stainless steel ports of a sampling manifold. The equivalence of the seven, 1-1/2" I.D. ports was assessed by parallel sampling with open-face filter holders connected to each port sampling with Sartorius Nylon filters. For two successive 3-hour trials run at 50% R.H. and 21°C, the means and standard deviations for measured HNO₃ concentrations were $16.0 \pm 1.2 \mu\text{g}/\text{m}^3$ (n=7) and $16.3 \pm 0.81 \mu\text{g}/\text{m}^3$ (n=7), respectively. We infer a precision of 7.5% or better for parallel sampling at equal flow rates.

Samplers operating at 16-28 Lpm were attached to 1.5" I.D. ports, and that at 10 Lpm was attached to a 5/8" port. Each device employed a 47 mm Nuclepore holder and Nylon filter attached at the downstream end. In addition to the seven devices, two open face Nylon filters were operated, attached directly to the sampling ports of each size. The filter on the 1-1/2" port ran at 20 Lpm while that on the 5/8" port ran at 10 Lpm. Transmission efficiency was evaluated relative to HNO₃ sampled with Nylon filters from the same size port ("control filters").

Table 9. Inlet Devices Evaluated for Nitric Acid Transmission Efficiency

<u>Device Code</u>	<u>Device</u>	<u>Volume, mL</u>	<u>Sampling Rate, Lpm</u>
a	AIHL-design PFA-coated Aluminum cyclone*	475 (with glassware)**	28***
b	Andersen stainless steel	85 (without extension) 250 (with s/s extension)	20 20
c	AIHL-design PTFE cyclone	83	20
d	RTI PTFE cyclone (Southern Research Institute design)	60	15.6
e	Teflon-coated glass cyclone†	75	16
f	Teflon-coated glass impactor†	35	16
g	U. Calgary PTFE cyclone (Southern Research Institute design)	62	10

* According to R.J. Chase Co. (Union City, CA) the PFA coating is applied in two steps. Initially the item to be coated is baked at 750°F to remove volatile organic matter. When cool, the surface to be coated is roughened by grit blasting with #80 garnet or #100 Al₂O₃. The surface is given a pre-coating with a TFE primer containing chromic and phosphoric acids to obtain a 5 to 8 μm film. The pre-coat is colored green or grey to indicate complete coverage. The primer is cured at 450°F. PFA is applied electrostatically as a free flowing powder (average particle size 37 μm) at minimum voltage to obtain a film 25 to 75 μm thick. The coating is baked at 750°F for at least 20 min causing the powder to coalesce into a transparent film covering the colored pre-coat.

** Volume without glassware is 85 ml.

*** The PFA-coated AIHL cyclone was operated at 28 Lpm but the nylon filter sampler downstream sampled at 20 Lpm.

† University Research Glassware, Carboro, NC.

All devices were precleaned with a 1 hour hot H₂O soak followed by a MeOH rinse and particle-free air dry. Filter holders were washed with deionized water and dried in particle-free air.

Three, 6-hr trials were performed at 50% R.H., 20°C and three at 80% ± 2% R.H., 13 ± 1°C. Following the third trials, the cyclones were rinsed with 2, 5 mL aliquots of standard IC eluent to assess NO₃⁻ recoverability from the walls.

C. Results

Results for three trials at 50% R.H. are given in Table 10, expressed as a percent of the relevant control filter result. The measured HNO₃ concentration was about 10% lower at 10 compared to 20 Lpm, consistent with greater loss to the walls of the manifold and/or sampler. Transmission efficiency ranged from 18% for the stainless steel cyclone, initial trial, to 114% for the Teflon-coated glass impactor. All inlets showed evidence of increased transmission with increased dosage. This effect is seen more clearly in Figure 5. The AIHL PFA-coated cyclone with attached glassware was initially quite inefficient, but showed a rapid increase in efficiency, never equalling, however, the cyclones constructed of solid Teflon or Teflon-coated glass.

Recoveries of nitric acid from the collection medium and from washing the cyclone interior are detailed in Table 11. Recoveries are nearly quantitative except for the stainless steel and PFA-coated cyclones. Both of the latter had attached sections whose surfaces were not washed, a possible cause of the low recoveries.

Since the AIHL-design PFA-coated cyclone (with connecting glassware) was previously used in the NSMCS, an effort was made to assess the degree of HNO₃ transmission after uninterrupted exposure to the acid. For this purpose, a pre-cleaned unit was conditioned by sampling about 10 µg/m³ HNO₃ for 24 hours at 50% R.H. Following this, its transmission efficiency was measured for an additional 6-hr period as described previously. Total calculated dosage following the 6-hr trial was 360 µg. The efficiency found, 85%, compares to 74% for the third 6-hr trial at this concentration, after a cumulative dosage of 325 µg HNO₃.

Table 12 and Figure 6 gives transmission efficiency results for trials with the seven inlet devices at simulated Southern California nighttime conditions, 80% R.H. and 13°C. Except for the stainless steel and PFA-coated cyclones, transmission efficiencies are consistently lower than at 50% R.H., 20°C. Greater retention of the acid by a thicker water layer on top of an inert surface of each device may be the cause. At both simulated daytime and nighttime conditions, the Teflon-coated glass impactor showed the highest efficiency. In contrast to daytime conditions, the PFA-coated and stainless steel cyclones showed higher initial efficiency at the higher R.H. These results may indicate some degree of passivation of a reactive surface by the thicker water layer provided at 80% R.H.

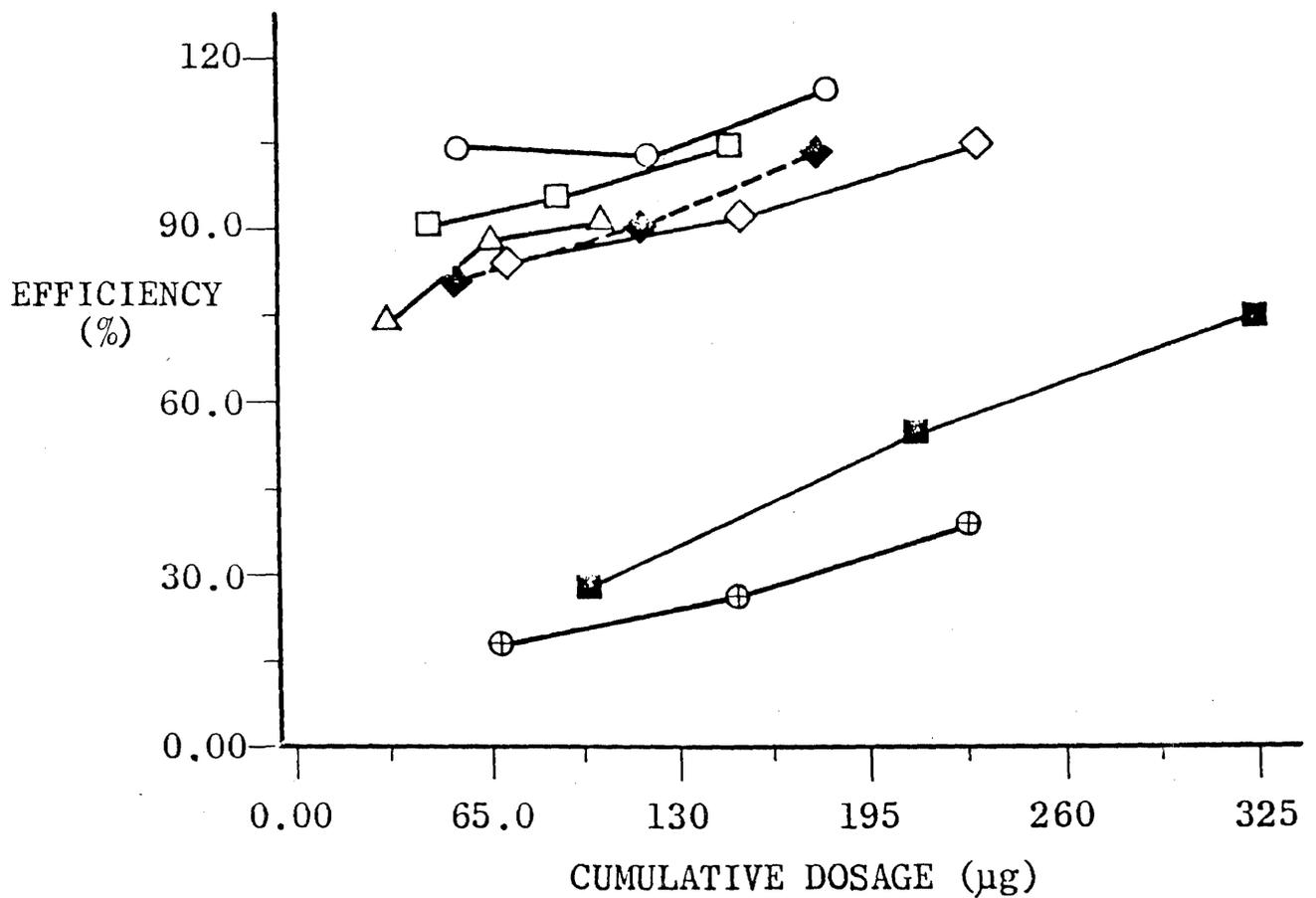
Table 10. Efficiency of Transmission of Nitric Acid Through Inlet Devices at 50% R.H. (Percent)*

Device Code **	Trial		
	A	B	C
a	28.0	54.3	74.1 ^a
b	18.0	26.5	38.4
c	85.1	92.7	105
d	81.3	90.5	103
e	91.3	95.5	105
f	104	102	114
g	74.3	88.4	91.9
<u>HNO₃ Concentrations (μg/m³)</u>			
20 Lpm:	9.90	11.0	11.2
10 Lpm:	9.07	9.66	11.1

* Conditions: 6 hour sampling
21°C

** See Table 9.

NITRIC ACID TRANSMISSION EFFICIENCY
50% R.H.



- PFA-COATED AIHL CYCLONE (ALUMINUM)
- ⊕ STAINLESS STEEL (SIERRA-ANDERSEN)
- ◇ AIHL CYCLONE (PTFE)
- ◆ RES. TRIANGLE INST. PTFE CYCLONE
- EPA FEP-COATED GLASS CYCLONE
- EPA FEP-COATED GLASS IMPACTOR
- △ U. CALGARY PTFE CYCLONE

Figure 5.

Table 11. Recovery of HNO₃ from Inlet Devices in 50% R.H. Trials ($\mu\text{g NO}_3^-$)

<u>Sampler</u> *	<u>Transmitted NO₃⁻</u>	<u>Recov. in Wash</u>	<u>Cumulative Dosage</u>	<u>% Recovery</u>
a	121	69.2	324	58.6
b	63.8	90.6	229	67.4
c	218	11.3	232	98.8
d	162	11.5	178	97.5
e	144	6.2	148	101
f	192	4.8	181	109
g	89.4	5.4	105	90.3

* See Table 9

Table 12. Efficiency of Transmission of Nitric Acid Through Inlet Devices at Simulated Nighttime Conditions (%)*

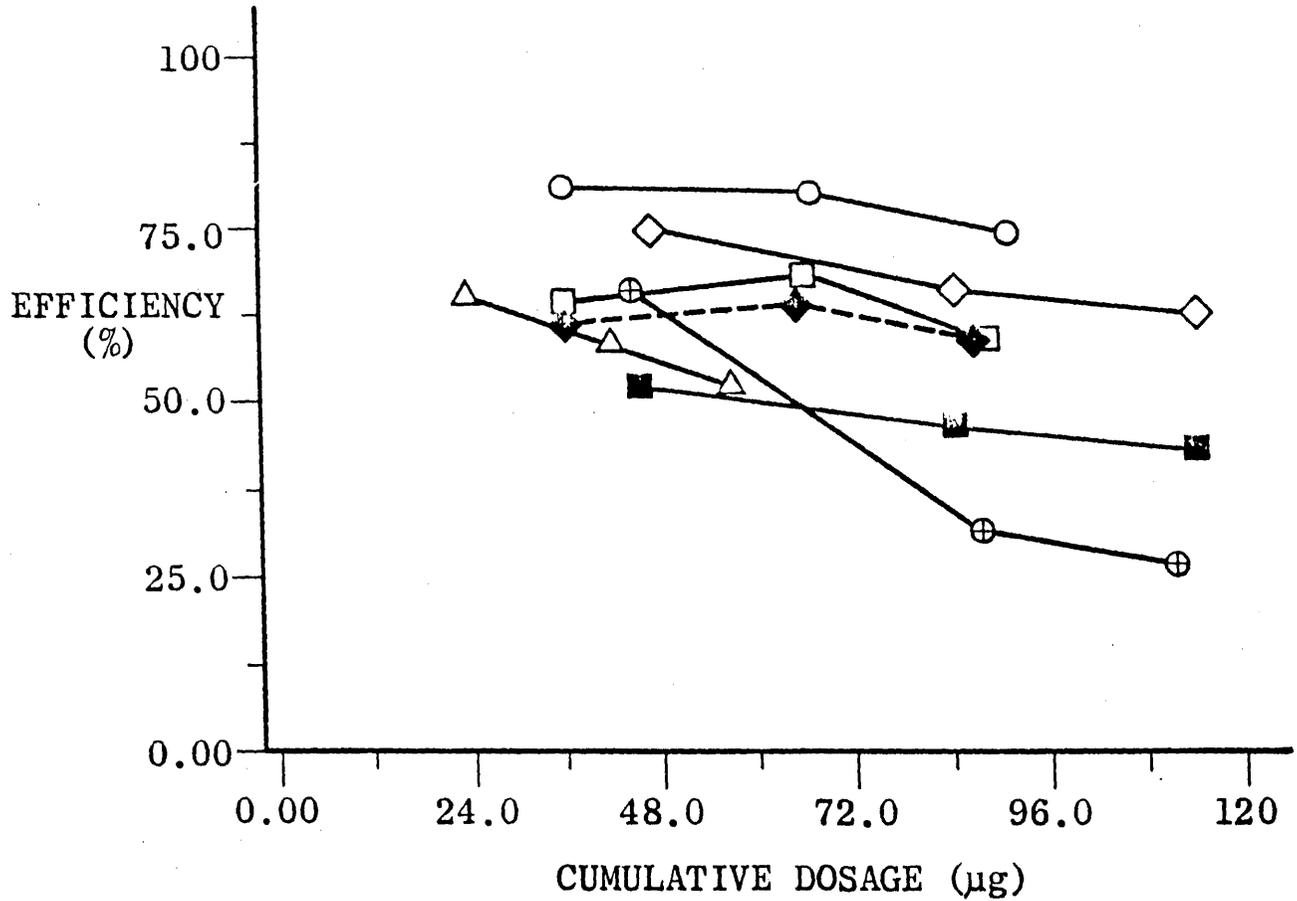
Device Code **	Trial		
	E	F	G
a	52.4	46.9	43.4
b	65.4	31.8	27.1
c	74.8	66.1	63.3
d	62.1	65.1	59.7
e	65.0	68.8	59.5
f	81.2	80.5	75.1
g	65.6	58.4	53.2
<u>HNO₃ Concentrations (μg/m³)</u>			
20 Lpm:	6.22	5.48	4.17
10 Lpm:	(7.98)***	5.45	4.17

* Conditions: 6 hour sampling
80% R.H.
13°C

** See Table 9.

*** Suspect result, not used for calculation.

NITRIC ACID TRANSMISSION EFFICIENCY
80% R.H.



- PFA-COATED AIHL CYCLONE (ALUMINUM)
- ⊕ STAINLESS STEEL (SIERRA-ANDERSEN)
- ◇ AIHL CYCLONE (PTFE)
- ◆ RES. TRIANGLE INST. PTFE CYCLONE
- EPA FEP - COATED GLASS CYCLONE
- EPA FEP - COATED GLASS IMPACTOR
- △ U. CALGARY PTFE CYCLONE

Figure 6.

Recoveries of nitrate from the samplers in the simulated nighttime trials are given in Table 13. These ranged from 72 to 104% (discounting an apparently contaminated sample). The high recovery of nitric acid with the stainless steel cyclone is notable and suggests that, with a substantial water layer, the nitric acid was rapidly removed such that nearly all of it remained within the cyclone rather than penetrating to the (unextracted) stainless steel extension downstream.

An important factor influencing nitric acid wall loss may be revealed in Figure 7. This shows nitric acid transmission efficiencies for the first, 6-hr trial at 50% R.H. against calculated average residence times with the devices (including the glassware of the AIHL cyclone and the steel extension for the stainless steel cyclone). An excellent negative correlation is observed regardless of wall composition or design. Devices with residence times < 0.2 sec. showed > 80% transmission efficiency without previous conditioning.

The AIHL design PTFE and PFA-coated cyclones are nearly identical except for wall composition. To permit a direct comparison, and to eliminate ambiguity resulting from the attached glassware with the PFA-coated cyclone, the cyclones, followed immediately by Nylon filters, were run in parallel at 20 Lpm to provide nearly equal geometries. Table 14 gives results for three, 3-hr trials. The dosages were about half those for the preceding trials at 50% R.H. Even without the glassware, the PFA-coated cyclone showed lower transmission of nitric acid. Little or no conditioning was evident for this cyclone, whereas a small effect can be seen with the PTFE cyclone.

The reproducibility of the behavior of the PFA-coated AIHL design cyclone was assessed by sampling HNO_3 in parallel through two such cyclones with filter holders directly attached at the outlets. Units 1 and 2 were employed by us in the DDM during the 1985 Nitric Acid Intercomparison Study. Unit 3, identical except for the addition of a pyrex pipe and Teflon-coated adaptor between the cyclone outlet and the filter holder, was also included. Table 15 shows transmission efficiency results for three successive trials. The results for the three units are similar although unit 3, with the attached glassware, failed to exhibit a conditioning effect. The NO_3^- dosage for each trial was about 30 μg compared to about 80 μg for the trials described in Tables 2 and 4. In recovery trials for unit 3, only the cyclone interior was washed. Recoveries of NO_3^- ranged from 93 to 106%.

The degree of agreement shown among the three cyclones tested argues that damage to the Teflon coating is unlikely to be influencing transmission efficiency.

D. Comparison to Earlier Work

Following the NSMCS, during which about 2400 μg HNO_3 was sampled through each cyclone, the still-dirty PFA-coated AIHL cyclone plus its associated glassware, was tested for HNO_3 transmission efficiency. The cyclone evaluated was used to sample total fine inorganic nitrate, TFIN, (i.e. nitric acid plus fine particle nitrate).

Table 13. Recovery of HNO_3 from Inlet Devices in Simulated Nighttime Trials
($\mu\text{g NO}_3^-$)

<u>Device Code</u> *	<u>Transmitted</u>	<u>Recov. in Wash</u>	<u>Cumulative Dosage</u>	<u>% Recovery</u>
a	55	98 ^a	114	134**
b	49	68	112	104
c	79	40	115	103
d	55	8	88	72
e	58	25	90	92
f	72	20	91	101
g	34	19	57	93

* See Table 9.

** High SO_4^{2-} observed indicating likely sample contamination. Result considered unreliable.

HNO₃ TRANSMISSION vs. RESIDENCE TIME
50% R.H.
FIRST TRIAL

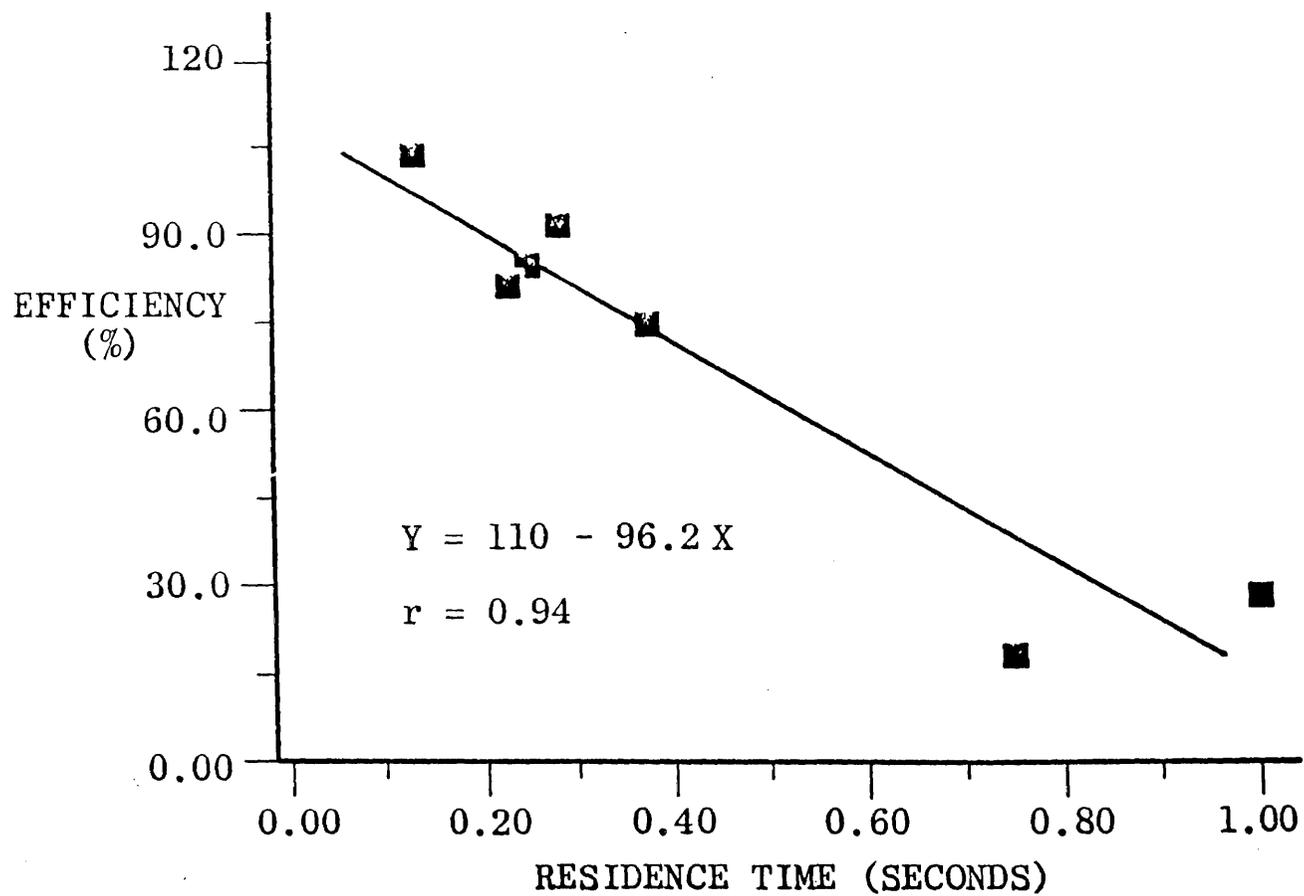


Figure 7.

Table 14. Comparison of AIHL Design PFA-Coated and Solid PTFE Cyclones for HNO₃ Removal (% Transmission)^a

Device\Trial:	A	B	C
PFA-Coated	47.5	43.0	51.1
Solid PTFE	71.2	75.7	78.6
HNO ₃ Conc. (μg/m ³) ^b :	11.8 ± 0.1	10.7 ± 0.1	13.1 ± 0.4

a. Conditions: 3 hour sampling
 20 Lpm
 50 % R.H.
 20°C

b. Mean based on two Nylon filters sampling in parallel.

Table 15. Comparison of Three PFA-Coated AIHL Design Cyclones for HNO₃ Transmission Efficiency (%)^{a, b}

Device\Trial	H ^c	I ^d	J ^e
1 ^f	35.7	40.3	47.9
2	30.9	47.0	46.3
3	43.7	38.7	44.0
HNO ₃ Conc. (μg/m ³):	7.9 ± 0.6	8.6 ± 0.4	7.0 ± 0.05

- a. Conditions: 3 hr sampling
20 Lpm
20°C
- b. Filter holder attached directly to outlet of cyclone for device 1 and 2. With device 3, a unit employed by W. John and co-workers, the filter holder was attached to the end of a 3.8 cm I.D. tube consisting of 6 cm of PVC, 14 cm of Pyrex preceded by a Teflon-coated metal reducing adaptor connected to the cyclone outlet.
- c. R.H. range 53-57%.
- d. R.H. range 59-64%.
- e. R.H. range 61-64%.
- f. The unit identified as "a" in Tables 9-13.

The results, given in Appendix B, showed minimal loss of nitric acid passing through this inlet device. Consistent with these findings, comparison of our atmospheric HNO₃ results with those by spectroscopic techniques showed no measurable loss of HNO₃ (16). Indeed, our HNO₃ results averaged about 15% higher than those by Fourier transform infra-red spectroscopy (FTIR). Thus if loss of HNO₃ was experienced within our cyclones and attached glassware, such comparison fails to reveal it. A significant caveat to these results is the restriction to daytime results since the limit of detection by FTIR prevented measurement of HNO₃ during nighttime hours, when HNO₃ levels are relatively low.

In addition to FTIR, our NSMCS atmospheric HNO₃ results by the DDM were compared to those by J. Horrocks, ARB, who employed the DDM with AIHL design cyclones of solid PTFE. The regression equation between the data sets was:

$$\begin{aligned} \text{ARB} &= 9.25 + 0.839 (\text{AIHL}) \\ r &= 0.93 \\ n &= 39 \end{aligned}$$

Based on ratios of means, the AIHL results were higher by about 10%. If only the initial sampling periods are compared such that the cumulative HNO₃ dosage sampled through our PFA-coated cyclone was 270 μg (similar to the present laboratory trials):

$$\begin{aligned} \text{ARB} &= -5.2 + 1.18 (\text{AIHL}) \\ r &= 0.97 \\ n &= 5 \end{aligned}$$

Based on ratios of means, for the initial five periods the ARB results averaged higher by 4%. This is far less than the difference in HNO₃ transmission efficiency found for the solid PTFE and PFA-coated cyclones in the present laboratory studies. Of course, any differences between laboratories in recovery and analysis of NO₃⁻ are also reflected in these comparisons. For the first five sampling periods the mean HNO₃ dosage collected was low, only 11 μg. The recovery of 9.9 μg NO₃⁻ spiked on to Nylon filters was found during the NSMCS to be 71% and 101% for AIHL and ARB laboratory (7). If this observed difference were relevant to the atmospheric samples, then, corrected for recovery, the AIHL values would be higher than the ARB's by about 25%. Thus with and without correction for NO₃⁻ recovery at low dosage, the atmospheric results as well as subsequent laboratory trials with the dirty cyclone stand in contrast to the present findings.

The cause of these differences is unknown. The sampling strategy and conditions for the laboratory evaluations were nearly identical, except for preconditioning. The earlier lab work was deliberately done with the inlet system as retrieved from the field. As noted previously, this included conditioning by sampling about 2400 μg HNO₃. The present trials followed a rigorous precleaning. It appears that, in the absence of other ambient air components, sampling of up to 360 μg nitric acid is insufficient to permit efficient transmission of nitric acid through the PFA-coated AIHL cyclones.

A possible cause of the difference in results, remaining unexplored, is that conditioning for nitric acid sampling in ambient air is more efficient than that under laboratory conditions. Perhaps the deposition of NO_3^- -containing particles enhances the transmission efficiency for HNO_3 .

E. Conclusions

1. Inlet devices can vary substantially in nitric acid transmission efficiency.
2. Residence time and reactivity of the surface of the device appear to be the predominant variables influencing nitric acid transmission efficiency in the devices tested.
3. Inlet devices with relatively inert walls show increased nitric acid loss at higher relative humidities and/or lower temperatures.
4. Metal or Teflon-coated metal cyclones should be avoided for use in nitric acid sampling. Teflon-coated glass or solid Teflon (e.g. PTFE) should be used to minimize nitric acid loss.
5. Residence times for HNO_3 within the inlet device should be as short as possible, preferably ≤ 0.2 sec to minimize HNO_3 loss.
6. The inconsistency between the current laboratory results with the PFA-coated AIHL cyclone and prior studies indicates that current transmission efficiency values are probably lower limits for atmospheric sampling.
7. Additional work is needed to reconcile laboratory and atmospheric results and, thereby, assess the relevance of this work to atmospheric sampling.

VI. COMPARISON OF THE ANNULAR DENUDER AND DENUDER DIFFERENCE METHOD FOR HNO_3

A. Introduction

Laboratory-generated HNO_3 was sampled in parallel by the annular denuder (ADM) and denuder difference (DDM) methods under conditions of constant concentration, temperature and relative humidity. To minimize ambiguity in interpretation, the DDM and ADM were employed without a preceding cyclone and associated glassware. Thus differences in results reflect a direct comparison of the collection efficiency and recovery of NO_3^- from a carbonate-coated annular denuder compared to that from a Nylon filter. With the DDM, the filter-collected total inorganic NO_3^- is corrected for the particulate NO_3^- measured downstream of an MgO-coated denuder. Two ADM units were coupled in series permitting assessment of single tube collection efficiency. In addition to the comparison with laboratory-generated HNO_3 , atmospheric sampling trials were done on Emeryville outdoor air for 3, 24 hr periods.

B. Experimental

Annular denuders were purchased from University Research Glassware, Carboro, NC. The denuders (Figure 8) include plastic screw caps for each end, and a plastic coupler with PTFE gasket for joining two units in series. Coating and extraction of each device are described in Appendix C.

Two ADM were coupled together for all trials. In the front end of each annular denuder, the inner rod has been shortened, leaving a one inch cylindrical section ahead of the annulus. All devices sampled from separate 1-1/2" I.D. stainless steel ports, connections being made to minimize contact between HNO_3 and rubber gaskets or Tygon sleeves used to achieve air-tight seals to the manifold. The following devices were similarly attached to the ports of the sampling manifold:

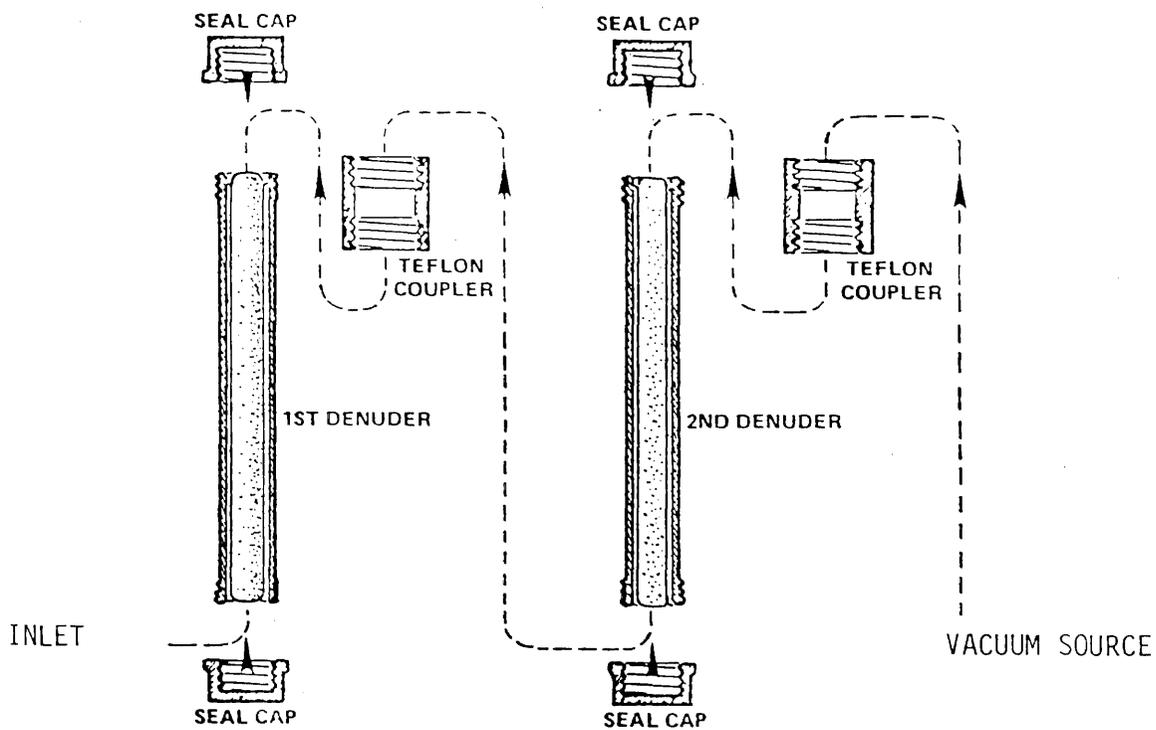
1. MgO denuder plus Nuclepore filter holder, with Nylon filter (20 Lpm)
- 2 & 3. Nuclepore filter holders, Nylon filters (20 Lpm)
4. Nuclepore filter holder, Nylon filter (16.7 Lpm)
- 5 & 6. Annular denuders each containing two denuder sections (16.7 Lpm)

DDM values were obtained by subtracting sampler 1 results from those for the mean of samplers 2 and 3. The recovery of HNO_3 by the DDM was calculated relative to the mean of samplers 2 and 3 NO_3^- . ADM denuder efficiencies were calculated employing only the NO_3^- from the front denuder, and were relative to the NO_3^- on sampler 4 (i.e. that collected at the same flow rate). For trials at 80% R.H., two Nylon filters sampled in parallel at 16.7 Lpm.

To permit parallel atmospheric sampling of atmospheric HNO_3 with the ADM and DDM, the glass and stainless steel manifold employed in laboratory trials was relocated adjacent to a laboratory window.

Figure 3.

ANNULAR DENUDER SYSTEM



Outdoor air was drawn in through a 1-1/2" glass pipe with a squirrel cage blower (flow rate 16 cfm) from which four units sampled in parallel:

- a. PFA-coated AIHL cyclone with Nuclepore filter holder and Sartorius Nylon filter at 20 Lpm. Filter holder was attached directly to the downstream outlet of the cyclone.
- b. As in a. but with a 24-tube MgO denuder between the cyclone and the Nylon filter.
- c. PFA-coated AIHL cyclone + two annular denuder sections in tandem followed by a Nuclepore filter holder and Nylon filter, all sampling at 16.7 Lpm.
- d. Same as c.

Throughout sampling, the air temperature and relative humidity were also monitored. The three sampling periods were consecutive with about 1 hour between sampling periods. Denuders from the ADM were extracted with IC eluent immediately following each trial and the extracts refrigerated at ca. 5°C. IC analyses for NO_2^- and NO_3^- were done within 24 hr of the third trial.

Results for NO_3^- are discussed below. Since the NO_2^- results have greater relevance to the problem of HONO measurements, these data are included in Section VII.

C. Results

Table 16 compiles results at 50% R.H. for the DDM and the two ADM units, relative to the NO_3^- collected on a Nylon filter. On average, the open face Nylon filters at 16.7 Lpm measured 97.2% of the NO_3^- measured at 20 Lpm. The efficiencies of the MgO and Na_2CO_3 coated denuders were very high; the NO_3^- penetrating the MgO denuder was 0, 0.2 and 0.2 $\mu\text{g}/\text{m}^3$ for the three trials. Thus the values shown for DDM are very close to those for the mean of the two, 20 Lpm Nylon filters. With the ADM, in only one case was the NO_3^- recovered from the second denuder in series significantly above the NO_3^- blank value.

Recoveries with the DDM ranged from 99 to 100%. With the ADM, 5 of the 6 trials ranged from 88% to 91.7%. The sixth value, 105%, is considered an outlier. Based on these results accuracies, as measured by mean recoveries, were $99.5 \pm 0.5\%$ (n=3) and $89.0 \pm 2.1\%$ (n=5) for the DDM and ADM, respectively.

Table 17 shows similar results at 80% R.H. In no case was penetration of NO_3^- observed through the MgO denuder or the first annular denuder. Therefore, DDM HNO_3 equalled Nylon filter (20 Lpm) results, making recoveries 100%. Nitrate recovered from Nylon filters sampling at 16.7 Lpm averaged 4.4% lower than those at 20 Lpm. The accuracy of the ADM averaged $93.1 \pm 6.5\%$ (n=6). As with the results at 50% R.H., the ADM provided slightly lower recovery.

Table 16. Comparison of the Annular Denuder and Denuder Difference Method for HNO_3 at 50% R.H. ($\mu\text{g}/\text{m}^3$ as NO_3^-)^{a, b}

Technique	Trial A		Trial B		Trial C	
	$\mu\text{g}/\text{m}^3$	%Recovery ^c	$\mu\text{g}/\text{m}^3$	%Recovery ^c	$\mu\text{g}/\text{m}^3$	%Recovery ^c
DDM	21.7	100	19.1	99.0	21.5	99.5
ADM1 ^c	19.2 0	88.0	19.2 0	105	18.8 0	90.4
ADM2 ^c	20.0 0.5	91.7	15.8 0	86.3	18.4 0	88.5
Nylon filter @ 16.7 Lpm	21.8		18.3		20.8	
Nylon Filter @ 20 Lpm	21.7 ± 0		19.3 ± 0.6		21.6 ± 0.1	

- a. Experimental conditions: 20°C
50% R.H.
5 hr trials
47 mm filters
- b. Both DDM and ADM run without a cyclone to minimize errors introduced by losses of HNO_3 . The denuders were attached directly to the HNO_3 sampling manifold without preceding glassware. Recovery for DDM relative to NO_3^- on Nylon filter at 20 Lpm. Recovery for ADM relative to Nylon filter at 16.7 Lpm.
- c. NO_3^- results for the second denuder in series are shown immediately below that for the first denuder. Recoveries based only on first denuder. Results corrected for the mean denuder blank, $2.8 \pm 0.4 \mu\text{g NO}_3^-$ (n=3).

Table 17. Comparison of the Annular Denuder and Denuder Difference Method for HNO_3 at Simulated Nighttime Conditions ($\mu\text{g}/\text{m}^3$ as NO_3^-)^{a,b}

Technique	Trial A		Trial B		Trial C	
	$\mu\text{g}/\text{m}^3$	%Recovery ^c	$\mu\text{g}/\text{m}^3$	%Recovery ^c	$\mu\text{g}/\text{m}^3$	%Recovery ^c
DDM	11.5 ± 1.8	100	9.35 ± 0.3	100	9.56 ± 0.2	100
ADM1 ^c	9.98 0	89.9	8.32 0	98.0	9.31 0	98.3
ADM2 ^c	9.03 0	81.4	8.15 0	96.0	8.98 0	94.8
Nylon filter @ 16.7 Lpm	11.1 ± 0.4		8.49 ± 0.5		9.47 ± 0.2	
Nylon Filter @ 20 Lpm	11.5 ± 1.8		9.35 ± 0.3		9.56 ± 0.2	

- a. Experimental Conditions: 12.8 ± 1°C
80% R.H.
5 hr trials
47 mm filters
- b. Both DDM and ADM run without a cyclone to minimize errors introduced by losses of HNO_3 . The denuders were attached directly to the HNO_3 sampling manifold without preceding glassware. Recovery for DDM relative to NO_3^- on Nylon filter at 20 Lpm. Recovery for ADM relative to Nylon filter at 16.7 Lpm.
- c. NO_3^- results for the second denuder in series are shown immediately below that for the first denuder. Recoveries based only on first denuder. Results corrected for the mean denuder blank, 2.8 ± 0.4 μg NO_3^- (n=3).

Atmospheric sampling results for three 24 hr periods with the ADM and DDM are given in Table 18. The two ADM units showed fair agreement. The ratio of means for all periods for the two units was 0.90. The mean C.V. for ADM sampling was 16%. Average HNO_3 concentrations for the three trials by the ADM ranged from 0.7 to $0.9 \mu\text{g}/\text{m}^3$. With the DDM, the measured HNO_3 ranged from 0.17 to $0.6 \mu\text{g}/\text{m}^3$. The agreement between the two techniques was poor at these low concentrations, with the DDM consistently lower. Since losses of HNO_3 ahead of the collection media should have been about equal, the results are considered to reflect differences involving the collection and recovery process, itself. Possible sources of the observed differences include:

1. Partial conversion of NO_2^- to NO_3^- following collection by the ADM units.
2. Incomplete retention and/or recovery of NO_3^- from Nylon filters at very low HNO_3 levels.
3. Incomplete retention of HNO_3 by the MgO denuder.

Of these possible sources, the first is almost unavoidable (see Section VII) and becomes more significant at low HNO_3 levels. Possible source 3 is judged to be highly unlikely based on trials at $10\text{-}15 \mu\text{g}/\text{m}^3$ HNO_3 (as NO_3^-). Possible source 2 cannot be ruled out based on presently available data. Extraction and IC analysis of Nylon filters spiked with $10 \mu\text{g}$ NO_3^- yielded a recovery of 70% (16).

Fine particulate NO_3^- (FPN) measurements with both methods involved recovery of NO_3^- from Nylon filters. The agreement between the ADM and DDM FPN was good, with a ratio of means, $\text{ADM}/\text{FPN} = 1.14$. The principle conclusion from this is that the CO_3^{2-} -glycerol coated ADM was about equally efficient to the MgO-coated denuder for HNO_3 removal.

D. Conclusions

Employing equivalent inlet devices, with laboratory-generated HNO_3 at 50% and 80% R.H., the DDM showed an accuracy of $\geq 99\%$ whereas that for the ADM was 89% to 93%. However, with atmospheric trials at low HNO_3 , the ADM showed significantly higher results, suggesting interference from collection of other NO_x species and/or incomplete recovery of NO_3^- from Nylon filters at low dosages.

Table 18. Comparison of the ADM and DDM in Ambient Air HNO₃ Sampling Through Equivalent Inlet Devices (μg/m³)

<u>Sampler</u>	<u>Trial</u>	<u>Stage 1 NO₃⁻</u>	<u>Stage 2 NO₃⁻</u>	<u>Nylon Filter NO₃⁻</u>	<u>HNO₃ by Difference</u>
ADM-1	Q	0.63	0.04	1.13	
	R	0.67	0	1.69	
	S	0.76	0	2.51	
ADM-2	Q	0.82	0.06	1.29	
	R	0.72	0	1.66	
	S	1.09	0.09	2.55	
TFIN ^a	Q	-	-	1.21	0.17
	R	-	-	1.77	0.28
	S	-	-	2.82	0.60
FPN ^b	Q	-	-	1.04	
	R	-	-	1.49	
	S	-	-	2.22	

a. Total fine inorganic NO₃⁻.

b. Fine particle NO₃⁻.

VII. INTERFERENCE IN NO_x MEASUREMENTS WITH THE ANNULAR DENUDER METHOD

A. Introduction

Tubular and annular denuders coated with Na₂CO₃ or Na₂CO₃-glycerol have been used for the collection and subsequent extraction and analysis measurement of atmospheric HNO₃ and HONO (17-19). Measurement of HONO on such denuders appears to be subject to error due to the partial retention of NO₂ on the annular denuder (17).

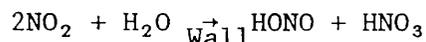
Figure 9 provided by D. Lawson, ARB, compares HONO measurements obtained with four devices at the NSMCS. These included two ADM systems, as well as a UV spectroscopy method, referred to as DOAS, and the tungstic acid technique, identified here as HT for heated tube, as employed by R. Braman. DOAS was taken to be the reference method, showing that all of the alternative techniques were subject to a positive bias.

Figure 10 is a scatter diagram of the difference in apparent HONO with the two ADM units against NO₂ concentrations. A moderate positive correlation (r=0.70) was observed providing some support for the involvement of NO₂ in producing different results. The higher ADM results were obtained by Allegrini et al. and the lower set, by E. Peake. The former employed a PTFE cyclone and PTFE manifold ahead of the collection medium whereas Peake's sampler used only a PTFE cyclone. Thus greater surface area was available ahead of the collector in Allegrini's system.

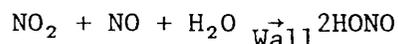
If NO₂ is retained on such denuders, the initially-retained species exists as nitrite ion (NO₂⁻) but undergoes slow oxidation to NO₃⁻. Nitrous acid is believed to be collected with high efficiency on the carbonate-coated denuder where it is analyzed as NO₂⁻. Since NO₂ retention produces the same ionic species, NO₂ retention is an interferent in HONO measurement.

If NO₂ is retained with low efficiency (e.g. < 5%), then a second denuder sampling in tandem should collect about an equal amount of NO₂. Subtracting the NO₂⁻ value obtained for the second denuder from that on the first would provide a more nearly error-free measurement of HONO.

The potential for NO₂ interference in HONO measurement is enhanced because of the reaction:



Ferm (17) noted some evidence for HONO formation on a bare glass surface, either by the above reaction or an alternative involving NO:



Atkinson et al. (20) considered the latter to be insignificant; their chamber data supported the surface catalyzed reaction of NO₂ and water as an important pathway to HONO formation in the absence of sunlight (21).

Figure 9

HONO MEASUREMENTS AT THE NSMCS

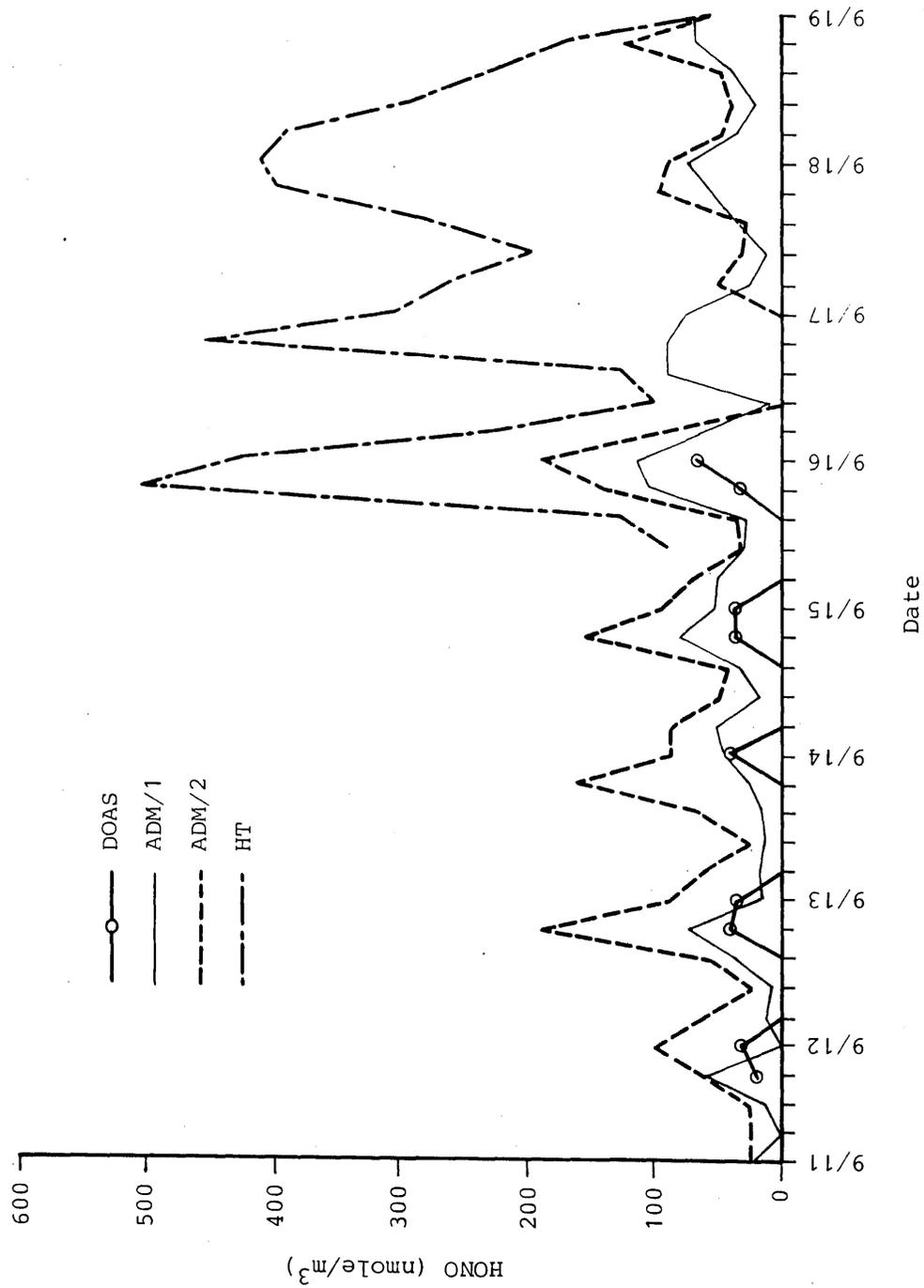
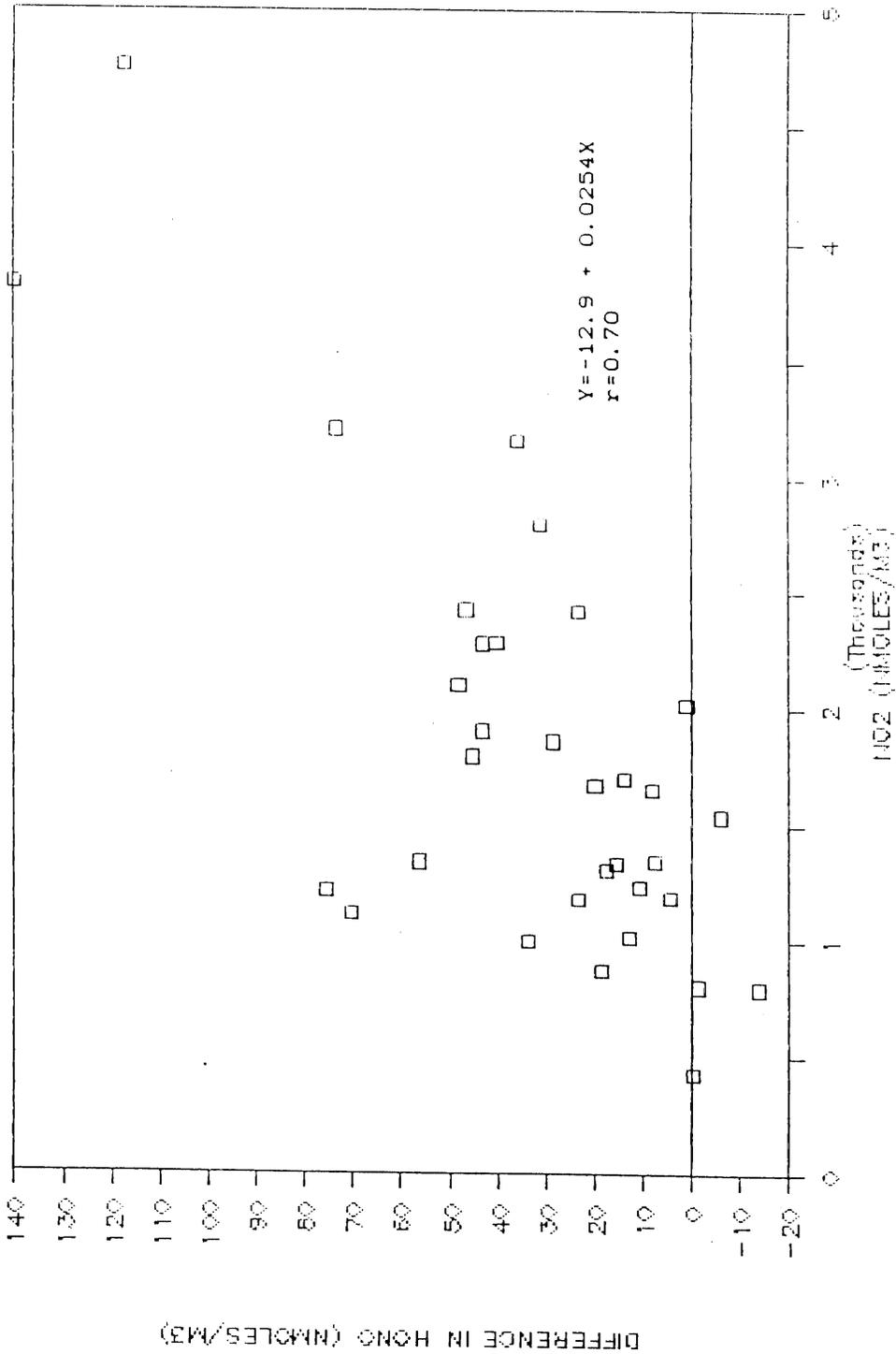


Figure 10.

DIFFERENCE IN HONO VS. NO2 FOR TWO ADM SYSTEMS



The possibility of such reactions creates both the potential for atmospheric sampling errors and for an experimental artifact which hampers laboratory assessment of the sampling error due to NO_2 . If one or both of the above reactions occur within the sampler, then such a process would probably occur both in chamber and atmospheric trials. About equal conversion would be expected on each successive denuder. If, however, conversion to HONO occurred on the surfaces of the exposure system used for the laboratory evaluation (i.e. ahead of the samplers) then the resulting HONO would be almost completely retained on the first denuder in series. NO_2 on the second denuder would represent the sum of actual NO_2 retention, NO_2 to HONO conversion within the sampler, and the very low percentage of HONO penetrating the first denuder which is captured by the second.

Ferm (17) assessed the measurement of the true atmospheric HONO concentration [HONO], with two tandem denuders as follows:

$$\begin{aligned}
 a &= 0.96 [\text{HONO}] + \delta_1 \\
 b &= 0.0384 [\text{HONO}] + \delta_2 \\
 \text{where} \quad a &= \text{NO}_2 \text{ on first denuder} \\
 b &= \text{NO}_2 \text{ on second denuder} \\
 \delta_1 &= \text{NO}_2 \text{ on first denuder from other than HONO} \\
 \delta_2 &= \text{NO}_2 \text{ on second denuder from other than HONO}
 \end{aligned}$$

The single denuder efficiency for HONO was taken to be 96%. To solve these two equations (with three unknowns), Ferm assumed $\delta_1 = \delta_2$, from which one calculates:

$$\text{HONO} = (a-b) \times 1.085$$

The validity of this assumption appears to be inconsistent with Ferm's own laboratory results. With 50 ppb NO_2 and excess O_3 (to consume any NO present) in humidified air; he reported about 0.4% retention (as NO_2) on the first denuder and less than 0.04% retention (as NO_2) on the second denuder.

The retention of HNO_3 on the first denuder should also occur with an efficiency of $\geq 96\%$. The $\leq 4\%$ NO_3 penetrating to a second denuder would be trapped as NO_3 . If oxidation of NO_2 to NO_3 occurs following NO_2 retention, it should provide NO_3 in nearly equal amounts on the first and second denuder. If substantial HONO were sampled, then NO_3 formed by oxidation would be significantly greater on the first denuder.

Subtracting NO_3 measured with the second denuder from NO_3 on the first to correct the HNO_3 measurement is not necessarily meaningful. Nitrate on the second denuder due to HNO_3 penetration should be added whereas that due to NO_2 oxidation should be subtracted. A better strategy is to operate with the residence time providing nearly 100% HNO_3 efficiency for the first denuder and minimize NO_2 oxidation by analyzing the samples quickly after collection, with refrigeration of samples during any storage periods.

The present experiments were done to test the effectiveness of the correction procedure for NO_2 retention under varying relative humidity conditions.

In addition to laboratory trials, atmospheric sampling trials were done with two ADM units for 3, 24-hour periods. The principal objective of this work was to compare ADM and DDM HNO₃ results, so the experimental procedures followed were those described in Section VI. The NO₂⁻ results from these trials are presented here. Since no independent measurement of atmospheric HONO was available, data assessment can only be based on comparisons to levels of HONO which could be expected.

B. Experimental

Denuder preparation was as detailed in Appendix B.

NO₂ was provided from cylinders in N₂ (Scott Lab, 184 or 190 ppm), with flow rates established by a mass flow controller. The NO₂ was introduced into a 227 Lpm purified air stream, humidified to 50 or 80% R.H. For the trial at 50% R.H., the NO₂ in N₂ was passed through a Nylon filter just before entering the glass and stainless steel exposure system, in an effort to remove HNO₃ possibly present with NO₂ in the cylinder. In addition, the trials at 50% R.H. employed two dual nylon filter packs sampling in parallel with the annular denuder. The final NO₂ concentration calculated from the degree of dilution agreed within 4% of that measured with a TECO Model 14BE chemiluminescent NO_x analyzer.

Prior to the first NO₂ trials (those at 80% R.H.) the exposure system was thoroughly water-washed and dried. NO₂ conditioning was done for about two hours before the first trials. A 9-hour chamber blank air trial was run to assess the cleanliness of the system and collectable NO_x in the purified ambient air.

Analytical procedures for annular denuder samplers were similar to those described in Section VI. Analyses for NO₂⁻ and NO₃⁻ were done in an eluent medium (2.14 mM CO₃⁼, 2.70 mM HCO₃⁻) by ion chromatography. Under the conditions used, retention times were as follows:

<u>Species</u>	<u>Retention Time, Min</u>
F ⁻ , Cl ⁻ , formate, OAc ⁻	3.75 ± 0.25
NO ₂ ⁻	6.3
NO ₃ ⁻	17.5

C. Results

For quality assurance on the NO₂⁻ determination, two samples were analyzed by two analysts using independently prepared standards and different IC units. In addition, standards prepared by one analyst were analyzed, as unknowns, by the second analyst. The results given in Table 19 show excellent agreement.

Results for the chamber blank and NO₂ trials at 80% R.H. are given in Table 20. Chamber blank results for NO₂⁻ were about one-sixth of those with added NO₂ on the first denuder (Stage 1) and one

Table 19. Comparison of Nitrite Analyses Between Two Analysts^a

<u>Sample</u>	<u>Analyst 1 NO₂⁻ (μg/ml)</u>	<u>Analyst 2 NO₂⁻ (μg/ml)</u>
Standard, 1.0 μg/ml	1.0 ^b	0.96
Standard, 10.0 μg/ml	10.0 ^b	9.9
PISA	3.0	2.8
OISA	7.1	7.1

- a. Analyst 1 used a Dionex Model 10 with manual sample injection. Analyst 2 used a Dionex Model 14 with automated sample injection. Both instruments used HCO₃⁻-CO₃⁼ eluents of similar (but not identical) concentrations.
- b. Theoretical value of standard prepared by Analyst 1 for use in instrument calibration. Analyst 2 employed independently prepared standards in analyzing the standards from Analyst 1.

Table 20. Collection^{a, b} of NO₂ in Two-Stage Annular Denuders at 80% R.H.
($\mu\text{g}/\text{m}^3$)

Trial	Sampler 1		Sampler 1		Sampler 2		Sampler 2	
	<u>S1</u>	<u>S1</u>	<u>S2</u>	<u>S2</u>	<u>S1</u>	<u>S1</u>	<u>S2</u>	<u>S2</u>
	NO ₂	NO ₃						
Blank Air	5.5	0.3	0.2	0.1	6.8	0.25	0.19	0.11
L	33.3	2.7	2.1	0.2	35.1	3.3	2.5	0.4
M	37.2	2.1	2.9	0.2	40.4	2.7	2.3	0.07
N	27.5	3.2	1.9	0.1	31.4	2.1	1.7	0.07

a. Experimental Conditions: 0.50 ± 0.02 ppm ($928 \pm 37 \mu\text{g}/\text{m}^3$) NO₂
 20°C
 80 ± 2% R.H.
 16.7 Lpm

b. Blank trial for nine hours. Trials L, M and N for 3 hours each.

c. S = Stage.

tenth, of those with added NO_2 on the Stage 2. Concentrations of NO_2 during the chamber trial, measured with the NO_x analyzer, ranged from 0.01 to 0.02 ppm.

The notable feature of the results with added NO_2 is the very low NO_2 observed on the second stage denuders, relative to Stage 1 levels. The mean NO_2 observed on Stage 1, corrected for chamber blank, $28 \mu\text{g}/\text{m}^3$, corresponds to about three percent retention of the initial NO_2 , while that on Stage 2, corresponds to about 0.2% retention. The results suggest that whatever NO_2 species is (are) being retained, the predominant species has relatively high retention efficiency on the annular denuder. The results are consistent with about 3% conversion of NO_2 to HONO, the resulting HONO then being trapped on the first denuder. Failure to observe an equivalent amount of HNO_3 might reflect loss of HNO_3 to the walls of the exposure system.

The Stage 1/Stage 2 ratio of NO_3^- results was at least 10, again suggesting relatively efficient retention of a NO_3^- species. This was probably HNO_3 , either present with NO_2 in the cylinder or formed in reaction with H_2O .

Results at 50% R.H. with added NO_2 are given in Table 21 for two trials. Trial O employed the same NO_2 cylinder used in Trials L, M and N at 80% R.H. Because of insufficient remaining NO_2 , a different cylinder, containing 185 ppm NO_2 in N_2 (1/10/84), was used. In contrast to Trials L, M and N, Trials O and P employed a Nylon filter in the NO_2 source line, through which NO_2 in dry N_2 passed. Results for Trial O strongly resemble results at 80% R.H. with NO_2 retention decreased by about one-third. In both cases $\text{NO}_2^-/\text{NO}_3^-$ ratios \geq on the first denuder stages were observed. The Stage 1/Stage 2 NO_2^- ratios similarly were at least 10. Thus at both R.H. levels, the NO_2^- species retained was collected with high efficiency.

In trial P, however, the $\text{NO}_2^-/\text{NO}_3^-$ ratio on Stage 1 was only about 4. The Nylon filter pack results showed relatively high NO_3^- on the first filter. This, as well as the low NO_2^- recovered on the first denuders, suggest that a substantial fraction of the NO_x entering through the Nylon filter was not NO_2 . Possibilities include HNO_3 transmitted through Nylon in a stream of dry N_2 conditions from a cylinder of NO_2 which was more than 3 years old. The efficiency of HNO_3 retention under such conditions have not been assessed previously, to our knowledge. The observation of about 0.5 ppm NO_2 with the chemiluminescent NO_x analyzer is not definitive since species convertible to NO over the Mo catalyst and able to reach the catalyst (e.g. HNO_3) would be indistinguishable from NO_2 .

However, even in trial P, the Stage 1/Stage 2 NO_2^- ratio was > 10 . The first stage Nylon filter data for NO_3^- are similar to those on the first annular denuder stage, supporting HNO_3 in the air stream sampled as the probable source in Trial P.

Table 21. Retention of NO₂ in Two-Stage Annular Denuders and Nylon Filter Packs at 50% R.H. ($\mu\text{g}/\text{m}^3$)^{a, b}

Sampler	Trial	Stage 1 ^c	Stage 1	Stage 2 ^c	Stage 2
		NO ₂	NO ₃	NO ₂	NO ₃
Denuder 1	O	21.7	1.09	1.06	0.29
	P	9.90	2.10	0.48	0.48
Denuder 2	O	22.9	1.06	1.06	0.29
	P	9.45	2.44	0.81	0.41
Filter Pack 1	O	0.19	0.60	0.19	0.1
	P	0.48	2.80	0.48	0.0
Filter Pack 2	O	0.21	0.60	0.26	0.1
	P	0.53	2.80	0.48	0.0

a. Conditions: 50 ± 2% R.H.
 19.5 ± 0.1°C
 0.48 ± 0.02 ppm NO₂
 3 hour trials

b. Trials O and P used different cylinders of NO₂ in N₂, both of which gave, after dilution, measured NO₂ levels of 0.48 ± 0.02 ppm.

c. Stage 1 indicates the first annular denuder or Nylon filter in filter pack samplers, and Stage 2, the corresponding second annular denuder or Nylon filter.

Aside from the probable contaminant NO_3^- source, results at 50% R.H. are similar to those at 80% R.H. All fail to support the usefulness of a strategy for HONO measurement based on subtracting NO_2 retention on a second tandem denuder from that on the first.

Atmospheric HONO results are given in Table 22 based on the assumption that HONO is the only source of NO_2^- . The results are similar to those for laboratory trials with NO_2 ; most of the NO_2^- is found on the first denuders. Applying the correction strategy proposed by Ferm had little impact. The apparent 24 hr HONO averaged about $2.6 \mu\text{g}/\text{m}^3$ (ca. 1.4 ppb).

These results can be compared to those by the DOAS for Claremont in September 1985. HONO peaked at nighttime at around 2 ppb ($3.7 \mu\text{g}/\text{m}^3$) and was below detectable limits during the day, consistent with its photochemical instability. The present results are much higher than expected 24-hr average levels of HONO. It is likely that some conversion of NO_2 to HONO occurred on the glass and/or stainless steel surfaces of the sampling manifold.

D. Conclusion

The retention of 0.5 ppm NO_2 , itself, on glycerol-carbonate coated annular denuders is $< 0.2\%$. Conversion of NO_2 to HONO is relatively small within the denuders but probably substantial in the glassware and/or stainless steel preceding the denuders. Since HONO was readily retained on the first denuder, subtraction of NO_2^- on the second denuder was not a meaningful strategy in these laboratory trials.

The assumption made by Ferm (17), that the non-HONO nitrite formed or collected on each of two denuders in tandem was equal, was not be tested adequately. What is needed are laboratory trials in which real-time measurements of HONO and NO_2 are made (e.g. by spectroscopic techniques) just before entry into the samplers, including necessary inlet devices (e.g. cyclones). Such measurements, together with recoveries of NO_2^- from the denuders, would permit assessment of HONO formation within the sampler and inlet, and as a result, better appraisal of the accuracy of HONO measurement by the ADM method. A simpler strategy to be used in continuations of this work involves removal of reactive nitrites (e.g. HONO) immediately ahead of each sampler to be evaluated. Based on the present work, CO_3^{2-} -impregnated filters can be used for this purpose.

Table 22. Collection of Nitrite in Atmospheric Sampling with Annular Denuders and Nylon Filters ($\mu\text{g}/\text{m}^3$)^a

Sampler	Trial	Stage 1 NO ₂ ⁻	Stage 2 NO ₂ ⁻	Nylon filter NO ₂ ⁻
ADM-1	Q	1.83	0.03	0.01
	R	2.62	0.04	0.01
	S	3.54	0.49	0.01
ADM-2	Q	2.05	0.23	0.02
	R	3.06	0.38	0.01
	S	2.60	1.28	0.01
TFIN ^b	Q	-	-	0.03
	R	-	-	0.03
	S	-	-	0.04
FPN ^c	Q	-	-	0.02
	R	-	-	0.03
	S	-	-	0.04

- a. Each trial was for 24 hr. R.H. during the three trials ranged from 42% to 50%.
- b. Total fine inorganic nitrate sampler.
- c. Fine particulate nitrate sampler.

VIII. HCl MEASUREMENT BY THE DENUDER DIFFERENCE METHOD

A. Introduction

Data from the NSMCS suggested that the DDM was providing a measure of gas phase chloride in addition to HNO_3 . The most likely form for such chloride was as HCl. For such measurements to be quantitative required that HCl be retained with high efficiency on both MgO coated denuder tubes and on Nylon filters. Such retention data had not been determined previously, to our knowledge.

B. HCl Retention on MgO-Coated Denuder Tubes

1. Experimental

HCl in N_2 was provided from a cylinder with concentration of 30.4 ± 1.1 ppm determined using midget impinger collection in 0.01N NaOH. Employing a mass flow controller, stainless steel fittings and the shortest possible lengths of Teflon tubing, the HCl was diluted with filtered room air for a total flow of 1.0 Lpm, and HCl concentration of 0.30 ppm ($442 \mu\text{g}/\text{m}^3$). HCl penetration through the denuder tube was measured by sampling with two midget impingers in series, each containing 0.01M NaOH with negligible Cl^- blank. The impinger solutions were analyzed for Cl^- by ion chromatography.

The flow rate through the denuder tube, 1 Lpm compares to a total flow of 20 Lpm through 24 tubes in parallel in atmospheric sampling. Accordingly, residence time within the sampling tube in the present experiment was 25% shorter than in atmospheric sampling. Thus, retention efficiencies for and HCl are considered lower limits to those expected in atmospheric sampling.

2. Results

Results for HCl retention on a single denuder tube are given Table 23, indicating an efficiency of about 94% at a cumulative dosage of up to 3.4 mg (as Cl^-). Assuming $10 \mu\text{g}/\text{m}^3$ to represent an upper limit concentration expected for ambient air, the calculated capacity of the denuder for HCl at this level exceeds 286 days of sampling (in the absence of other strong acid gases).

C. HCl Retention on Nylon and Carbonate-Impregnated Filters

1. Introduction

Results from the NSMCS (22) suggested at least partial retention of atmospheric HCl on Nylon filters. Chloride values on the Nylon filters from the total fine NO_3^- samplers were higher than those on the fine particulate NO_3^- sampler. The difference in Cl^- results between the paired samplers would be a measure of atmospheric HCl if 1) Nylon filters retained HCl efficiently, 2) the MgO acid gas denuder removed HCl efficiently, and 3) gaseous chloride was equivalent to HCl.

Table 23. Capacity of an MgO Denuder Tube for HCl^a

Date	Total HCl Dosage (μg as Cl^-)	Equiv. No. Days _b at $10 \mu\text{g}/\text{m}^3$	MgO Denuder Efficiency (%)
7/10/86	397	33	91.9
7/14/86	2226	186	91.0
7/15/86	2862	239	96.4
7/16/86	3426	286	96.4
			Mean: 93.9 ± 2.9

a. Sampling conditions: 1.0 Lpm
 4 mm I.D. tube coated for 30 cm
 $441 \pm 16 \mu\text{g}/\text{m}^3$ HCl (as Cl^-)
 room temperature

b. Calculated for a 24-tube denuder sampling at 20 Lpm.

2. Experimental

To assess the efficiency of Nylon filters at a face velocity equal to that used in NO_3^- sampling, cylinder HCl in N_2 was introduced into purified room air ahead of two Nylon filters in series. Air purification consisted of passage through H_3PO_4 -coated glass wool (to remove NH_3), an NaCl-impregnated Whatman 41 filter to remove HNO_3 and a glass fiber filter to exclude acidic gases plus particles. The total flow through the 47 mm Nylon filters, (20 Lpm) provided a face velocity equal to that used in NO_3^- sampling. Gelman Nylasorb (Batch 871) filters were evaluated.

3. Results and Conclusions

For HCl dosages of 100-200 μg (as Cl^-), Gelman Nylasorb (Batch 871) filters showed an efficiency of $88 \pm 1.7\%$ ($n=4$) (Table 24). These results are based on a comparison of the Cl⁻ recovered from a Gelman Nylasorb (Batch 871) filter and the calculated dosage. Using the estimation technique of Smith, as described in the Table, an HCl collection efficiency of $82 \pm 22\%$ is calculated.

We conclude that chloride results from the NSMCS should have yielded estimates of HCl concentration which are accurate within 20%, assuming complete removal of HCl with the MgO denuder.

The efficiency of HCl retention on 47 mm Whatman 41 filters impregnated with 0.8 ml of 5%w Na_2CO_3 solution ($\text{CO}_3/\text{W41}$), was assessed, after drying, employing the same experimental procedures used for Nylon filters. Table 25 lists results for two trials plus a blank trial; the efficiency was $95 \pm 6.7\%$ based on total HCl dosage, and 99.9% based on the method of Smith.

Table 24. Efficiency of Gelman Nylasorb Filters for HCl^a

Trial	HCl Dosage ^b ($\mu\text{g Cl}^-$)	Nylon Prefilter ^c ($\mu\text{g Cl}^-$)	Nylon Afterfilter ^c ($\mu\text{g Cl}^-$)	Prefilter Collection Efficiency (%)	
				Basis Dosage	Basis Smith ^d
1	102	89.5	2.5	88.0	97
2	181	156	35.5	86.2	77.1
3	203	183	87.5	90.0	52.4
4	122	106	-5	86.9	100

a. Sampling conditions: Total flow rate 20 Lpm
 T = 20-24°C
 R.H. = 55-60%
 47 mm filters

b. Based on cylinder concentration measured by two midjet impingers in series with standard IC eluent as trapping medium. Found 29.6 ppm (42,876 $\mu\text{g}/\text{m}^3$).

c. Results corrected for mean Cl^- filter blank, $8.5 \pm 1.6 \mu\text{g}$.

d. The procedure of J.R. Smith (J. Air Pollution Cont. Assoc. 29:969-970 (1979)), provides an estimate of the overall efficiency of the two filters in series:

$$x_{12} = 2/y - 1/2$$

where x_{12} = overall efficiency expressed as a fraction.

y = ratio of the first sampler catch to the total retained by the two samplers combined.

From x_{12} , the total recovered Cl^- and the amount recovered from the prefilter, the prefilter efficiency can be estimated.

Table 25. Efficiency of Na₂CO₃-Impregnated Filters for HCl^a

Trial	HCl ^b Dosage ($\mu\text{g Cl}^-$)	CO ₃ ⁼ Prefilter ^c ($\mu\text{g Cl}^-$)	CO ₃ ⁼ Afterfilter ^c ($\mu\text{g Cl}^-$)	Prefilter Collection Efficiency (%)	
				Basis Dosage	Basis Smith ^e
1	1044	945	29	90.5	99.9
2	840	891	3	100	100
3 ^d	0	44	1	-	-

a. Conditions: 47 mm filters
20 Lpm
60 ± 5% R.H.
Room Temperature

b. Based on an apparent cylinder concentration of 43.6 ± 4.0 ppm (63,155 $\mu\text{g}/\text{m}^3$) measured by the total recovered Cl⁻ from trials 1 and 2. The higher measured cylinder concentration compared to that reported in Table 24 may reflect transfer of Cl⁻ (probably as HCl) from the NaCl prefilter used in scrubbing ambient air. The estimation by the technique of Smith is, therefore, probably more reliable compared to that based on the calculated dosage.

c. Corrected for mean Cl⁻ blank, 2 ± 0 $\mu\text{g}/\text{filter}$.

d. Sampled filtered room air about 16 hours. Based on this value, estimate 8 and 6 $\mu\text{g Cl}^-$ found on the prefilter in trials 1 and 2, respectively, from room air.

e. See Table 24, footnote d.

IX. CONTINUOUS MONITOR FOR PARTICULATE SULFUR SPECIES

A. Description of System

A system to monitor particulate sulfur species was assembled following the design of G. Allen (23). The system is intended to provide quantitation of H_2SO_4 , the sum of $(NH_4)_2SO_4$ and NH_4HSO_4 , and non-volatile S compounds (e.g. Na_2SO_4). The concepts employed, hardware and limitations are detailed in Appendix A. At ambient temperature, a voltage representing total particulate sulfur is obtained. Heating the sample to ca. $125^\circ C$ ahead of a PbO-coated denuder allows removal of relatively volatile H_2SO_4 , but might include some normally particle-phase organic S compounds as well. A voltage decrease is observed, corresponding to the volatile S removed. Accordingly, the design employed by Allen and other investigators was modified by addition of NH_3 to the sample (ahead of the heater) to convert H_2SO_4 to $(NH_4)_2SO_4$, causing an increase in S reaching the detector (i.e. a voltage increase). With non-acidic, organic sulfur compounds volatilized at $125^\circ C$, no voltage change is expected. This change was intended to enhance the selectivity of the method for H_2SO_4 . At $300^\circ C$, both $(NH_4)_2SO_4$ and NH_4HSO_4 volatilize causing another decrease in voltage. Finally the sample is replaced by particle-free air. The corresponding further voltage decrease measures S compounds not volatilized at $300^\circ C$.

To insure adequate performance during atmospheric sampling a portable H_2SO_4 aerosol generator was constructed. The system (Figure 11), based on the design of Allen et al. (23), employed a Lovelace aerosol nebulizer (INTOX Products, Part No. 01-100) and required a dilution air flow of 10-12 Lpm. The unit was installed in a carrying case, and was designed to use ambient air provided by a compressor and a purification train.

B. System Response

The response of the sulfur monitor to H_2SO_4 is shown in Figure 12. The generator provided an H_2SO_4 aerosol which was relatively free of neutralization. The response of the S-monitor was similar to that observed by Tanner et al. (24). In these trials, at $140^\circ C$ about 10% H_2SO_4 penetrated the denuder compared with 5% achieved by Tanner et al. Thus if $140^\circ C$ was selected for H_2SO_4 analysis, the resulting H_2SO_4 would be corrected for the 10% of the acid not volatilized with the pure acid.

The optimal temperature for discrimination of sulfate species is the highest one at which loss of ammonium sulfates remains insignificant. Figure 13 shows insignificant loss of both $(NH_4)_2SO_4$ and NH_4HSO_4 aerosols at up to $145^\circ C$. As expected from other studies (23,24), these two salts respond about equally to temperature change in the range $150-300^\circ C$.

* In subsequent work the residual signal was reduced to $< 5\%$. The cause of the higher initial residual signal is unknown, but presumably reflects neutralization by NH_3 in the aerosolized solution or from the dilution air.

Figure 11.

Schematic of H₂SO₄ Aerosol Generator

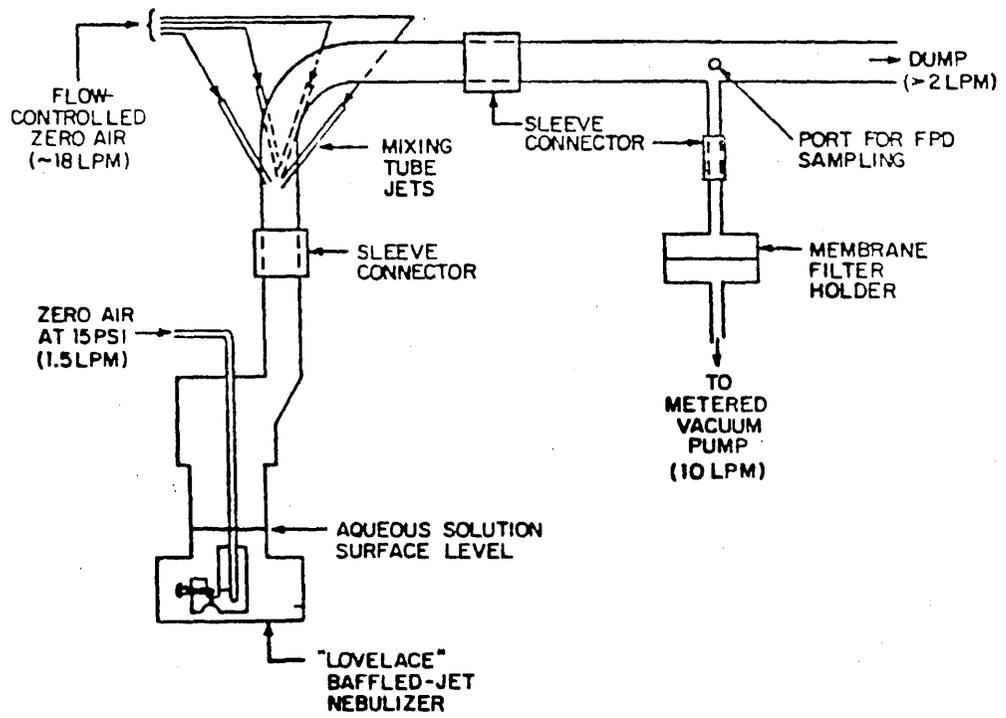


Figure 12

RESPONSE OF PARTICLE SULFUR ANALYZER TO H_2SO_4

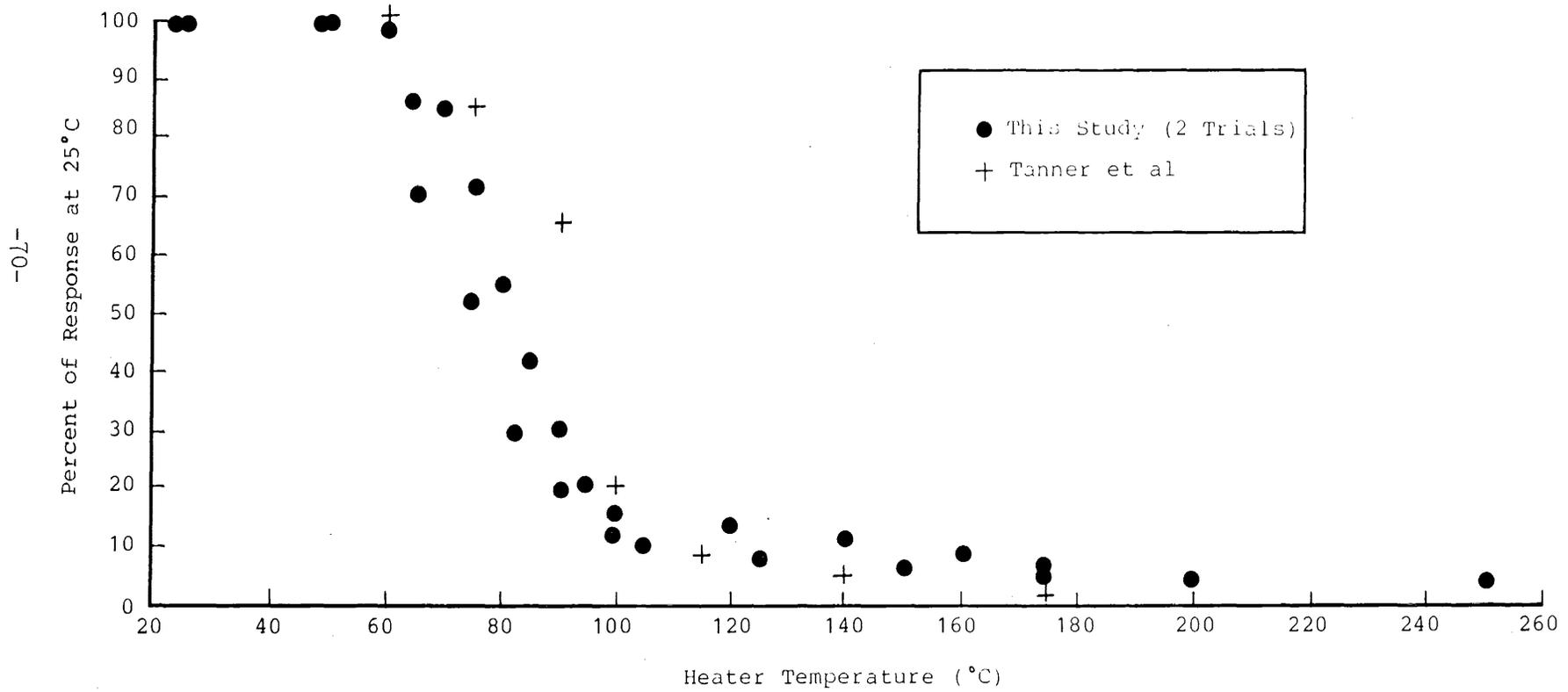
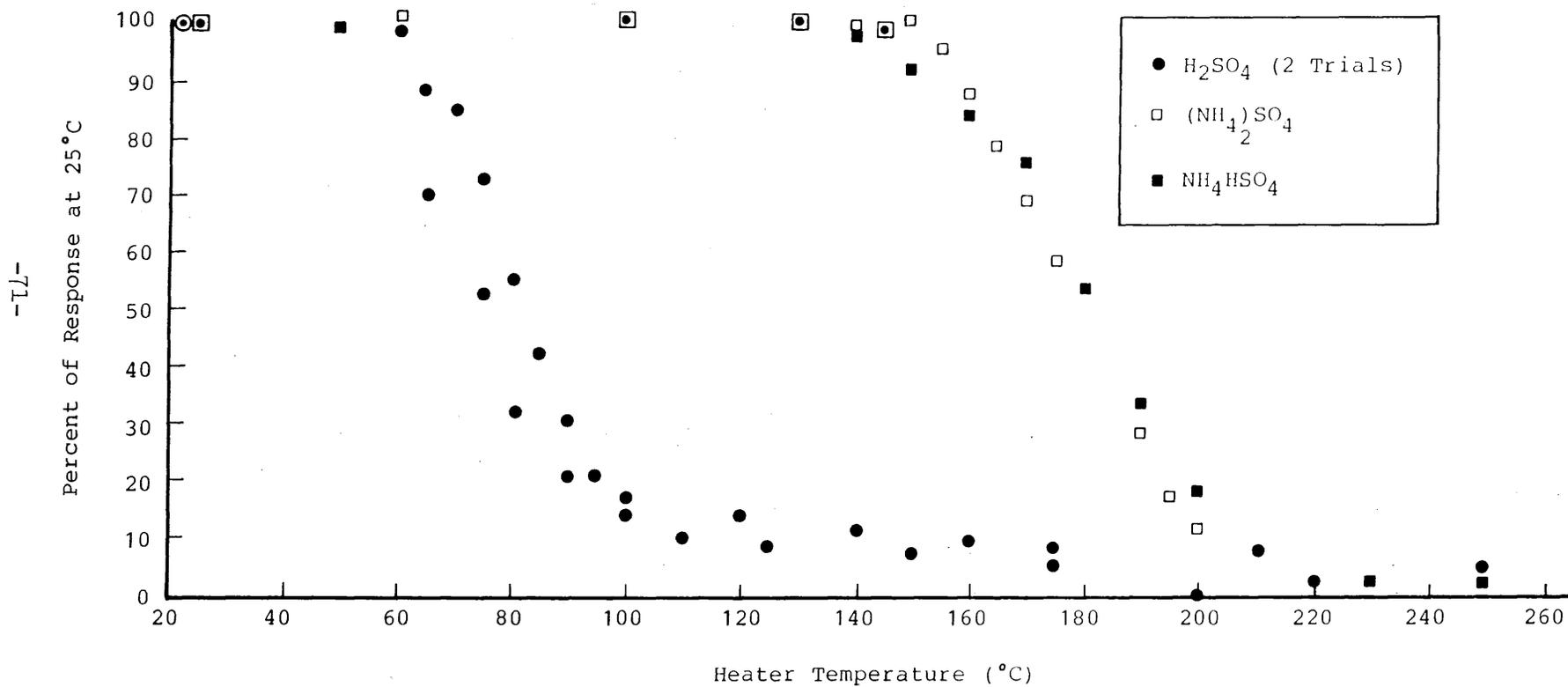


Figure 13

RESPONSE OF PARTICLE SULFUR ANALYZER TO SULFURIC ACID AND AMMONIUM SULFATES



The presence of relatively volatile sulfur species other than H_2SO_4 provides potential positive interference in measuring atmospheric H_2SO_4 . Such species include hydroxymethane sulfonates (as the sulfonic acid or sulfonate salt) (25) bis-hydroxymethyl sulfone (26), and alkylsulfonic acids (27).

A technique to improve the selectivity of the sulfur monitor for H_2SO_4 measurement was assessed, involving the addition of a second criterion for its measurement. Sulfuric acid was measured by the increase in FPD sulfur response when NH_3 was added ahead of the analyzer inlet while the heater tube was at the temperature required to efficiently volatilize H_2SO_4 . The resulting ammonium salt re-condensed causing an increase in S response.

C. Operating Program for Atmosphere Sampling

Figure 14 illustrates the temperature and operational program for a 20 minute instrument cycle. Also shown are five sections, (S(1) to S(5)). These represent the time periods over which signal averaging is done. The response of the analyzer to H_2SO_4 is shown in idealized form (i.e. square-wave responses changes). Here an S(1) voltage of 75 mV corresponds to about $35 \mu\text{g}/\text{m}^3 \text{H}_2\text{SO}_4$. Sections S(1) to S(5) are intended to provide responses following approach to steady state at the new conditions.

Based on this program the measured species are defined by the voltage changes given in Table 26. Note that both H_2SO_4 and volatile SO_4 (i.e. all S compounds volatilized at $\leq 300^\circ\text{C}$) are measured two ways. The parameter H_2SO_4 (1) is subject to positive error due to other volatile S compounds, whereas H_2SO_4 (2), the increased response following NH_3 addition, should be less subject to this error. Volatile SO_4 (1) would include organic S compounds (if present), whereas volatile SO_4 (2) excludes materials not reacting with NH_3 to produce a particle-phase material at 125°C .

D. Calibration with SO_2 and H_2SO_4 Aerosol

The TECO S monitor was calibrated with SO_2 , from a cylinder containing 3.7 ppm in N_2 (Scott certified value). The cylinder concentration was checked against an NBS certified permeation tube SO_2 source and found to have a concentration of 3.8 ppm. Using the latter value and quantitative dilutions, a log-log response curve was obtained and employed for data reduction.

$$\ln (\text{mV}) = -0.215 + 1.256 \ln (\mu\text{g}/\text{m}^3 \text{SO}_4)$$

This was rearranged to provide the equation:

$$\text{SO}_4 (\mu\text{g}/\text{m}^3) = 1.22 [\text{EXP} (0.796 \text{Ln} (\text{mV}))]$$

FIGURE 14. Idealized Response of S Monitor to about $35 \mu\text{g}/\text{m}^3 \text{H}_2\text{SO}_4$

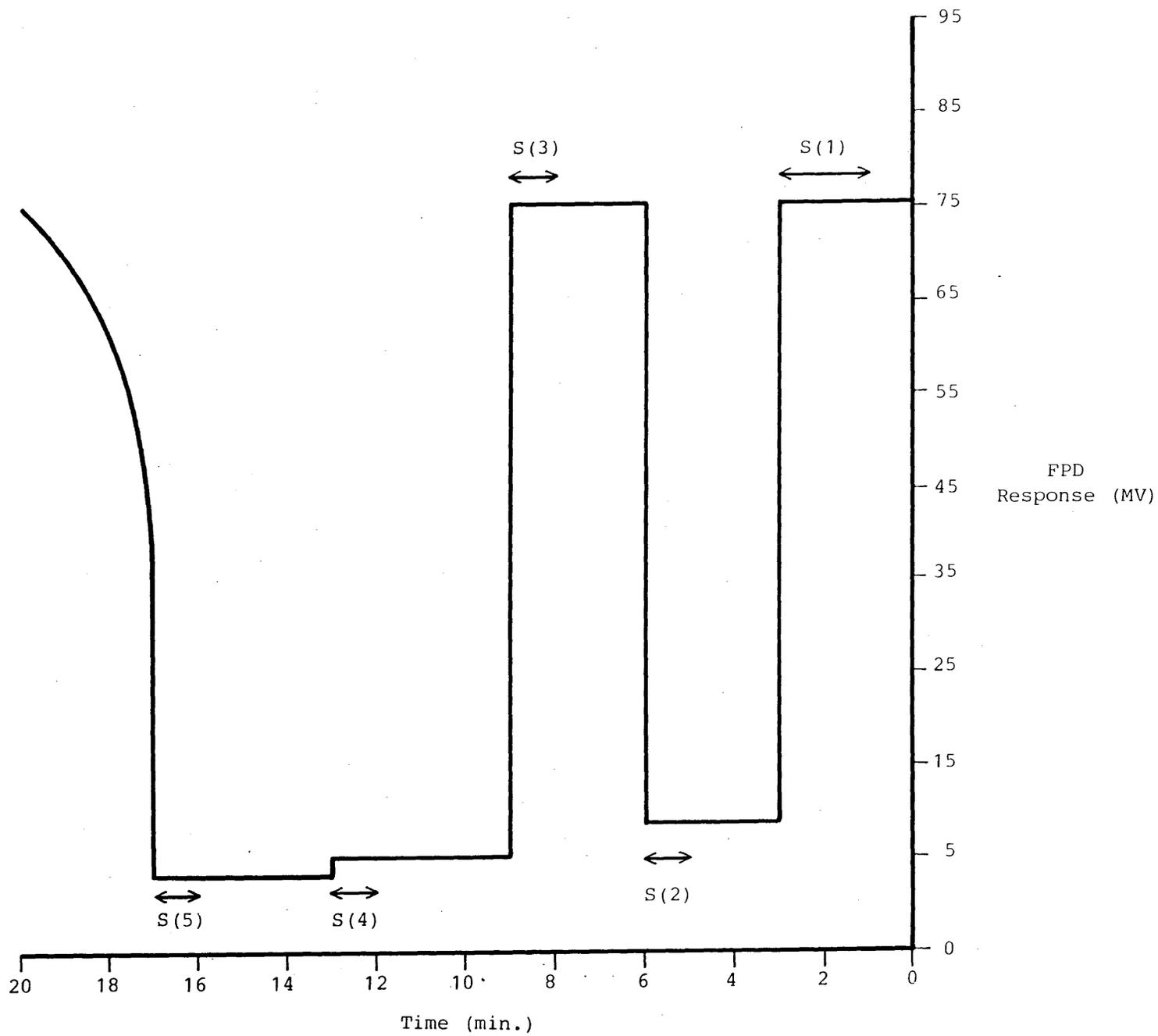


TABLE 26. Scheme for Analysis of S Monitor Response

<u>Parameter</u>	<u>Equation</u>
H_2SO_4 (1)	S (1) - S (2)
H_2SO_4 (2)	S (3) - S (2)
Volatile $SO_4^{=}$ (1)	S (1) - S (4)
Volatile $SO_4^{=}$ (2)	S (3) - S (4)
$NH_4H_xSO_4^a$	Volatile $SO_4^{=}$ (1) - H_2SO_4 (1)
MSO_4^b	S (4) - S (5)

a. The sum of $(NH_4)_2SO_4$ and NH_4HSO_4 .

b. Indicates sulfates less volatile than $(NH_4)_2SO_4$ (e.g. Na_2SO_4).

To insure that the analyzer efficiently transported particulate S to the detector, the calibration of the analyzer with H₂SO₄ aerosol was compared to that with SO₂. The latter was done by sampling SO₂ directly into the S monitor (i.e. bypassing the aerosol sampling inlet, heater tube and denuder). Aerosol calibration was done introducing H₂SO₄ aerosol (0.1-0.4 μm optical diameter) through the aerosol inlet, heater and denuder tubes. For some data points at high S concentration only the maximum S signal was measured (i.e. the response at 25°C). In such cases, instrument drift may have produced some change in the zero. For other points, the net response change at 25°C vs. ca. 125°C was used. In these cases, instrument drift is no longer a significant variable. However, 5%-10% H₂SO₄ was observed to remain non-volatile at ca. 125°C. The total particulate S calibration was not corrected for this effect.

Figure 15 includes the calibration results with H₂SO₄ as well as with SO₂. The calibration with H₂SO₄ for the range 8-45 μg/m³ was linear and similar to that with SO₂ in slope and intercept.

E. Effect of Inlet Pressure on Meloy FPD Response

1. Introduction

The response of the Meloy FPD sulfur analyzer used in the particle S monitor is known to vary with atmospheric pressure. Changes in sample inlet tubing lengths are a potential source of variable inlet pressures. The change may be a simple shift in the baseline response leaving the slope unchanged, or a shift in the overall slope. The analyzer must, therefore, be calibrated under the same inlet pressure restriction conditions as during normal sampling. To evaluate the magnitude of the FPD response to reduced pressure, the analyzer's signal output was determined at two reduced inlet pressures, 0.4 and 0.9 inches H₂O vacuum.

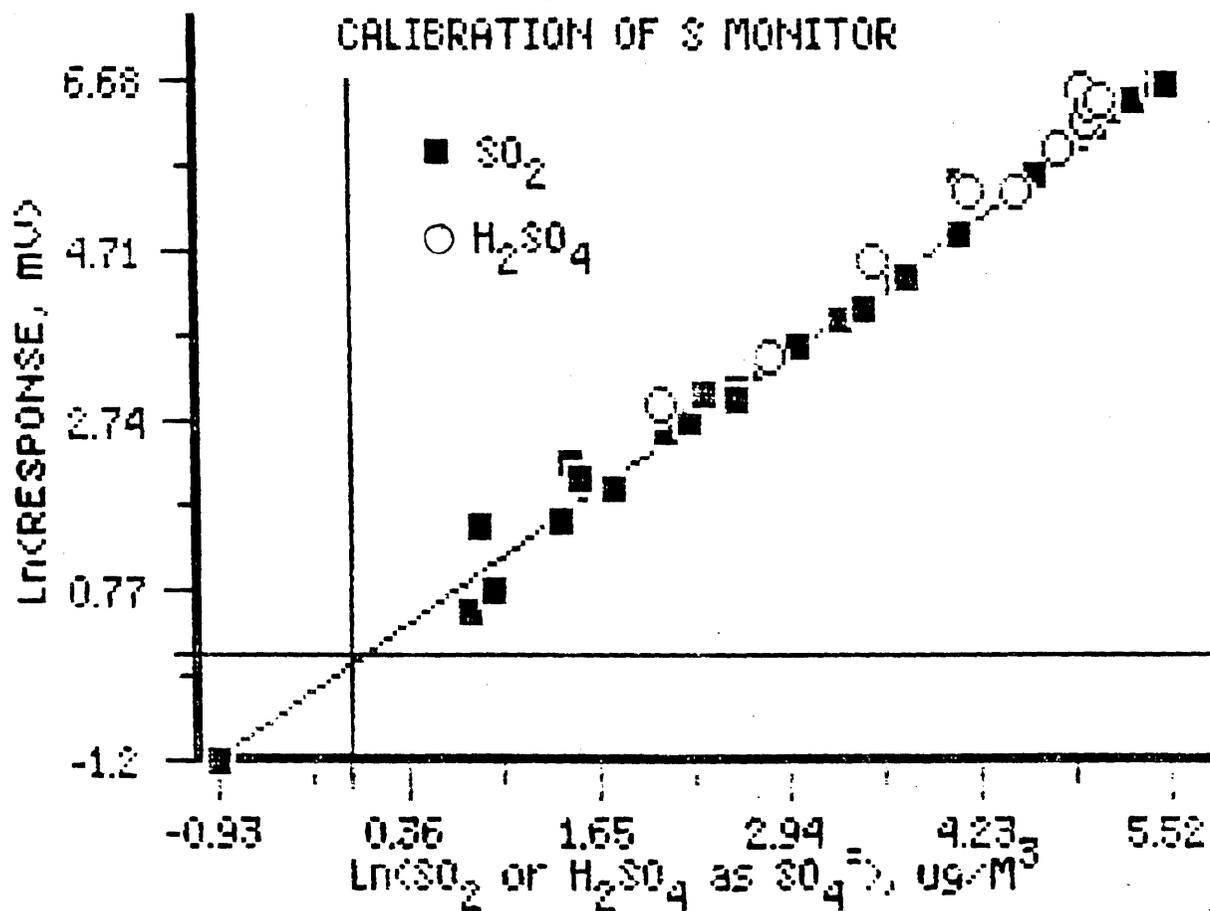
2. Experimental

The 0.4 inch H₂O vacuum was obtained by adding a 27 inch length of 0.085 inch I.D. (1/8 inch O.D.) stainless steel tubing to the analyzer sample inlet. The 0.9 inch inlet vacuum was achieved by adding an additional 20 inch section. The pressures were monitored with a 0-1 inch H₂O Magnahelic vacuum gauge attached to a Tee in the inlet line as close as possible to the analyzer detector chamber. A 0-30 inch vacuum gauge monitored the chamber pressure.

Cylinder SO₂ (3.8 ppm) was diluted with SO₂-free room air, with both flows controlled by mass flow controllers. The analyzer baseline at zero SO₂ concentration was adjusted to 0.0 mV output at each pressure.

* During atmospheric sampling the aerosol inlet was extended by about two meters to permit sampling of air surrounding our mobile laboratory. Possible loss of SO₄ in this extended line can be assessed by comparing S and filter SO₄ (Section XII A).

Figure 15.



3. Results

Figure 16 shows the FPD response to SO_2 at the two pressure conditions. The data plotted on 2 cycle log paper show that the slopes are essentially equal at both pressures, and that the change in response is due a shift in the baseline. Thus, in normal operation, once the analyzer baseline is set to coincide with zero at 0.0 SO_2 concentration, it is sufficient to reset the analyzer zero when any change in analyzer inlet configuration is made.

F. Response of Potential Interferents (Single-Components Systems)

For the ammonia addition technique to be effective, potential interferents must behave differently. Bis-hydroxymethyl sulfone is not expected to show a change upon NH_3 addition, but hydroxymethane sulfonic acid (HMSA) and other sulfonic acids should form NH_4^+ salts of possibly lower volatility.

A 1.0%w solution of HMSA was prepared from the commercially available sodium salt of the HSO_3^- -HCHO adduct by passing a 1.23%w aqueous solution of the salt through a strong acid ion exchange resin. The NH_4^+ salt was prepared by titrating a portion of the strong acid solution to neutrality with NH_4OH . Aerosols were prepared by nebulizing 0.02%w solutions.

The responses of HMSA and its NH_4^+ salt are compared to those of H_2SO_4 and the ammonium sulfate in Figure 17. The free acid HMSA does not differ substantially from H_2SO_4 in response.

The NH_4^+ salt of HMSA, while somewhat more volatile, is similar in response to the ammonium sulfates. These results do not, therefore, suggest that NH_3 addition would enhance the selectivity of the method for sulfate speciation in relation to HMSA and its salts.

To assess the effectiveness of the NH_3 addition strategy with bis-hydroxymethyl sulfone, this unstable material was synthesized by the method of Binz (28). Figure 19 shows the response of the S monitor to this material with and without NH_3 addition. Without NH_3 addition, 50% of the material was volatilized at about 50°C . With added NH_3 , this shifted to about 80°C . In both cases, however, the S monitor would volatilize at least 80% of the material at 125°C . The addition of NH_3 to the system at 125°C would have only a slight effect on this sulfone. Thus the NH_3 addition strategy would be useful in distinguishing H_2SO_4 from this sulfone.

Figure 16.

MELOY RESPONSE TO INLET PRESSURE CHANGE

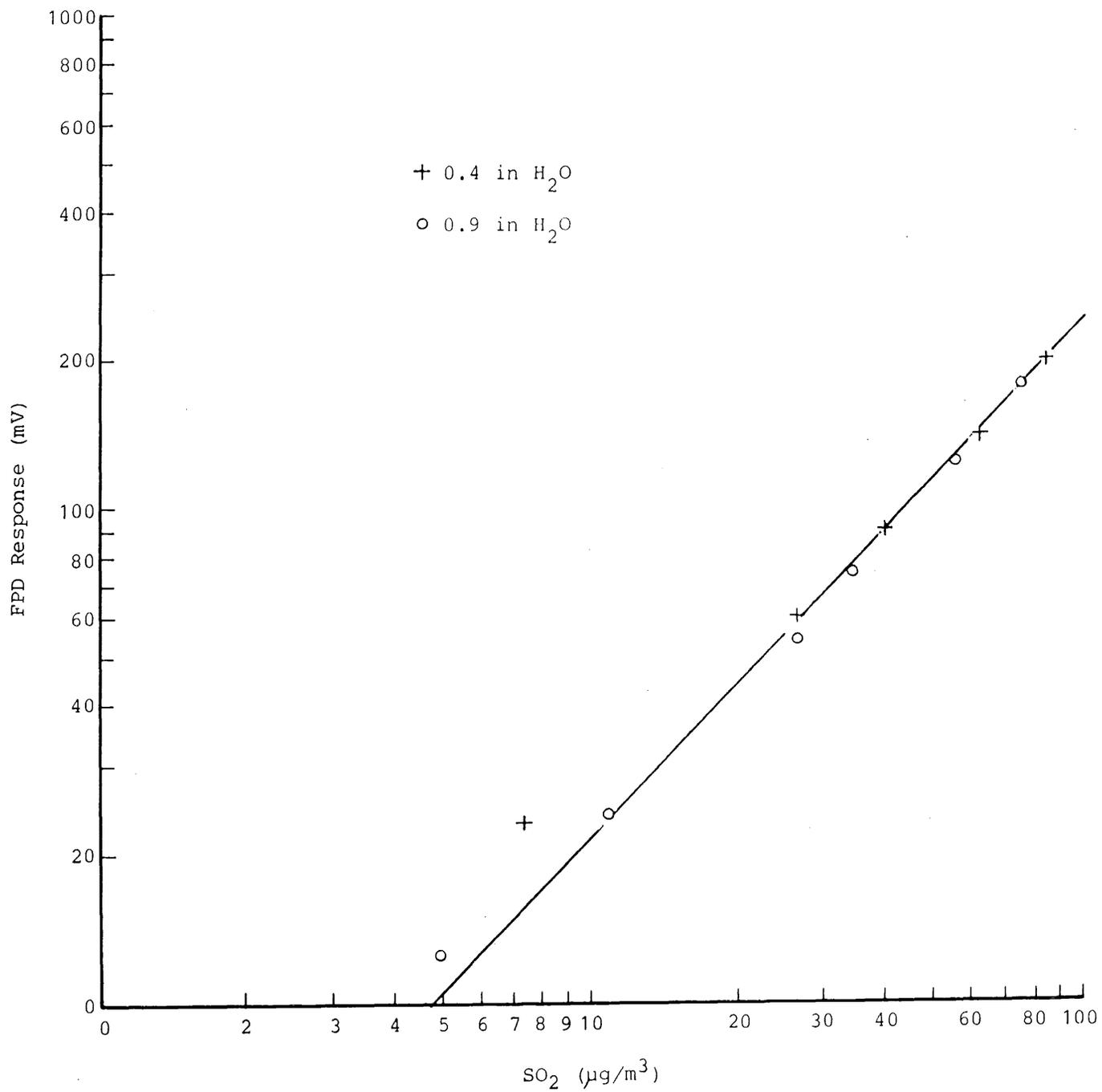


Figure 17.

RESPONSE OF PARTICLE SULFUR ANALYZER
TO SULFATE AND HYDROXYMETHANE SULFONATE SPECIES

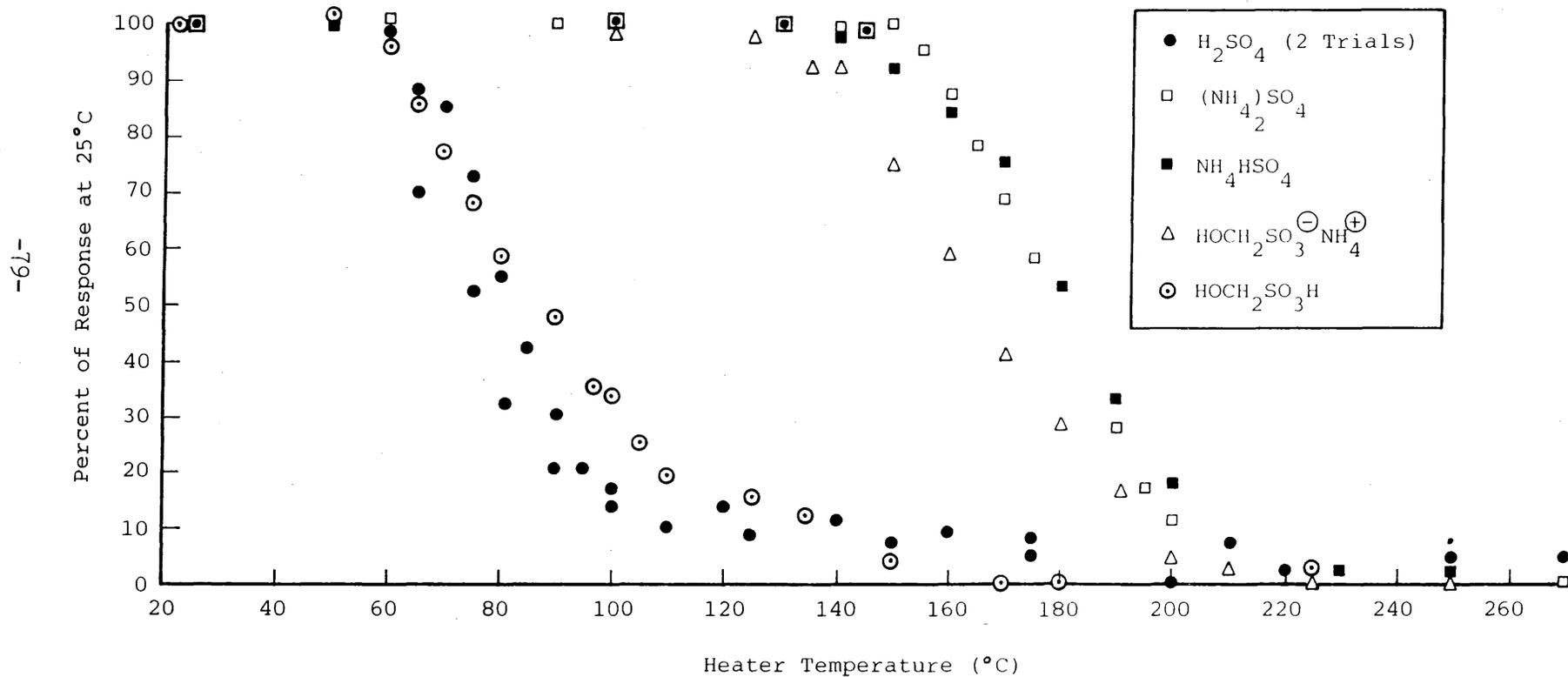
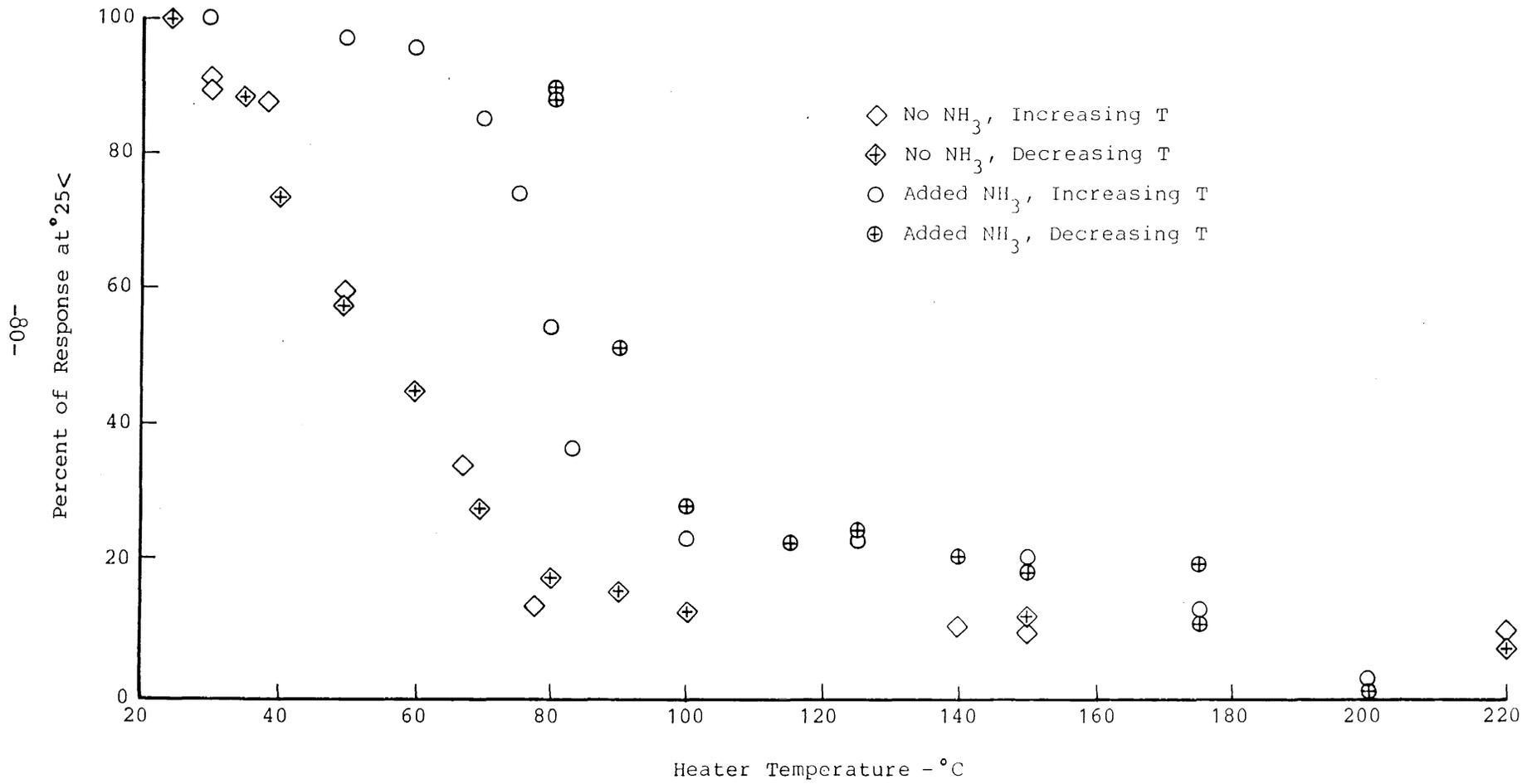


Figure 18.

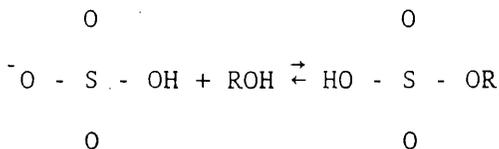
RESPONSE OF PARTICLE SULFUR ANALYZER TO BIS-HYDROXYMETHANE SULFONE



G. The Effect of Methanol Addition on Sulfur Response with NH₄HSO₄

1. Introduction

One of the major limitations of the continuous sulfur monitor is its inability to distinguish NH₄HSO₄ and (NH₄)₂SO₄. In principal, the volatility of NH₄HSO₄ could be altered by the reaction:



The resulting sulfate ester should have a vapor pressure substantially greater than that of the NH₄HSO₄. A literature search revealed insufficient data upon which to assess whether the rate of this reaction could be sufficient to permit reaction with NH₄HSO₄. Thus it was judged expedient to try the procedure.

2. Experimental

Methanol was introduced from a diffusion tube by varying the methanol temperature from room temperature to about 40°C. The vapor concentration was not assessed. Relative humidity of the system was maintained at 80% so that the expected reaction medium would be aqueous droplets containing high concentration of HSO₄⁻, SO₄²⁻ and H⁺.

Methanol (MeOH) was chosen because its high vapor pressure, relatively low toxicity and higher expected reaction rate compared to higher homologs. The reaction time was either about 10 seconds or about 100 seconds. The longer time was achieved by adding a 20 L glass vessel in line between the source of the reactants and the sulfur monitor. The flow rate through the reactant source and glass vessel, ca. 12 Lpm, provided about 100 seconds mean residence time. In addition to NH₄HSO₄, trials were also made with H₂SO₄.

3. Results

In the absence of methanol, the influence of changing the R.H. of the purified air stream with and without added H₂SO₄ aerosol was evaluated in the range between ambient (ca. 50%) and 80%. No significant effects were noted on either the zero response or with H₂SO₄.

The addition of vapor phase MeOH did not alter the response of the Meloy S monitor unless large quantities of MeOH were introduced (e.g. by adding liquid MeOH directly to the 20 L glass vessel). In that case the Meloy response was driven off scale (in a positive direction).

* The pKa of HSO₄⁻ is 1.9.

The addition of MeOH in the presence of NH_4HSO_4 or H_2SO_4 failed to alter appreciably the volatility of the sulfate compound over the range of conditions explored.

4. Conclusions

As performed, the reaction rate of MeOH and acidic sulfates is insufficient to be useful. Efforts to distinguish NH_4HSO_4 from $(\text{NH}_4)_2\text{SO}_4$ during field trials must rely on indirect means, e.g. comparison of sulfur monitor results with those for particulate H^+ and NH_4^+ concentrations.

X. RESPONSE OF THE PARTICLE S MONITOR TO EXTERNAL AEROSOL MIXTURES

A. Introduction

Airborne aerosol constituents might interfere in S compound measurements by particle-particle reaction within the sampler inlet line or the analyzer, itself, or by volatilization of the interferent followed by reaction with the sample during heating but prior to loss of vaporized S to the denuder walls. In addition, aerosols might cause interference by deposition on internal surfaces of the inlet and analyzer followed by interaction with the airborne sample. Finally, interference might be possible by altering the FPD response to the target compounds.

The interference in analysis of H_2SO_4 and ammonium sulfates due to the presence of a second, externally mixed aerosol was evaluated employing as potential interferents NH_4NO_3 , NH_4Cl , Na_2SO_4 , NH_4HSO_4 , $(NH_4)_2SO_4$ and $NaCl$.

B. Experimental

Potential interferents and H_2SO_4 were aerosolized from separate Lovelace nebulizers, and turbulently mixed immediately ahead of the monitor inlet. The calculated residence time available for reaction of the two components before entering the sampler was about 2 seconds.

To establish an interference effect, the response due to H_2SO_4 , alone, was compared to that due to the aerosol mixture as well as to that for the second component, alone. The degree of air dilution remained constant for periods with one or two aerosols; during single aerosol measurements, the second nebulizer operated with distilled water and the usual dilution air flow. The solution concentration for the second component was set equal, on a weight basis, to that of H_2SO_4 . For a survey of interferent effects, airborne particle concentrations were not measured. That for sulfur-containing aerosols could be estimated from prior calibrations, however. Based on such calibrations the estimated H_2SO_4 aerosol concentrations in two-component mixtures were in the range 100-175 $\mu g/m^3$.

To insure equal performance for the two nebulizers, the response with H_2SO_4 was measured for each by aerosolizing H_2SO_4 alternately in one generator and then the other, with H_2O in the second nebulizers. Flow parameters were then adjusted to provide equal sulfur outputs. Table 27 summarizes the system response to H_2SO_4 at the various temperature conditions after such adjustments. Table 28 shows the final operating parameters obtained for the two generators as well as the operating parameters used by the FPD sulfur analyzer.

The FPD response for at least three cycles with H_2SO_4 in generator 1 and H_2O in generator 2 was followed by trials with H_2SO_4 plus the potential interferent. The results tabulating the voltage response for each operating temperature, are given in the following tables for three or four cycles, followed by the mean response for that temperature.

Table 27. FPD Response to H_2SO_4 From Two Lovelace Nebulizers (0.024% w Solution)

Trial	Solution in Nebulizer		RESPONSE (mV)		
	1	2	25°C	130°C	300°C (zero air)
1	H_2SO_4	H_2O	450	40	20
1	H_2O	H_2SO_4	457	42	20
2	H_2SO_4	H_2O	550	40	20
2	H_2O	H_2SO_4	550	40	20
3	H_2SO_4	H_2O	640	41	20
3	H_2O	H_2SO_4	648	42	21

Table 28. Operating Parameters for Equivalent S Output from Aerosol Generators

<u>PARAMETER</u>	<u>GENERATOR 1</u>	<u>GENERATOR 2</u>	<u>MELOY FPD</u>
Nebulizer Pressure, psig	20	19	-
Dilution Air Flow, Lpm	5.1	2.1	-
Sample Inlet Pressure, in. H ₂ O	-	-	0.92

C. Results

1. NH₄Cl

In addition to particle-particle interactions, a potential gas-particle pathway is possible. Dissociation of NH₄Cl to NH₃ and HCl is expected at and above the temperature used to volatilize H₂SO₄, 125°C. A rapid reaction of H₂SO₄ with NH₃ would then produce an ammonium sulfate species, decreasing the response of H₂SO₄. However, at that temperature, removal of H₂SO₄ by the denuder wall surfaces is rapid. The PbO denuder to remove vapor phase SO_x is preceded by a tube heated at varying temperatures. During some fraction of the residence time in the heater, the gas temperature is sufficient to volatilize H₂SO₄ prior to its removal in the denuder. The species formed when H₂SO₄ is volatilized may include SO₃, H₂O and SO₂ as well as H₂SO₄. Reaction with NH₃ to produce a less volatile S species than H₂SO₄ would be a another possible source of interference.

The results in Table 29 show that the response to H₂SO₄ was substantially the same whether NH₄Cl was present or not, indicating no measurable interference.

2. NH₄NO₃

Ammonium nitrate is well known to undergo volatilization forming NH₃ and HNO₃. At 25°C, the equilibrium partial pressure of NH₃ is about 2 μg/m³, sufficient to convert 12 μg/m³ H₂SO₄ to NH₄NHSO₄. Nearly complete dissociation would be expected at 125°C. Thus substantial interference in H₂SO₄ measurement might occur by reaction in the heater tube ahead of the denuder. At 25°C, no change in the observed S response would be expected. At 125°C, the expected interference would be similar to that from NH₃ addition, although the latter has greater time for reaction. Thus the response at 125°C due to particulate S should be increased relative to that for H₂SO₄, alone.

Table 30 shows, in contrast to these expectations, a depressed response at 25°C. The data shown were obtained on two successive days. The decrease on the first day was 48% and on the second, 25%. The latter result is considered less reliable since only a single cycle of data was obtained for H₂SO₄, alone, on this day.

At 125°C, in contrast to the expected large increase in response, the small residual signal showed a further small decrease. The H₂SO₄ concentration is inferred from the difference in response at 25°C and 125°C. The apparent H₂SO₄ concentration was decreased by 50% and 27% for the two days of data.

In addition to depressing the H₂SO₄ response, a short term, full scale voltage spike was introduced which started 2-3 seconds after the program switched from 125°C to the 300°C mode and the temperature started to rise. The signal, which

Table 29. Effect of NH_4Cl Aerosol on the Response Due to H_2SO_4

Nebulizer Solution		RESPONSE - mV			
1	2	25°C	130°C	300°C	300°C (zero air)
H_2SO_4 (0.024%)	H_2O	630	36	35	34
		645	38	35	34
		<u>610</u>	<u>37</u>	<u>35</u>	<u>24</u>
		628	37	35	31
H_2SO_4	NH_4Cl	628	37	35	31
		620	41	25	23
		625	42	27	25
		635	42	32	27
		<u>664</u>	<u>38</u>	<u>30</u>	<u>24</u>
636	41	28	25		

Table 30. Effect of NH_4NO_3 Aerosol on the Response Due to H_2SO_4

Nebulizer Solution		RESPONSE - mV ^a				
		25°C	125°C	300°C	300°C (zero air)	
<u>1</u>	<u>2</u>					
H_2SO_4 (0.024%)	H_2O	659	76	2	1	
		<u>596</u>	<u>72</u>	<u>3</u>	<u>0</u>	
		Mean:	628	74	2	1
H_2SO_4 (0.024%)	NH_4NO_3 (0.020%)	283	20	2	2	
		290	33	30	20	
		330	57	24	10	
		<u>410</u>	<u>70</u>	<u>32</u>	<u>15</u>	
		Mean:	328	53	29	15
H_2SO_4 (0.024%)	NH_4NO_3 (0.020%)	415	24	10	8	
		365	19	11	8	
		464	26	13	12	
		<u>430</u>	<u>32</u>	<u>17</u>	<u>13</u>	
		Mean:	418	21	13	11
H_2SO_4 (0.024%)	H_2O	560	19	18	11	

a. In addition to the results tabulated, a short term full scale (747 mV) deflection in response was observed switching from 125°C to 300°C which peaked in 7 sec and returned to baseline in 35-37 sec.

peaked in about 7 sec. and was over in about 35-37 sec, persisted even after water was substituted for the NH_4NO_3 . Thorough washing of all tubing components of both generators carrying H_2SO_4 did not correct the problem, but it was eliminated by thorough cleaning of the S monitor burner block.

3. NH_4HSO_4

Ammonium acid sulfate was not expected to alter the response of the analyzer to H_2SO_4 . The evaluation with this salt required that the sulfate concentrations be reduced by half since the response (as total sulfates), although semilogarithmic, is not greatly different from additive in this range. Results are given in Table 31. At 25°C the average response of H_2SO_4 , alone, (185 mV) corresponded to $78 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$, using the calibration in Section D. The mean response due to NH_4HSO_4 , 250 mV, corresponded to $99 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$. The calculated total for the mixture, $177 \mu\text{g}/\text{m}^3$, compares to an observed $174 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$, based on the mean 509 mV response.

At 125°C , the response from H_2SO_4 , alone, was about 7% of that at 25°C , based on calculated $\mu\text{g}/\text{m}^3 \text{SO}_4^{=}$, whereas that for NH_4HSO_4 was unchanged. The particulate $\text{SO}_4^{=}$ measured at 125°C from the mixture, $93 \mu\text{g}/\text{m}^3$, compares to the value $104 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$ from the combined responses of the individual components. The results indicate essentially no interference in H_2SO_4 measurement from NH_4HSO_4 aerosol.

4. $(\text{NH}_4)_2\text{SO}_4$

Ammonium sulfate could serve as an interferent in H_2SO_4 measurement if particle-particle reaction were significant. This would produce NH_4HSO_4 , either airborne or following initial deposition of one component on an interior surface. Experimental results are shown in Table 32.

At 25°C the average response of H_2SO_4 (410 mV) corresponded to $147 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$ using the calibration given in Section D. The mean response due to $(\text{NH}_4)_2\text{SO}_4$, 344 mV, corresponded to $127 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$. The calculated total for the mixture, $274 \mu\text{g}/\text{m}^3$, compared to an observed $237 \mu\text{g}/\text{m}^3$, based on the mean 750 mV response at 25°C .

At 125°C , the H_2SO_4 response was much higher than usually observed, perhaps reflecting partial neutralization by contaminants in the system. The response due to $(\text{NH}_4)_2\text{SO}_4$ was unchanged from that at 25°C , as expected. The observed response from the mixture (563 mV) corresponded to $189 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$, suggesting that about 40% neutralization of H_2SO_4 had occurred.

Further evidence of neutralization of H_2SO_4 as well as wall losses of H_2SO_4 is indicated by the lower H_2SO_4 response at 25°C and higher response at 125°C in the single component H_2SO_4 trials following those for the mixture.

Table 31. Effect of NH_4HSO_4 Aerosol on the Response Due to H_2SO_4

Nebulizer Solution		RESPONSE - mV			
1	2	25°C	125°C	300°C	300°C (zero air)
H_2SO_4 (0.013%)	H_2O	220	5	6	3
		175	5	6	3
		<u>162</u>	<u>9</u>	<u>6</u>	<u>4</u>
		Mean: 185	6	6	3
H_2SO_4 (0.013%)	NH_4HSO_4 (0.012%)	510	250	10	7
		518	228	10	3
		<u>498</u>	<u>220</u>	<u>10</u>	<u>3</u>
		Mean: 509	232	10	4
H_2O	NH_4HSO_4 (0.012%)	258	260	14	4
		245	238	15	5
		<u>248</u>	<u>249</u>	<u>17</u>	<u>9</u>
		Mean: 250	249	15	6

Table 32. Effect of $(\text{NH}_4)_2\text{SO}_4$ Aerosol on the Response Due to H_2SO_4

Nebulizer Solution		RESPONSE - mV			
1	2	25°C	125°C	300°C	300°C (zero air)
H_2SO_4 (0.013%)	H_2O	365	70	55	50
		430	75	60	52
		<u>435</u>	<u>77</u>	<u>66</u>	<u>58</u>
		Mean: 410	74	60	53
H_2O	$(\text{NH}_4)_2\text{SO}_4$ (0.013%)	315	315	67	62
		325	325	65	60
		340	340	63	60
		360	360	65	60
		<u>380</u>	<u>380</u>	<u>63</u>	<u>60</u>
Mean: 344	344	65	60		
H_2SO_4 (0.013%)	$(\text{NH}_4)_2\text{SO}_4$ (0.013%)	732	518	95	88
		738	577	96	90
		<u>781</u>	<u>595</u>	<u>96</u>	<u>93</u>
		Mean: 750	563	95	90
H_2SO_4 (0.013%)	H_2O	207	98	63	60
		210	90	60	60
		228	93	60	60
		<u>250</u>	<u>95</u>	<u>60</u>	<u>60</u>
		Mean: 224	94	60	60

The present data suggest both a loss of $\text{SO}_4^{=}$ from H_2SO_4 by reaction on interior surfaces as well as partial neutralization of airborne H_2SO_4 . Further work with this salt is justified.

5. NaCl

Whether by airborne particle-particle interaction, or collision after depositing on interior walls, a $\text{NaCl-H}_2\text{SO}_4\text{-H}_2\text{O}$ system would result in substantial loss of H^+ as HCl , a process strongly favored thermodynamically (29). Table 33 shows that NaCl aerosol had no significant influence on the response of the S monitor to H_2SO_4 .

6. Na_2SO_4

Sodium sulfate was expected to interact with H_2SO_4 similarly to $(\text{NH}_4)_2\text{SO}_4$. However, the expected behavior of the acidic salt, NaHSO_4 , is unclear since decomposition may occur. The metal $\text{SO}_4^{=}$, Na_2SO_4 should not volatilize at up to 300°C . Thus, with only Na_2SO_4 aerosol, one would expect constant response at all three temperature conditions and no response with zero air. As indicated in Table 34, in the absence of H_2SO_4 , a substantial signal (56%) remained with zero air, corresponding to 63% of the measured $\text{SO}_4^{=}$; in the runs with the mixed aerosol, 41% of the signal attributable to Na_2SO_4 aerosol remained. These results are consistent with deposition of a portion of the total sulfate on the walls of the analyzer, with some re-intrainment of sulfate into the sample stream. The pattern of response to H_2SO_4 appeared normal, even immediately after exposure to Na_2SO_4 , but the response was about half that expected. This suggests loss to the walls ahead of the analyzer. The H_2SO_4 solution concentration had to be doubled, from 0.013% to 0.024%, to obtain a response similar to that obtained initially. Moreover, exposing the system to high H_2SO_4 solutions to restore full response provided only temporary improvement.

The influence of Na_2SO_4 is not straight-forward. The concentration of H_2SO_4 is measured by the decrease in response at 125°C relative to 25°C . On this basis the measured H_2SO_4 showed no decrease with the mixed aerosol. However the response of the analyzer to H_2SO_4 in subsequent single-component trials was sharply depressed. Obviously contamination of the analyzer walls was substantial. Further work is needed with this salt, especially at realistic concentrations, to assess its influence.

D. Conclusions

The interference studies with dual aerosols reveal that NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ significantly depress the measured H_2SO_4 . Species showing little or no interference in H_2SO_4 measurement were NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . The behavior of Na_2SO_4 was too complex to permit conclusions.

Table 33. Effect of NaCl Aerosol on the Response Due to H₂SO₄

Solution in Nebulizer		RESPONSE - mV			
1	2	25°C	130°C	300°C	300°C (zero air)
H ₂ SO ₄ ^a (0.072%)	H ₂ O	310	3.0	2.5	1.5
		310	3.5	3.0	1.5
		<u>380</u>	<u>3.5</u>	<u>3.0</u>	-
		Mean: 333	3.5	3.5	1.5
H ₂ SO ₄ ^a (0.072%)	NaCl (0.072%)	365	6.0	6.0	2.0
		330	5.0	5.0	2.0
		305	5.5	5.5	2.0
		<u>300</u>	<u>6.5</u>	<u>1.0</u>	<u>0.5</u>
		Mean: 325	6.0	5.4	2.0
H ₂ SO ₄ ^a (0.072%)	H ₂ O	245	1.2	1.2	1.0
		<u>270</u>	<u>2.0</u>	<u>1.2</u>	<u>1.0</u>
		Mean: 258	1.5	1.2	1.0

a. The higher H₂SO₄ concentration, relative to those in Tables 27-32, was employed because of a change in the aerosol nebulizers. The jets were changed yielding about a 3-fold decrease in aerosol S output.

Table 34. Effect of Na₂SO₄ Aerosol on the Response Due to H₂SO₄

Nebulizer Solution		RESPONSE - mV			
1	2	25°C	125°C	300°C	300°C (zero air)
H ₂ O	Na ₂ SO ₄ (0.013%)	468	480	488	265
		487	487	486	270
		<u>518</u>	<u>514</u>	<u>514</u>	<u>290</u>
		Mean: 491	494	496	275
H ₂ SO ₄ (0.013%)	H ₂ O	322	32	5	3
		355	35	10	5
		<u>377</u>	<u>37</u>	<u>10</u>	<u>7</u>
		Mean: 351	37	8	5
H ₂ SO ₄ (0.013%)	Na ₂ SO ₄ (0.013%)	703	330	327	190
		688	327	334	210
		<u>649</u>	<u>318</u>	<u>308</u>	<u>205</u>
		Mean: 680	325	323	202
H ₂ SO ₄ (0.024%)	H ₂ O	325	33	13	12
		<u>350</u>	<u>33</u>	<u>17</u>	<u>15</u>
		Mean: 338	33	15	14

XI. PROCEDURES FOR ATMOSPHERIC SAMPLING AND QUALITY ASSURANCE STUDIES

A. Sampling Design

Atmospheric sampling was done for five days at El Camino College in Torrance, CA, in September 1986. The sampling design is shown in Table 35. The emphasis was on validating the sulfur monitor as follows:

- (1) Comparison of measured sulfur (as sulfate) with co-collected, fine particle sulfate on Teflon and quartz filters.
- (2) Comparison of H_2SO_4 acid events, as indicated by the sulfur monitor, with strong particulate acidity measurements by titration of filter-collected particulate samples.
- (3) Measurement of potential interferents in the sulfur monitor by analysis of total S (IV) and SO_3^- in co-collected filter samples.

The nature of the particulate acid species was assessed by measuring total acidity (titration to $pH = 7.0$), and strong acidity estimated from the pH of an aqueous extract. These measurements were supplemented by simultaneous measurements of NH_4^+ and SO_4^{2-} . In addition, evidence for sorption of HNO_3 and strong particle acidity was sought. For this purpose HNO_3 was measured by the denuder difference method (DDM). Hydrochloric acid was also measured by the DDM to provide a more complete description of the gaseous strong acids. Ammonia data were obtained to aid in rationalizing the time dependence of strong particulate acidity.

B. Analytical Strategy for Atmospheric Particulate Sulfur (IV) and Organo-Sulfur Species

Working under a synthetic air atmosphere, six 47 mm discs were removed from each 8" x 10" quartz filter sample immediately following sampling. Two discs were cut up and immersed in 10 ml 0.1% formaldehyde solution to complex and stabilize sulfite (SO_3^-) from air oxidation. On return to the laboratory this extract was analyzed directly by IC for the bisulfite-formaldehyde adduct. The second and third pairs of discs were cut up and transferred to plastic screwcap test tubes and stored in the dark over dry ice to retard oxidation. On return to the lab, the second pair of discs was extracted in aqueous MnO_4^- , to convert non-sulfate S compounds to SO_4^{2-} . The difference in SO_4^{2-} between the MnO_4^- extract (disc pair 2) and an aqueous extract (disc pair 3) is a lower limit measure of non-sulfate S, some of which might serve as an interferent in measuring H_2SO_4 and/or $NH_4HSO_4 + (NH_4)_2SO_4$ with the semi-continuous monitor.

C. Recovery of Sulfuric Acid Aerosol from Filter Samples

Previous studies (30) assessed recoveries of H_2SO_4 aerosol from initially clean and atmospheric particulate-preloaded filters. A brief recovery experiment was done to insure the adequacy of current procedures and sampling media prior to initiating atmospheric sampling.

Table 35. Plan for Atmospheric Sampling at El Camino College, September 1986

Sampler No.	Sampler	Collection Medium	Flow Rate, Lpm	Samples/day (Collection time, Hr)	Species Measured
1	Semi-Real Time S Monitor	-	0.6	72	H_2SO_4 , $(NH_4)_x H_2SO_4^y$, non-volatile S
2	Cyclone, H_3PO_3 denuder, Teflon filter	2 μm pore Zefluor	28	5 (4 or 8)	H^+ , $SO_4^{=}$
3	Cyclone, MgO denuder, Nylon filter	Sartorius Nylon, 0.65 μm pore	20	5 (4 or 8)	Fine partic. NO_3^- , Cl^- , $SO_4^{=}$
4	Cyclone, Nylon filter	same as 3	20	5 (4 or 8)	Total fine NO_3^- , Cl^- (HNO_3 , HCl by difference)
5	Cyclone and Hi-Vol	acid washed quartz ^a	40 cfm	5 (4 or 8)	$SO_3^{=}$, $SO_4^{=}$ and H^+ w/ and w/o oxidation for total S (IV)
6	NH_3 denuder	OA-GL ^b	1.5	2 (12)	NH_3 as NH_4^+
7	NH_3 by dual filter	Teflon prefilter, OA-GL/quartz after-filter	25	5 (4 or 8)	particulate NH_4^+ NH_3 as NH_4^+
	TECO 43	-		continuous	SO_2
	DASIBI	-		continuous	Ozone
	EG & G R.H., T Monitor	-		continuous	R.H., T
	Meteorological Unit	-		continuous	Wind speed and direction

a. Pallflex 2500 QAO.

b. OA-GL = oxalic acid-glycerol, two 47 mm impregnated quartz filters contained in the same after-filter section of a dual filter holder.

Recovery of H_2SO_4 aerosol was assessed by loading blank 47 mm acid-washed quartz fiber and Teflon (Zefluor) filters with H_2SO_4 , immediately cutting up and transferring the filters to screw-capped polystyrene test tubes in a synthetic air (i.e. NH_3 -free) atmosphere, extraction in 10 mL glass-distilled water, pH measurement and microtitration for H^+ of an N_2 -flushed aliquot and ion chromatographic analysis for SO_4^- . With quartz filters, extractions were by 1-hour mechanical shaking at room temperature. With Zefluor filters, such shaking was followed by 1-hour agitation on a Fisher RotoRack at room temperature.

Table 36 summarizes the H_2SO_4 loadings measured by IC and the recovered H^+ . The recovery from acid-washed quartz filters, $84 \pm 13\%$, compares to $94 \pm 6\%$ previously found (30). The recovery with Zefluor filters, $74 \pm 7\%$, compares to $88 \pm 8\%$ previously found with polyolefin-backed Teflon filters. The lower mean recovery with the present quartz filters is probably not significant. However, the Zefluor results appear to be consistently lower than those with the previously-used Teflon filters.

D. Measurement of Particle-Phase Non-Sulfate Sulfur

1. Introduction

Section IX F demonstrated interference in the H_2SO_4 measurement with the semi-real time sulfur monitor from the HCHO adduct of SO_2 , hydroxymethanesulfonic acid. To discriminate between such species and H_2SO_4 , an analytical strategy was evaluated to measure non-sulfate sulfur. Silver oxide has been used to oxidize bis-hydroxymethane sulfone to SO_4^- , with IC analysis before and after oxidation, to assess the total concentration of this and possibly other non-sulfate sulfur species in atmospheric particulate matter (31). For the present study, a series of semi-quantitative experiments were performed to compare three oxidizers for this purpose: Ag_2O , KMnO_4 and H_2O_2 .

2. Experimental

A series of sulfur compounds was selected to represent a range of structural types. A quantity of the compound which would produce $20 \mu\text{g SO}_4^-$, with complete conversion, was oxidized in alkaline solutions containing each oxidizer, heating for 10 min at 90°C .

3. Results

Results are shown in Table 37 suggesting that 1) many organosulfur compounds are difficult to oxidize to sulfate, and 2) that Ag_2O is inferior to MnO_4^- for this purpose. Accordingly, MnO_4^- oxidation was employed in the present atmospheric trials.

* $1 \mu\text{m}$ pore size Fluoropore filters (Millipore Corp.)

Table 36. Recovery of H₂SO₄ Aerosol from Blank Filters

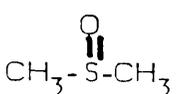
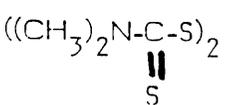
Filter Type	Sample No.	H ₂ SO ₄ Loading μg as SO ₄ ⁼ = b	H ₂ SO ₄ by H ⁺ Titration = μg as SO ₄ ⁼	Recovery %	Mean Recovery %
Pallflex Quartz 2500 QAO ^a	QAO-9	38	42	90.5	84.3 ± 13
	QAO-10	42	39	92.9	
	QAO-11	95	66	69.5	
Gelman Zefluor 2 μm pore size	Z2-1	29	23	79.3	73.9 ± 6.9
	Z2-2	47	32	76.2	
	Z2-3	56	37	66.1	

a. Pre-washed with H₃PO₄ as detailed by Tanner et al. (See Reference 30.)
For 5, 47 mm discs from the same 8" x 10 " sheet, residual PO₄⁼ = 32.6 ± 1.8 μg per disc.

b. Based on ion chromatographic analysis for SO₄⁼.
Filter blank corrections:

Quartz = 9.5 ± 6.4 μg SO₄⁼ per 47 mm filter (n=2)
Zefluor = 1 ± 0 μg SO₄⁼ per 47 mm filter (n=2)

Table 37. Efficiency of Oxidation of Sulfur Compounds (% Conversion)

Compound	Heat Only		Ag ₂ O		MnO ₄ ⁻		H ₂ O ₂	
	SO ₄ ⁼	SO ₃ ⁼	SO ₄ ⁼	SO ₃ ⁼	SO ₄ ⁼	SO ₃ ⁼	SO ₄ ⁼	SO ₃ ⁼
S ₂ O ₃ ⁼	-	-	ca.50		100		100	
S ₂ O ₄ ⁼	20	35	80		100		100	
S ₂ O ₅ ⁼	40	55	90		100		100	
HOCH ₂ -SO ₃ H	-	-	90		100		65	35
			0		100		88	
NH ₂ SO ₃ H	-	-	< 1		5		< 1	
	-	-	0	0	4	0	0	0
	-	-	65		75		50	
	-	-	trace		23		9	
			trace	0	7	0	6	0

E. Precision of Strong Acid Measurements

Following about two months storage at 5°C, three quartz fiber filter samples and two filter blanks were re-analyzed for strong acid. The results indicated a sharp decrease in strong acid. The slope of the titration curve in the first determinations suggested organic acids as the principal contributor to total acidity. In the samples repeated after two months, the slope of the titration curve had altered dramatically and was now similar to that for a mineral acid (e.g. HSO_4^-). These results suggest the loss of strongly acidic organic acids by bacterial action or other chemical change during storage.

XII. ATMOSPHERIC RESULTS

A. Continuous Sulfur Monitor

1. General Description of Results

During the five days for which the S monitor was operated, S response ranged up to $12 \mu\text{g}/\text{m}^3$ (as sulfate), with the analyzer exhibiting a limit of detection of about $1 \mu\text{g}/\text{m}^3$. There was no evidence of atmospheric sulfuric acid or other particulate S compound of similar volatility. Relatively large decreases in S response accompanied the increase in temperature from 125 degrees to 300 degrees, consistent with the presence of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 as the predominant S species. Efforts to measure non-volatile sulfur compounds were hampered by the sensitivity of the monitor to pressure changes as small as 0.01 inch H_2O . The change from ambient air to filtered (zero particulate S) air caused a slight pressure change (0.01 - 0.02 in H_2O) which resulted in a response change. This masked the change due to a real decrease in S reaching the detector if such S compounds were present in the unfiltered sample air. Manual reduction of stripchart results was employed. Field calibration of the unit with SO_2 as well the response of the unit to sulfuric acid aerosol from a portable aerosol generator showed results similar to those in laboratory trials.

2. Comparison of Particulate S Monitor and Filter Sulfate Results

Because S volatilized at 125°C was absent, sulfate was measured by the response change between the system at 300°C and at 25 to 125°C . Atmospheric particulate S remained $< 2 \mu\text{g}/\text{m}^3$ (as sulfate) until the final 24-hour period. Figure 19 and Table 38 report one hour average S results, as sulfate for this period. A pronounced diurnal maximum around 0800 hours was observed on 9/30/86. Figure 19 also shows 1-hr average SO_2 concentrations. The maximum for sulfate preceded by one hour that for SO_2 . Wind speed and direction for this 24-hr period are listed in Table 39. The location of the sampling site immediately to the north of a football stadium effectively restricted wind from the south. The observed wind direction during the S maxima was ESE with low wind speeds.

Four hour average values with the continuous S monitor are calculated and compared to quartz and Teflon filter samples in Table 40 and Figure 20. The continuous monitor and filter results are highly correlated, but show about 20% higher values by the continuous monitor.

B. Fine Particulate Acidity with Filter Samples

Tables 41 and 42 list strong acid, total acidity and sulfate measurements made with Teflon and acid-washed quartz fiber filters, respectively. Teflon filter samples were collected following an ammonia denuder while those on quartz had no denuder. Results are

Figure 19.

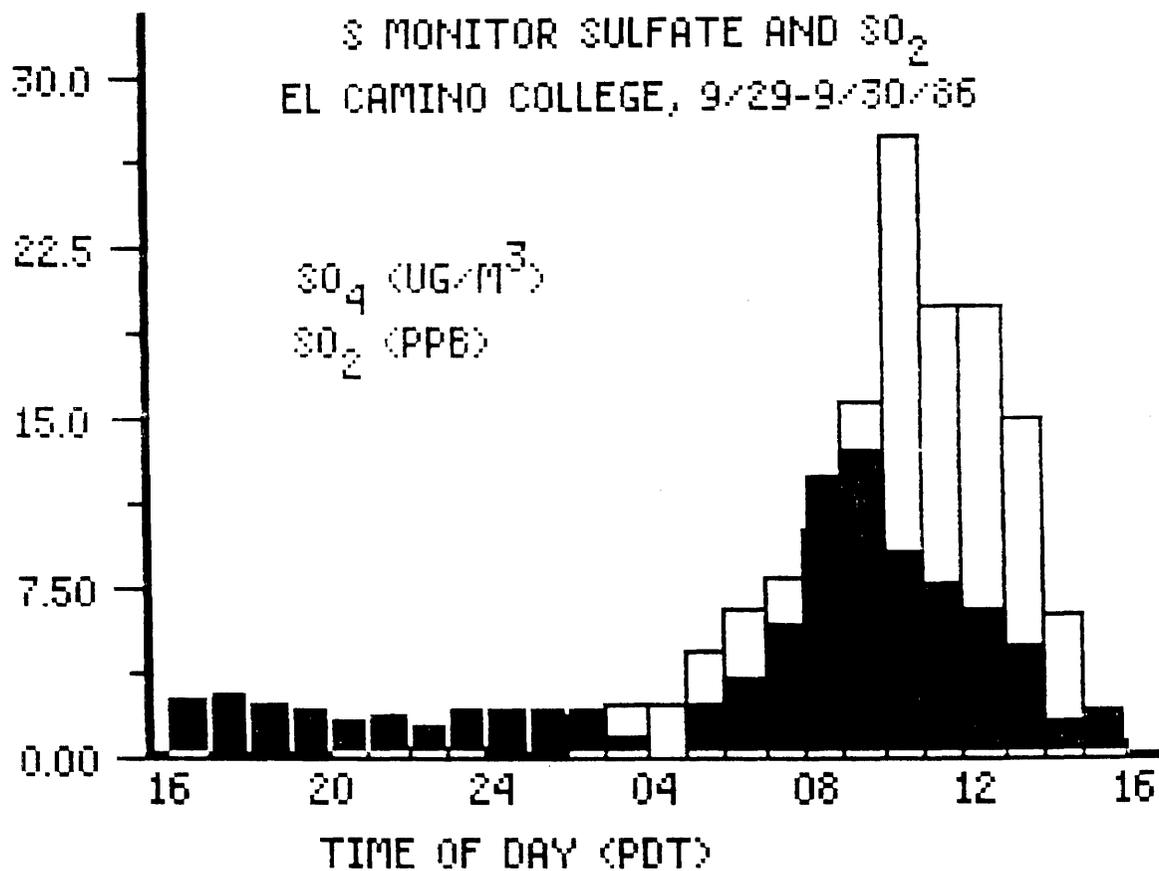


Table 38. Continuous S Monitor Measurement of Total Sulfate at El Camino College ($\mu\text{g}/\text{m}^3$)

Sample Date	Time Interval (PDT)	SO ₄ ⁼ Conc.	Mean Sulfate Values			
			Time (PDT)	Concentration		
9/29/86	1600 - 1700	2.6	1600 - 2000	2.5		
	1700 - 1800	2.8				
	1800 - 1900	2.3	2000 - 2400	1.7		
	1900 - 2000	2.2				
	2000 - 2100	1.7				
	2100 - 2200	1.8				
	2200 - 2300	1.3				
	2300 - 2400	2.2				
9/30/86	0000 - 0100	2.1	0000 - 0800	2.7		
	0100 - 0200	2.2				
	0200 - 0300	2.1	0800 - 1200	10.7		
	0300 - 0400	1.0				
	0400 - 0500	N/D*				
	0500 - 0600	2.3				
	0600 - 0700	3.6				
	0700 - 0800	5.8				
	0800 - 0900	12.4				
	0900 - 1000	13.7				
	1000 - 1100	9.1				
	1100 - 1200	7.7				
	1200 - 1300	6.6			1200 - 1600	3.8
	1300 - 1400	4.9				
	1400 - 1500	1.6				
	1500 - 1600	2.0				
1600 - 1700	1.1					

* Not Determined.

Table 39. Wind Speed and Direction for the 24-Hour Period with Highest Sulfur Levels at El Camino College

<u>Time</u>	<u>Wind Speed, mph</u>	<u>Wind Dir.</u>
1600 - 1700	5	W
1700 - 1800	4	W
1800 - 1900	2.5	W
1900 - 2000	1.5	W
2000 - 2100	0.5	W
2100 - 2200	calm	-
2200 - 2300	0.5	W
2300 - 2400	0.2	W
0000 - 0100	0.2	SW
0100 - 0200	0.2	W
0200 - 0300	0.5	W
0300 - 0400	calm	-
0400 - 0500	0.4	S
0500 - 0600	0.5	ESE
0600 - 0700	1.0	ESE
0700 - 0800	2.0	ESE
0800 - 0900	2.0	ESE
0900 - 1000	3.0	ESE
1000 - 1100	3.5	ESE
1100 - 1200	2.5	ESE
1200 - 1300	3.0	ESE
1300 - 1400	4.5	W
1400 - 1500	6	W
1500 - 1600	5	W

Table 40. Comparison of S Monitor and Filter Sulfate Results at El Camino College ($\mu\text{g SO}_4^-/\text{m}^3$)

<u>Date</u>	<u>Time (PDT)</u>	<u>S Monitor (as SO_4^-)</u>	<u>Teflon Filter</u>	<u>Quartz Filter</u>
9/29/86	1600 - 2000	2.45	2.1	1.84
	2000 - 2400	1.73	1.5	1.19
9/30/86	0000 - 0800	2.71	2.2	1.93
	0800 - 1200	10.7	8.5	9.02
	1200 - 1600	3.78	3.5	3.35
Ratio of Means:		1.2	1.00	1.03
<p>S Monitor = $-0.287 + 1.28$ (Teflon filter)</p> <p>r = 0.998</p> <p>S Monitor = $0.31 + 1.14$ (Quartz filter)</p> <p>r = 0.998</p>				

Figure 20.

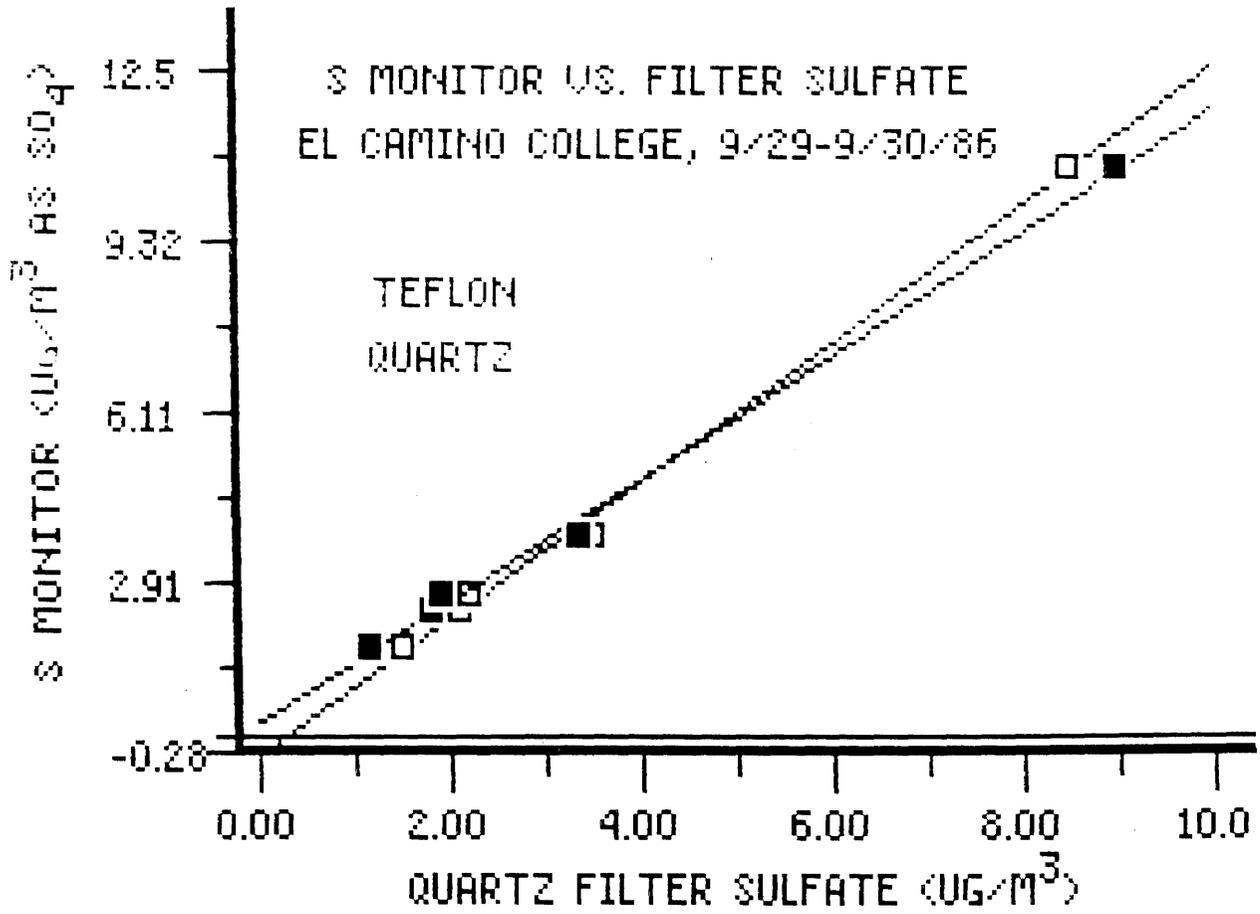


Table 41. Acidity and Sulfate Determinations with Teflon Filter Samples at El Camino College (nequiv/m³)

Sample ID	Date	Time	Strong Acid	Total Acidity	SO ₄ ⁼
203Z5	9/25/86	1600-2000	14.8	24.5	28.8
204Z5		2000-2400	23	25.1	27.2
205Z5	9/26/86	0000-0800	12.2	27.6	44.2
301Z5		0800-1200	27.8	40.0	88.3
302Z5		1200-1600	14.2	22.2	49.0
303Z5		1600-2000	18.0	26.8	73.8
304Z5		2000-2400	14.4	19.0	17.2
305Z5	9/27/86	0000-0800	7.8	13.8	34.4
401Z5		0800-1200	29.9	45.7	138
402Z5		1200-1600	23.2	31.6	70.8
403Z5		1600-2000	16.8	26.3	37.3
404Z5		2000-2400	17.0	25.6	27.1
405Z5	9/28/86	0000-0800	14.2	27.9	51.2
501Z5		0800-1200	< 2.0	5.6	39.2
502Z5		1200-1600	3.4	6.4	26.7
503Z5		1600-2000	< 2.0	5.6	25.6
504Z5		2000-2400	2.8	7.8	24.6
505Z5	9/29/86	0000-0800	12.4	20.6	38.5
601Z5		0800-1200	19.0	33.2	95.8
602Z5		1200-1600	11.2	18.0	52.2
603Z5		1600-2000	11.0	9.0	43.3
604Z5		2000-2400	15.2	0	31.9
605Z5	9/30/86	0000-0800	29.2	28.1	45.7
701Z5		0800-1200	71.4	75.4	177
702Z5		1200-1600	46.2	41.0	73.0

a. Filter field blank results for n=3, per 47 mm filter disc:

Total acidity: $4.7 \pm 0.6 \mu\text{g}$ as H₂SO₄ (96 ± 12 nequiv)
 Strong acidity: $1.0 \pm 0.3 \mu\text{g}$ as H₂SO₄ (20 ± 6 nequiv)
 SO₄⁼: $0.77 \pm 0.23 \mu\text{g}$ as SO₄⁼ (16 ± 5 nequiv)

Table 42. Acidity, Sulfate and Sulfite Determinations with Acid-Washed Quartz Filter Samples at El Camino College (nequiv/m³)^a

Sample ID	Date	Time	Strong Acid	Total Acidity	Sulfate ^b	SO ₃ ⁼
203Q6	9/25/86	1600 - 2000	< 10	62.3	20.6	0
204Q6		2000 - 2400	< 10	67.5	17.3	0.9
205Q6	9/26	0000 - 0800	< 5	15.3	38.8	2
301Q6		0800 - 1200	< 10	56.2	63.5	2
302Q6		1200 - 1600	< 10	N/D	N/D	N/D
303Q6		1600 - 2000	< 10	33.6	66.0	0
304Q6		2000 - 2400	< 10	32.5	18.8	< 0.9
305Q6	9/27	0000 - 0800	< 5	16.1	26.7	2
401Q6		0800 - 1200	< 10	42.4	102	0.9
402Q6		1200 - 1600	< 10	50.0	46.7	3
403Q6		1600 - 2000	< 10	25.4	28.8	0
404Q6		2000 - 2400	< 10	29.4	21.3	3
405Q6	9/28	0000 - 0800	< 5	37.6	13.1	2
501Q6		0800 - 1200	< 10	39.2	34.8	< 0.9
502Q6		1200 - 1600	< 10	13.9	18.8	0
503Q6		1600 - 2000	< 10	-11	21.7	< 0.9
504Q6		2000 - 2400	< 10	14.5	28.5	0.9
505Q6	9/29	0000 - 0800	< 5	N/D	N/D	N/D
601Q6		0800 - 1200	< 10	48.1	103	2
602Q6		1200 - 1600	< 10	31.2	66.4	< 0.9
603Q6		1600 - 2000	< 10	19.6	39.2	< 0.9
604Q6		2000 - 2400	< 10	26.8	25.4	< 0.9
605Q6	9/30	0000 - 0800	< 5	24.7	40.6	3.1
701Q6		0800 - 1200	22.6	56.0	188.8	< 0.9
702Q6		1200 - 1600	< 10	25.1	70.8	0

a. Filter field blank results for n=3, per two, 47 mm discs:

Total acidity: $71 \pm 8.7 \mu\text{g}$ as H₂SO₄ (1449 ± 177 nequiv)
 Strong acidity: $19.3 \pm 6 \mu\text{g}$ as H₂SO₄ (394 ± 122 nequiv)
 SO₄ : 0
 SO₃ : 0

b. Sulfate analysis in aqueous formaldehyde filter extract. Results should be relatively free of error due to conversion of any SO₃⁼ present to SO₄.

expressed in nequiv/m³. With Teflon samples, strong acid levels were, on average, 75% of total acidity, consistent with the contribution of carboxylic acids to the total acidity. For the two periods with highest strong acidity, 08-12 and 12-16 hr, 9/30/86, strong acidity and total acidity were not significantly different. The latter two would be expected to contribute to the measured strong acidity.

Because H₂SO₄ was not observed with the continuous S monitor, comparison of the acidity and S monitor results is not feasible. Sulfate concentrations greatly exceeded strong acid measurements. The results are consistent with the presence of a mixture of ammonium sulfate and ammonium acid sulfate as well as such materials as formic acid. The latter two are expected to contribute to the measured strong acid.

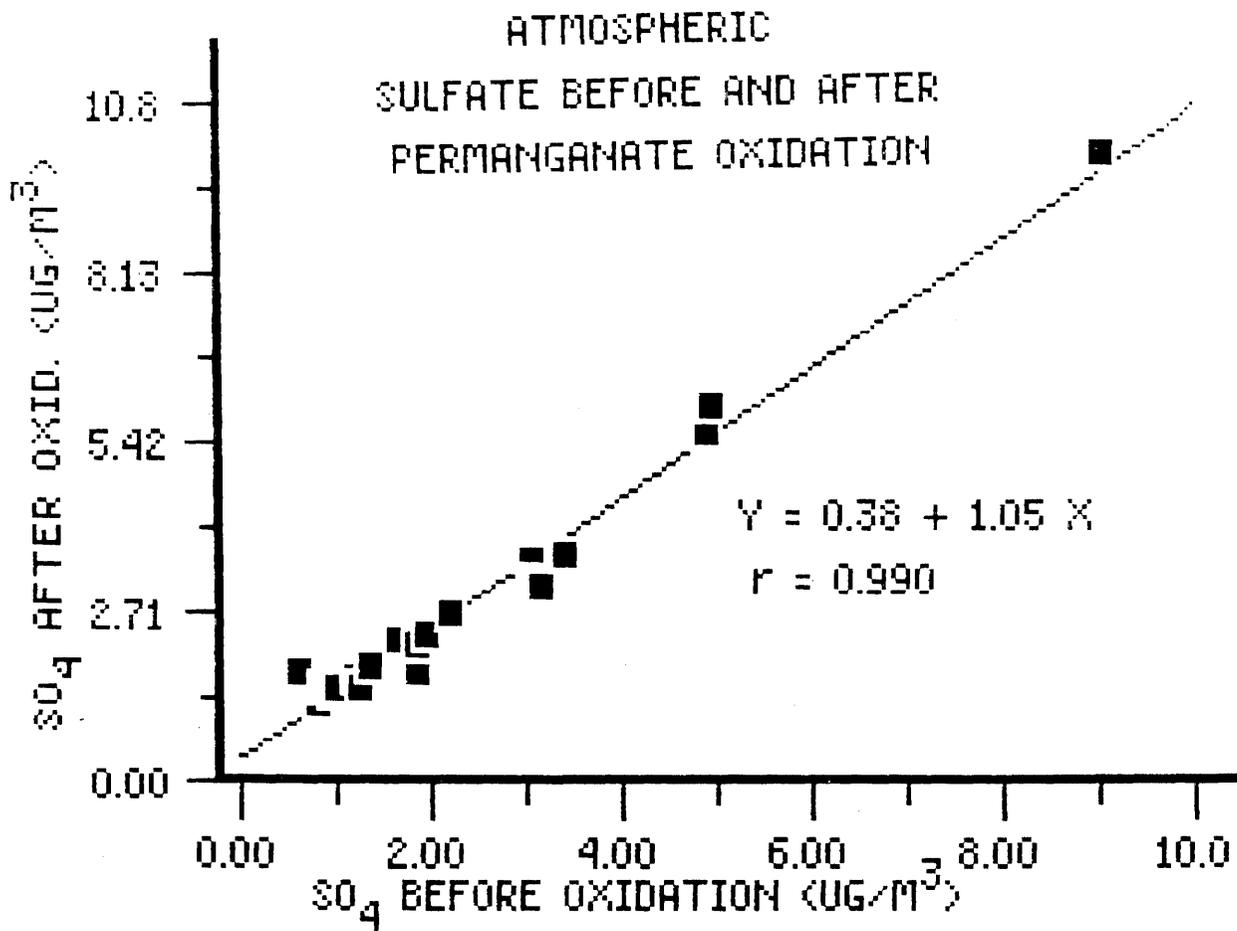
Acid washed quartz filters showed significant field blank values for strong and total acidity. The limits of detection for these measurements were 3-5 times higher than with Teflon filters. Strong acid measurements with acid-washed quartz filter samples were, with one exception, below our limit of detection, 10 nequiv/m³ (0.5 µg/m³). The latter was based on 2 σ of the field blanks. The exception corresponded to the period in which sulfate and Teflon filter sample acidity both exhibited maxima. The quartz filter result, 22.6, compares to 71.4 nequiv/m³ from the Teflon filter sample. Recovery of strong acid spiked on to quartz and Teflon filters showed somewhat higher recovery of strong acid with the acid-washed quartz material (Section XI B). Since 80% of the concentrations measured with Teflon filters were above the limit of detection for quartz filters, we conclude that the recovery of atmospheric strong acids from these quartz filter samples is less than from the Teflon filters. The cause of the lower recovery with quartz filters may reflect the effectiveness of the NH₃ denuder with the Teflon filter sampler, since the sampler with quartz filters lacked such a denuder.

Comparing total acidity measurements on quartz and Teflon filter samples, on average, the quartz filter total acidity results were substantially greater. This may relate to a greater degree of retention of carboxylic acids on the quartz filters, but this was not investigated.

C. Non-Sulfate Sulfur in Aerosol Samples

With Teflon filter samples, no precautions were taken to prevent oxidation of S species to sulfate after sampling other than storage at low temperature. Thus, such readily oxidized materials as sulfite would probably be oxidized to sulfate during aqueous extractions and/or storage periods prior to analysis. With quartz samples, aliquots were analyzed for sulfate before and after oxidation with permanganate. The "before" results were obtained with samples extracted in 0.1% formaldehyde solution immediately after sample collection, intended to stabilize from oxidation any sulfite present by formation of the adduct. Figure 21 compares sulfate results, in µg/m³, from the quartz filters before and after oxidation. Oxidation provided a small increase in SO₄ samples, averaging about 5%.

Figure 21.



The formaldehyde extracts of quartz filter samples were analyzed for the SO_3^- -HCHO adduct by ion chromatography. This analysis provides only an upper limit measure since, under the analytical conditions used, NO_2 elutes at the same position, if present in the sample. As shown in Table 42, only trace levels were observed; the maximum concentration was 3.1 nequiv/m^3 ($3.1 \text{ } \mu\text{g/m}^3$). The 5% average difference between sulfate concentrations observed before and after permanganate oxidation may include oxidation of species other than sulfite (e.g. organic sulfur compounds). However, the low concentrations of such materials, if present, hampers firm conclusions.

The formaldehyde extracts of the quartz filters were also analyzed for SO_4^- (Table 42). The results should be relatively free of error due to conversion of SO_3^- to SO_4^- by oxidation following sampling. This contrasts with results for Teflon filter samples which had no precautions regarding stabilizing SO_3^- . The SO_4^- results on the two filter types were highly correlated:

$$\begin{aligned} \text{SO}_4^- \text{ (Teflon)} &= 13.6 + 0.893 [\text{SO}_4^- \text{ (Quartz)}] \\ r &= 0.939 \quad n = 23 \end{aligned}$$

Based on ratios of means, the Teflon results averaged 18% higher. These differences reflect the combined influence of flow rate calibration errors, if any, and possibly decreased conversion of SO_3^- to SO_4^- on the quartz filters.

D. Particulate Ammonium and Ammonia Concentrations

Particulate ammonium and ammonia levels were measured with a filter pack method using 4 or 8-hr sampling. Ammonium nitrate can volatilize from the Teflon filter. Accordingly, NH_3 results are usually too high by this method (3). Ammonia was also measured for 12 hour periods with a denuder tube collection procedure. Filter pack results are given in Table 43. Particulate NH_4^+ results are given in both $\mu\text{g/m}^3$ and nequiv/m^3 . Ammonia levels were low, ranging from 0.6 to $3.7 \text{ } \mu\text{g/m}^3$. This is consistent with previous sampling performed at sites near the western edge of the South Coast Air Basin. Ammonia results by the denuder tube method are listed in Table 44 together with filter pack results averaged to permit comparison. Denuder tube results averaged about 40% smaller. Similarly, previous such comparisons made at higher concentrations, showed filter pack results to be higher by about 50% (16,22).

E. Nitric Acid, Particulate Nitrate, and HCl Concentrations

Table 45 lists concentrations for total fine NO_3^- , fine particle NO_3^- , and HNO_3 by the denuder difference method. Consistent with the sampling location near the western edge of the South Coast Air Basin, nitrate and nitric acid levels were low. A consistent diurnal pattern for nitrate was not observed; maxima were observed during morning, afternoon and evening periods. The highest concentration of HNO_3 observed was about $6 \text{ } \mu\text{g/m}^3$. The three periods of

Table 43. Summary of Particulate NH_4^+ and Ammonia Results by Filter Pack Sampling

Date	Time (PDT)	Sample Period	Particulate NH_4^+ ^b		NH_3 as NH_4^+ ^c
			$\mu\text{g}/\text{m}^3$	nequiv/ m^3	($\mu\text{g}/\text{m}^3$)
9/25/86	1600 - 2000	203	0.4 ^a	22	0.9
	2000 - 2400	204	0.8	44	1.1
9/26/86	0000 - 0800	205	1.1	61	1.9
	0800 - 1200	301	2.1	117	2.5
	1200 - 1600	302	0.5	28	1.9
	1600 - 2000	303	1.4	78	0.5
	2000 - 2400	304	0.4 ^a	22	1.2
9/27/86	0000 - 0800	305	1.0	56	2.2
	0800 - 1200	401	2.1	117	1.9
	1200 - 1600	402	1.0	56	1.0
	1600 - 2000	403	0.8	44	1.2
	2000 - 2400	404	0.4 ^a	22	1.2
9/28/86	0000 - 0800	405	0.7	39	2.8
	0800 - 1200	501	1.5	83	3.0
	1200 - 1600	502	0.6	33	1.3
	1600 - 2000	503	0.4 ^a	22	1.3
	2000 - 2400	504	1.1	61	0.6
9/29/86	0000 - 0800	505	1.6	89	2.5
	0800 - 1200	601	5.0	278	3.7
	1200 - 1600	602	1.4	78	2.0
	1600 - 2000	603	1.5	83	1.6
	2000 - 2400	604	1.6	89	1.8
9/30/86	0000 - 0800	605	2.6	144	2.2
	0800 - 1200	701	7.1	394	1.7
	1200 - 1600	702	1.7	94	2.9

- a. Result at the limit of detection.
- b. Results from Teflon prefilters.
- c. Results from oxalic acid-glycerol impregnated quartz filters.

Table 44. Ammonia Concentrations at El Camino College by the Denuder Tube and Filter Pack Methods ($\mu\text{g}/\text{m}^3$)

<u>Sample ID</u>	<u>Starting Date</u>	<u>Time (PDT)</u>	<u>Denuder Tube NH₃ as NH₄⁺</u>	<u>Filter Pack NH₃ as NH₄⁺</u>
207F3	9/25/86	2000 - 0800	< 0.5	1.6
306F3	9/26/86	0800 - 2000	0.6	1.6
307F3	9/26/86	2000 - 0800	0.7	1.9
406F3	9/27/86	0800 - 2000	1.2	1.4
407F3	9/27/86	2000 - 0800	1.2	2.3
506F3	9/28/86	0800 - 2000	1.1	1.9
507F3	9/28/86	2000 - 0800	1.5	1.9
606F3	9/29/86	0800 - 2000	1.4	2.4
607F3	9/29/86	2000 - 0800	1.3	2.1
706F3	9/30/86	0800 - 1600	1.2	2.3
			Mean: 1.13	1.94

Table 45. Fine Particulate Nitrate and Nitric Acid Determination at El Camino College ($\mu\text{g}/\text{m}^3$)

<u>Date</u>	<u>Time</u>	<u>Sample Period</u>	<u>Total Fine NO₃</u>	<u>Fine Particle NO₃</u>	<u>HNO₃ as NO₃</u>
9/25/86	1600 - 2000	203	0.8	0.9	0.1
	2000 - 2400	204	1.8	1.7	0.1
9/26/86	0000 - 0800	205	3.0	2.9	0.1
	0800 - 1200	301	7.6	7.6	0
	1200 - 1600	302	3.6	3.2	0.4
	1600 - 2000	303	2.0	4.5	- 2.5
9/27/86	2000 - 2400	304	5.1	1.9	3.2
	0000 - 0800	305	5.4	2.4	3.0
	0800 - 1200	401	10.2	10.0	0.2
	1200 - 1600	402	5.8	5.2	0.6
9/28/86	1600 - 2000	403	3.8	3.3	0.5
	2000 - 2400	404	1.5	1.6	-0.1
	0000 - 0800	405	3.2	3.1	0.1
	0800 - 1200	501	8.4	2.5	5.9
9/29/86	1200 - 1600	502	7.4	3.6	3.8
	1600 - 2000	503	2.1	1.7	0.4
	2000 - 2400	504	2.5	1.9	0.6
	0000 - 0800	505	4.3	4.1	0.3
9/29/86	0800 - 1200	601	18.4	17.3	1.1
	1200 - 1600	602	8.0	5.9	2.1
	1600 - 2000	603	4.8	3.5	1.3
	2000 - 2400	604	3.0	3.7	-0.7
9/30/86	0000 - 0800	605	5.5	4.9	0.6
	0800 - 1200	701	20.7	16.8	3.9
	1200 - 1600	702	10.8	8.1	2.7

highest HNO_3 were periods 501, 502 and 701. The first two coincided with unusually low strong particulate acidity concentrations. Thus, there is no contribution of HNO_3 to particulate acidity evident from these results.

Nylon filters were analyzed for chloride to permit measurement of HCl by the denuder difference method. Fine particulate chloride ranged from 0.4 to 5.3 $\mu\text{g}/\text{m}^3$. Concentrations of HCl by the difference technique ranged from 2.4 to -0.8 $\mu\text{g}/\text{m}^3$. Measurements by the difference technique were hampered by the substantial chloride blank of the Sartorius Nylon filters employed, $9.2 \pm 0.3 \mu\text{g}$ per disc ($n=3$), corresponding to $1.9 \pm 0.06 \mu\text{g}/\text{m}^3$ for four hour samples.

The blank correction represented a substantial fraction of the observed chloride, decreasing the precision of the measurements. The results are not considered acceptable for reporting.

* Attempts to pre-extract these filters to reduce the Cl^- blank value caused distortion of the filter disc sufficient to prevent their use; the filters dried with an oval shape.

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APPENDIX A

Tentative Method for the Semi-Continuous Measurement of Atmospheric Particulate Sulfur, Sulfuric Acid and Ammonium Sulfates

1. Principle of Method

- 1.1 Air containing gaseous and particulate sulfur compounds is passed through a heater and then through a diffusion denuder coated with lead oxide followed by a flame photometric detector (FPD).
- 1.2 The response of the FPD to sulfur-containing compounds is based on the light emitted near 400 nm from the excited S_2 band in a hydrogen-rich flame. Net current from the photomultiplier tube is approximately proportional to the square of the sulfur concentration.
- 1.3 With the heater at close to ambient temperature, only normally gaseous sulfur species are removed by the denuder, providing an FPD response due to particulate sulfur species.
- 1.4 With the heater at about 125°C, sulfuric acid volatilizes and is removed by the denuder together with normally gaseous sulfur species. In the absence of interferents, the decrease in FPD response, relative to that near ambient temperature, is related to the concentration of sulfuric acid present.
- 1.5 With the heater at about 300°C, sulfuric acid (H_2SO_4), ammonium sulfate ($(NH_4)_2SO_4$) and ammonium acid sulfate (NH_4HSO_4) volatilize and are removed together with the normally gaseous sulfur species. In the absence of interferents, the change in FPD response relative to that at about 120°C, is related to the sum of the concentrations of $(NH_4)_2SO_4$, NH_4HSO_4 and intermediate compounds (e.g. $(NH_4)_3H(SO_4)_2$).
- 1.6 The residual sulfur signal at 300°C, relative to that sampling clean air, is related to the concentration of non-volatile sulfur particulate species (e.g. metal sulfates).
- 1.7 The sensitivity of the FPD for sulfur is enhanced by continuous addition of a constant concentration of sulfur.
- 1.8 The method provides semi-continuous measurements employing typically a 10-15 minute temperature programming cycle.

2. Range and Sensitivity

- 2.1 A limit of detection of 1 to 2 $\mu g/m^3$ was reported for H_2SO_4 , implying that 5 to 10 $\mu g/m^3$ H_2SO_4 is required for a precision of 10% (1).

3. Interferences

- 3.1 Any sulfur compound in particle phase which volatilize at ≤ 125 or $\leq 300^\circ C$ is an interferent with respect to measuring the correspond-

ing inorganic sulfate species. Potential interferents include S-containing organic compounds (e.g. bis-hydroxymethane sulfone (2), hydroxymethanesulfonic acid (3), and alkyl sulfonic acids (4).

- 3.2 The ammonium salts $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 volatilize at about the same temperature and are, therefore, not distinguishable.
- 3.3 Ammonia addition to the sample inlet can aid in detecting interferents. A decrease in apparent H_2SO_4 upon NH_3 addition is consistent with the presence of H_2SO_4 and may exclude some potential interferents.
- 3.4 The response of the FPD is altered by change in levels of carbon dioxide (5,6), relative humidity (7), and barometric pressure (7).

4. Precision and Accuracy

An intermethod comparison, for total particulate sulfur (TPS), including three systems similar to that discussed herein, showed atmospheric results agreeing within about 13%, implying relatively good precision for TPS. Precision and accuracy have not been reported for measurement of H_2SO_4 , and ammonium sulfates by this technique (8).

5. Apparatus

- 5.1 Several investigators have constructed systems of this type (1,7,9-11). The unit detailed by Allen et al. (1) has attempted to incorporate the best features of each of the prior investigators. Accordingly, the present description is based largely on Reference 1.
- 5.2 Figure 1 is a flow diagram of the system.
- 5.3 The unit includes a source of NH_3 -free air, and an ammonia permeation tube. Ammonia is used to neutralize all sulfate species prior to their entry to the FPD. This minimizes errors resulting from differing responses for various inorganic sulfates (7). Ammonia can also be directed into the sample inlet.
- 5.4 Zero (i.e. particulate sulfur-free) air is supplied by filtration of ambient air.
- 5.5 The heater consists of a 15 cm section of 5 mm I.D., stainless steel tubing. Heating is provided by passing about 40 amp (at 0.5 to 1.3 VAC) through the tubing. The various temperatures in the thermal cycle may be controlled by a proportioning type electronic temperature controller. A single controller can be made to control at two temperatures (e.g. 120°C and 300°C) by wiring a second potentiometer across the original temperature setting potentiometer and switching between them with a relay.
- 5.6 The lead oxide denuder is prepared (13) by coating the inner surface of an 15 cm section of 5 mm I.D. stainless steel tubing with a thin slurry of PbO (e.g. 6 g PbO in 6 ml glycerine-water). The glycerine-water is removed by passing air through it while heating the tube initially at 110°C. Temperature is increased to 200°C gradually over a period of 4 hours. The orange color of PbO is replaced by a white to tan coating thought to be PbO_2 .

- 5.7 A microcomputer controller-timer (e.g. Chronrol Model CT, Lindberg Enterprises, Inc., San Diego, CA), not shown, can be used to operate the solenoid valves and heater.
- 5.8 Employing 66 ppb SF₆-doped H₂ fuel yields an increase in the signal/noise ratio of about 13 at 1 ppb S(11).

6. Reagents

- 6.1 Activated charcoal.
- 6.2 Silica gel.
- 6.3 PbO powdered.
- 6.4 5:1 v/v glycerine-water solution.
- 6.5 Ammonium sulfate.
- 6.6 H₂ doped with 50 to 75 ppb SF₆ (available from Scott Specialty Gases, Plumsteadville, PA)

7. Procedure

- 7.1 For a 3-5 minute period, the sample flows through the heater at < 50°C. The FPD response reflects all particle-phase S. (Point #1, Figure 2).
- 7.2 For a 4-minute period the heater is maintained at 120-130°C to volatilize H₂SO₄. The FPD response reflects all particle phase S species not volatilized at that temperature (Point #2, Figure 2).
- 7.3 For a 4-minute period the heater is maintained at 300°C to volatilize ammonium sulfates. The FPD response reflects only non-volatile S species (Point #3, Figure 2).
- 7.4 For a 3-7 minute period the system is permitted to cool down while sampling zero air (Point #4, Figure 2).
- 7.5 The difference in FPD response, Pt 1-Pt 2, Pt 2-Pt 3, and Pt 3-Pt 4, is used to measure H₂SO₄, ammonium sulfates and metal sulfates, respectively.

8. Calibration

- 8.1 Ammonium sulfate and H₂SO₄ aerosols are generated from dilute aqueous solutions employing a nebulizer or other appropriate system. The response of the analyzer to each aerosol is optimized by adjusting volatilization temperatures.
- 8.2 Primary calibration of the FPD can be done with known concentrations of SO₂ in air containing 315 to 385 ppm CO₂. Comparison of FPD total sulfate values, calculated from calibration with SO₂, and filter-collected sulfate concentrations showed relatively good agreement (Figure 3).

9. Sulfate concentrations are calculated using filtered air response (e.g. Point #4) as a baseline. Data are reduced as follows:

$$\mu\text{g}/\text{m}^3 \text{SO}_4^{=} = 3.93 \times A \left(\text{net chart div.} \times \frac{B \text{ volts}}{\text{chart div.}} \right) C$$

Parameters A and C are obtained from the calibration with SO₂. B is the volts per chart division of the recorder employed. The factor of 3.93 converts ppb SO₂ (at 25°C) to μg/m³ SO₄⁼.

It may be necessary to correct the observed H₂SO₄ concentration to allow for the fraction not volatilized at the midpoint temperature in the system. For the system described by Allen et al. (1), this correction amounted to 8%.

For the example given in Figure 2, with A = 3.06, B = 0.05 and C = 0.929:

Point #1 = 52.0 μg/m³ Total Sulfate

Point #3 = 2.7 μg/m³ Non-Volatile Sulfate

Point #2 = 14.2 μg/m³ Sulfate, so:

Sulfate as sulfuric acid = (52.0 - 14.2) x 1.08 = 40.8 μg/m³

Sulfate as ammonium sulfate

plus ammonium bisulfate = 52.0 - 40.8 - 2.7 = 8.5 μg/m³

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APPENDIX B

Laboratory Evaluation of the Loss of HNO_3 in Teflon-Lined Cyclones and Accuracy of the DDM (Following Atmospheric Sampling)

To assess loss of HNO_3 in the samplers and the accuracy of the denuder difference method (DDM) for HNO_3 under controlled conditions, HNO_3 from a diffusion tube source was diluted with purified ambient air to provide about $15 \mu\text{g}/\text{m}^3$ concentrations (as NO_3^-). This concentration represented close to the mid-range of the 4-6 hour average concentrations measured at Claremont. The purification system, Purafil and charcoal beds followed by a glass fiber filter, removed SO_2 , strong acids, and particulate matter and sharply reduced NO_2 and NO . The HNO_3 in air was adjusted to 50% R.H. and 20°C and sampled in parallel with four samplers.

1. A 47-mm Nylon filter (Gelman batch 871) at 20 Lpm.
2. As in 1 preceded by a Teflon-lined cyclone (1) and the same glass manifold as employed at Claremont. The total flow through the cyclone was 28 Lpm of which 20 Lpm was sampled through the Nylon filter. The cyclone was not cleaned from prior use at Claremont (where it had been cleaned after every 48 hr period).
3. Same as 1.
4. Same as 2 but with an MgO denuder between a second cyclone and the Nylon filter. The denuder tubes were the same ones used for the last half of the Claremont study (i.e. their efficiency represents a lower limit to that of a fresh denuder).

The results for three, 2-hour sampling trials are shown in Table B-1. HNO_3 concentrations decreased by about 25% between the first and the third trials which contributes to the 10%-20% C.V. shown for the mean NO_3^- concentrations by each sampler. Loss of HNO_3 in a cyclone (plus associated glass pipe) can best be assessed by comparing mean total fine NO_3^- results (Sampler 2), $15.2 \pm 1.5 \mu\text{g}/\text{m}^3$, against the mean NO_3^- recovered from samplers 1 and 3 for all trials, $15.7 \pm 2.1 \mu\text{g}/\text{m}^3$. The results are not significantly different, indicating no measurable loss of HNO_3 in a cyclone still dirty from 48-hr sampling in Claremont. Alternatively, the mean ratio, Sampler 2/Sampler 1 and 3, calculated from individual trials, 0.97 ± 0.07 , can be used to reach the same conclusion.

The accuracy of the DDM (in the absence of potential interferences) may be inferred by comparing the mean results (Total Fine NO_3^- -Fine Particulate NO_3^-), $14.3 \pm 1.5 \mu\text{g}/\text{m}^3$, to the mean of samplers 1 and 3, $15.7 \pm 2.1 \mu\text{g}/\text{m}^3$. Alternatively, the results may be determined separately by trial to eliminate the influence of the concentration change on the variance. Table B-2 indicates, by the latter approach, an accuracy for the DDM of $92 \pm 6\%$. The principal cause of the apparent 8% negative error is the NO_3^- measured with sampler 4. This NO_3^- represents the sum of HNO_3 penetrating the denuder (estimated to be about $0.5 \mu\text{g}/\text{m}^3$ or 3% penetration, employing the Gormley-Kennedy equation and the diffusion coefficient for unhydrated HNO_3), and particulate NO_3^- formed from HNO_3 and NH_3 not removed by the air purification system.

TABLE B-1. Loss of HNO₃ in Cyclone of Samplers for the DDM ($\mu\text{g NO}_3^-/\text{m}^3$)^a

<u>Trial</u>	<u>Nylon Filter (1)</u> ^b	<u>Total Fine NO₃⁻ (2)</u> ^b	<u>Nylon Filter (3)</u> ^b	<u>Fine Particulate NO₃⁻ (4)</u> ^b
1	17.5	16.4	18.9	0.8
2	15.7	15.8	14.7	1.0
3	13.5	13.5	14.1	0.8
Mean:	15.6 ± 2.0	15.2 ± 1.5	15.9 ± 2.6	0.9 ± 0.1

a. All results corrected for a laboratory filter blank, $1.2 \pm 0 \mu\text{g}/47 \text{ mm}$ filter (n=2).

b. Number in parenthesis is sampler number as discussed in text.

TABLE B-2. Laboratory Assessment of the Accuracy of the DDM ($\mu\text{g NO}_3^-/\text{m}^3$)

<u>Trial</u>	<u>Nylon Filter</u>	<u>DDM</u>	<u>DDM/Nylon Filter</u>
1	18.2	15.6	0.86
2	15.2	14.8	0.97
3	13.8	12.7	0.92
			Mean: 0.92 ± 0.06

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APPENDIX C

Procedure For Coating and Extracting Annular Denuders For Collection of HNO_3 , HONO and Other Acidic Species

COATING

- a. Prepare and check for NO_2^- and NO_3^- blank:
 1. 2%w Na_2CO_3 in H_2O
 2. 2%w glycerol in MeOH
- b. Just before coating, make sufficient volume of 50:50 v/v of solutions 1 and 2 for subsequent coating.
- c. Denuders and caps and coupler should be washed prior to first use with MeOH and then with H_2O . No need to dry completely, just drain.
- d. Sections A and B are coated separately. Cap bottom. Add 10 ml 50:50 solution. Cap top. Swirl to bathe uniformly the interior. Drain.
- e. Blow synthetic air through each section until dry.
- f. Cap both ends.
- g. When ready for sampling, join sections A and B with coupler.

EXTRACTING

- a. Following sampling, separate sections A and B and cap.
- b. To one tube add 5 ml standard IC eluent. Cap and rotate to wash surface. Drain with small funnel into 15 ml screw cap polystyrene test tube. Repeat with a second 5 ml aliquot. Note: about 0.3 ml remains in denuder.



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