

DETERMINATION OF ACIDITY IN AMBIENT AIR

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ABSTRACT

A laboratory and field study was performed to construct and evaluate an automated, semi-continuous monitor for ambient air concentrations of nitric acid (HNO_3) and ammonia (NH_3) utilizing tungstic acid-coated denuder tubes. In addition, atmospheric concentrations of hydrochloric acid (HCl) were determined. Manual techniques for atmospheric NH_3 measurement were also compared. Interference in HNO_3 measurements was determined with nitrogen dioxide, nitrous acid, and particulate ammonium nitrate. Atmospheric sampling for HNO_3 was done in Riverside, CA during September 1984 with the automated tungstic acid technique (TAT), and by the denuder difference method (DDM), considered the reference procedure for HNO_3 . Ammonia and HCl were measured with impregnated filter methods. In addition, NH_3 was measured by a denuder tube collection procedure.

Nitrous acid was the only material studied which exhibited significant interference in nitric acid response with the automated TAT. Atmospheric nitric acid levels with the automated TAT showed 1 hour average values up to $45 \mu\text{g}/\text{m}^3$ (17.5 ppb). These values yielded moderate correlation with O_3 ($r = 0.78$) and high correlation ($r = 0.94$) with HNO_3 by the DDM. However, the HNO_3 values averaged about 50% higher than those by the reference procedure. Ammonia measurements with impregnated filters showed high correlation ($r = 0.98$) with oxalic acid-coated denuder tube collected samples, but the former averaged 12% higher. Ammonia measurements with the automated TAT were not quantitative because of difficulties in calibration. Hydrochloric acid values ranged up to $3 \mu\text{g}/\text{m}^3$ with a pronounced diurnal variation, maxima occurring during the period 0800-1200 or 1200-1600 hr. Particulate chloride levels were similar in magnitude to those for HCl and showed no correlation with HCl .

The statements and conclusions in this report are those of the Contractor and not necessarily those of the State Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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I. SUMMARY AND CONCLUSIONS

A laboratory and field study was performed to construct and evaluate a semi-real time monitor for ambient air concentrations of nitric acid and ammonia utilizing tungstic acid (WO_x) coated denuder tubes. In addition, atmospheric concentrations of HCl were determined.

The laboratory study focussed on assessing the influence of design parameters to achieve a workable automated sampler for HNO_3 and ammonia. Utilizing a preliminary version of the automated tungstic acid technique (TAT), interference studies were done with NO_2 , HONO (nitrous acid), and particulate ammonium nitrate. Of these, only HONO showed significant interference. The apparent response corresponded to at least one third the molar response of nitric acid. The difficulties in preparation and quantitation of HONO made only lower limit measurements of TAT interference possible.

The efficiency of tungstic acid coated tubes at 1 Lpm with 340-1030 ng loadings of HNO_3 at ca. 50% R.H. ranged from 91 to 98%, decreasing with increasing loading. The automated system re-equilibrated from sampling HNO_3 or NH_3 to clean air within one or two cycles if the Teflon ball valve in the inlet was lined with pyrex tubing. Attempts to operate the automated TAT on purified ambient air for desorption and makeup gas flow yielded nonreproducible results and were, therefore, abandoned. Desorption of HNO_3 with helium was shown to provide about 30% higher response compared to desorption with synthetic air.

Alternative methods for NH_3 as well as a method for HCl collection and analysis were assessed with laboratory trials. Oxalic acid-coated denuder tubes yielded NH_3 results agreeing within 20% with those for oxalic acid impregnated quartz fiber filters with better agreement being obtained for 16 hr than for 4 hr trials. HCl collection with triethanolamine-KOH impregnated cellulose filters following a Teflon prefilter was evaluated with several sampling configurations. The procedure adopted was found to provide an efficiency for HCl of at least 92%.

Atmospheric sampling was done on the campus of the University of California (Riverside) with samplers mounted on the roof of a mobile laboratory. In addition

to the automated TAT, HNO_3 was measured with 4 or 8 hour resolution by the denuder difference method (DDM), considered the reference procedure for HNO_3 . Ammonia and HCl were measured with 4 or 8 hr resolution with impregnated filter methods. In addition, NH_3 was measured by a denuder tube collection method with 12 and 24 hr resolution.

Pollution levels ranged from extraordinarily light to moderate photochemical smog ($\text{O}_3 > 0.30$ ppm). Nitric acid levels with the automated TAT showed 1 hour average values up to $45 \mu\text{g}/\text{m}^3$ (17.5 ppb). These values showed moderate correlation with O_3 ($r = 0.78$) and high correlation ($r = 0.94$) with HNO_3 by the DDM. However, the HNO_3 values averaged about 50% higher than those by the reference procedure. The difference in results between the automated TAT and DDM showed positive correlation with NO_2 ($r = 0.6$) perhaps indicative of the retention on the WO_x tube of a species other than HNO_3 whose concentration correlates with NO_2 . The difference in results between methods is qualitatively similar to recent measurements made at a relatively remote site in Colorado (18).

Ammonia measurements with impregnated filters showed high correlation ($r = 0.98$) with oxalic acid-coated denuder tube collected samples but the former averaged 12% higher. This is consistent with partial volatilization of NH_4^+ salts from the Teflon prefilter. Ammonia measurements with the automated TAT were not quantitative because of difficulties in calibration. At relatively high concentrations, TAT response to NH_3 atmosphere appeared to be linear, however. Further modification of the TAT is needed to permit reliable NH_3 determinations.

Hydrochloric acid values, estimated by observed levels of gaseous Cl^- , ranged up to $3 \mu\text{g}/\text{m}^3$ with a pronounced diurnal variation, maxima occurring during the period 0800-1200 or 1200-1600 hr. Particulate chloride levels were similar in magnitude to those for HCl and showed no correlation with HCl.

The principal conclusions from this study are:

1. An automated WO_x denuder tube HNO_3 monitor can be reproducibly calibrated and used to obtain semi-real time ambient air measurements which are highly correlated with atmospheric HNO_3 .

2. Unidentified atmospheric nitrogen oxides are also retained on WO_x coated denuder tubes which, in the present study, caused a 50% positive interference. Without modification to improve its selectivity, the automated TAT may have limited applicability as a reference method for nitric acid.
3. NO_2 and particulate NH_4NO_3 do not appear to interfere in the method. However HONO shows a substantial positive interference. It is unlikely that HONO caused a substantial fraction of the observed interference, however.
4. Ammonia is more difficult to sample correctly with the automated TAT. Further work is needed to obtain a reliable, automated NH_3 monitor.
5. Atmospheric hydrochloric acid levels in Riverside are low ($\leq 3 \mu\text{g}/\text{m}^3$) with pronounced daytime maxima.
6. Triethanolamine-KOH impregnated cellulose filters cannot be recommended for HCl collection if ion chromatographic analysis is intended.
7. Phase II of this investigation should include further improvements in the automated TAT to permit NH_3 measurements, further interferent studies with the TAT, atmospheric trials at sites with both low and high levels of HCl, NH_3 and HNO_3 , and assessment of the contribution of gaseous acids to atmospheric particulate acidity.

II. INTRODUCTION

A. Gaseous Nitric Acid and Ammonia

Nitric acid is significant as an air pollutant for a variety of reasons; as an inhalation hazard, a precursor of NH_4NO_3 particles which cause visibility reduction, as a nitrating agent in forming nitro-PAH compounds of increased mutagenicity compared to the parent hydrocarbon, and as a contributor to the acidity of suspended particles, rain water, lakes and vegetation. Ammonia, while not hazardous at atmospheric levels, participates in aerosol formation with HNO_3 and can neutralize the acidity of gaseous and particle-phase acids. Knowledge of NH_3 levels is, therefore, very useful in interpreting visibility data and the spatial variability in atmospheric acidity.

Our preceding studies (1-4) evaluated and compared several procedures for nitric acid measurement. Ammonia was sampled by an impregnated filter procedure. These methods have in common the need for relatively long collection times (≥ 2 hr), water extraction and analyses for nitrate or ammonium ions. In addition, methods relying on dual filters (a prefilter to remove particulate matter with retention of the nitric acid or ammonia on an appropriate impregnated after-filter), are subject to positive errors caused by dissociation of materials such as NH_4NO_3 on the prefilter.

A recently developed procedure offers promise of overcoming many of these difficulties. The procedure employs a diffusion denuder coated with tungstic acid (5-8). This coating was reported to provide complete retention of both gaseous nitric acid and ammonia. After sample collection, both components are thermally desorbed, the NH_3 trapped by a transfer tube, and the evolved HNO_3 directly measured with a conventional chemiluminescent NO_x analyzer. Ammonia is subsequently desorbed thermally from the transfer tube, oxidized to NO and measured with the same analyzer.

Prior to the present study, only limited data were available comparing

this technique to the "denuder difference" method (4), currently favored as a reference procedure. Results obtained at Research Triangle Park, N.C. showed agreement within $\pm 20\%$ (9). However, no atmospheric comparisons had been made under conditions of relatively high nitrate such as found in California's South Coast Air Basin (SCAB).

In addition to this quasi-real time technique, a simple procedure for measuring atmospheric ammonia has been reported by Ferm in which air is drawn through a single 30 cm long oxalic acid-coated denuder tube at a low flow rate (e.g., 1-1.5 Lpm), trapping gas phase NH_3 (10). The coating and retained material are extracted by drawing water into the tube and the NH_3 determined as NH_4^+ with a specific ion electrode. The low flow rate required makes this technique appropriate for relatively long term (e.g., 12-24 hr) sampling. The accuracy and precision of this method are uncertain.

A continuous method for atmospheric NH_3 has also been reported relying on formation of a fluorescent derivative. Reproducible measurements of ≥ 0.1 ppb NH_3 are claimed, although the collection efficiency of the system for NH_3 was only 30% (11).

B. Hydrochloric Acid

Of the acids believed to exist in the polluted troposphere, probably least is known about HCl. Levels up to 8 ppb were observed in Tokyo (12), and it is possible that similar values would be observed in the SCAB. Atmospheric HCl probably results from hydrolysis of lead halides emitted from motor vehicles, from reaction of sea salt with strong acids (e.g. HNO_3), by liberation from cloud droplets containing a variety of acids and salts, and by combustion of waste products. The potential significance of HCl as an air pollutant include, an inhalation hazard possibly similar to HNO_3 , a contributor to the acidification of rain water, lakes, suspended particles and vegetation (by wet and dry deposition), and a source of errors in particulate nitrate values obtained in sampling with inert filters (14).

Consistent with the paucity of HCl data, methodology for HCl sampling remains comparatively primitive. Okita employed a dual filter procedure with the prefilter removing particulate matter and an Na_2CO_3 -impregnated after-filter collecting gaseous HCl (12). The resulting values probably represent upper limits to the true HCl levels since chloride can be released from the prefilter by reactions with strong acids.

C. Objectives of the Present Study

The present program has given principal emphasis to the semi-real time method for HNO_3 and NH_3 . The variables in design and operation were evaluated together with the influence of potential interferents. Atmospheric measurements were performed in Riverside, California to compare HNO_3 and NH_3 values with those measured by more conventional techniques. The site was chosen to provide what are probably the highest levels of both gases likely to be found in ambient air. In addition gaseous HCl was sampled to obtain what are, to our knowledge, the first urban ambient air HCl measurements in this country.

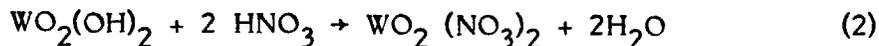
III. CONSTRUCTION AND INITIAL EVALUATION OF AN AUTOMATED MONITOR FOR HNO₃ AND NH₃

A. Chemistry of the Automated Tungstic Acid Technique (TAT)

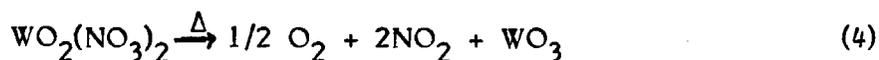
The automated tungstic acid technique (TAT) employs Vycor quartz tubes coated initially with blue tungsten oxide (W₁₈O₄₉ plus W₂₀O₅₈) which is converted by heating in O₂ to the yellow oxide, WO₃. The hydrate of this oxide H₂WO₄ or H₂W₂O₇ (also written WO₂(OH)₂), is a weak acid suggesting a surface pH of 3-4 (7). Collection of NH₃ is attributed to simple acid-base equilibria such as:



This equilibrium is reversed by heating to about 350°C. A color change appears to be associated with a change in crystal structure at 320°C. This provides a convenient method for adjusting heating temperature. The mechanism of HNO₃ sorption is unclear but was suggested (7) to involve:



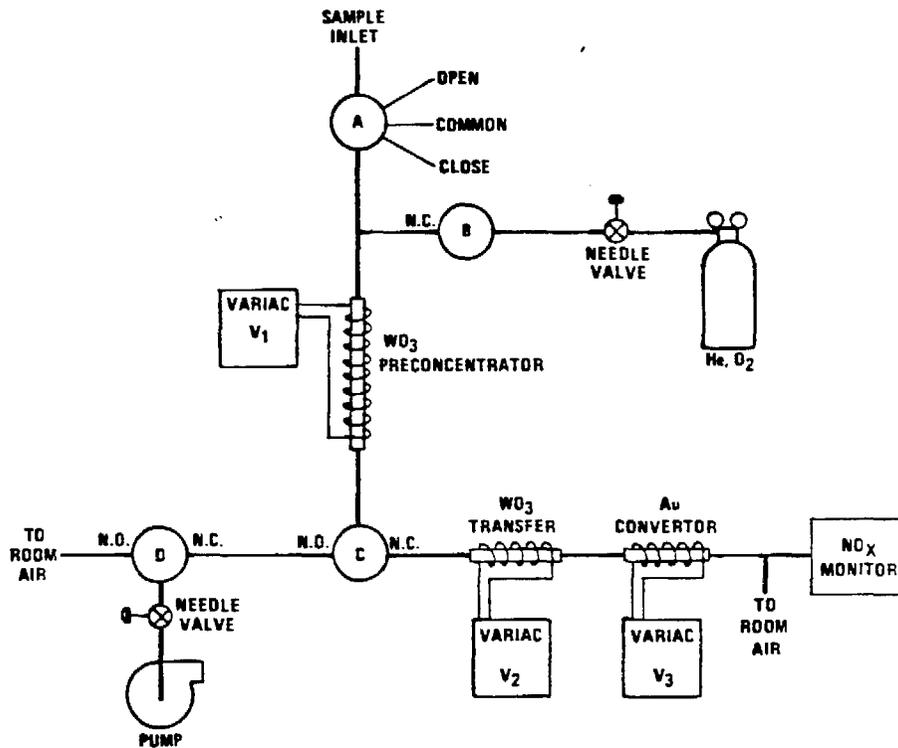
Thermal desorption is suggested (7) to proceed as follows to yield NO₂:



More recent studies (21) indicate that NO rather than NO₂ is the species formed following thermal desorption. The formation of NO rather than NO₂ is relatively insignificant, however, since, as shown below, a catalyst downstream of the preconcentrator would convert any NO₂ formed to NO.

B. Design

The automated TAT used by McClenny et al (6) is shown schematically in Figure 1. The automated TAT employed a denuder tube coated with



A = MOTOR-DRIVEN TEFLON BALL VALVE USING SEPARATE SIGNALS FOR OPENING AND CLOSING
B = NORMALLY CLOSED TWO-WAY SOLENOID VALVE
C, D = THREE-WAY TEFLON SOLENOID VALVES

Figure 1. Schematic of Automated Tungstic Acid Technique

tungstic oxide to retain both gaseous HNO_3 and NH_3 sampling ambient air at 1 Lpm (WO_3 preconcentrator). Following a sampling period of varying length depending on expected concentrations, the collected HNO_3 and NH_3 were desorbed by heating the preconcentrator tube to ca. 350°C (Variac V_1 and nichrome wire heater). The HNO_3 desorbed as NO or NO_2 , which passed through the WO_3 -coated transfer tube, was converted (if necessary) to NO on a gold catalyst heated at $> 600^\circ\text{C}$, and measured with a chemiluminescent NO_x analyzer. Ammonia desorbed from the preconcentrator column was retained on the transfer tube. Following analysis of the HNO_3 (as NO), the transfer tube was heated to ca. 350°C desorbing NH_3 which was also converted to NO on the gold catalyst and then analyzed.

McClenny's automated TAT system employed 80/20 v/v He/O_2 as a carrier during desorption. Oxygen was necessary to oxidize NH_3 to NO over the gold catalyst. However, in the automated system of Braman et al, only pure helium was used for desorption (15). Pure oxygen was introduced just ahead of the gold converter to oxidize the NH_3 . As a consequence a slow loss of preconcentrator tube activity, apparently by reduction with organic material, was experienced in this system. Consequently, periodic treatment with O_2 was necessary.

The AIHL system began with the McClenny design. The timing for activation of ball valves, solenoid valves, variacs, and integrator was provided by a Chronrol CT 5 four channel (10 program) timer unit. The unit was initially programmed for a 30 minute cycle time consisting of ten minutes sampling, seven minutes heating of the preconcentrator tube, seven minutes heating of the transfer tube and the remaining six minutes, for cool down before re-cycling. Peaks were integrated by a Hewlett-Packard Model 3380A recorder-integrator. In the prototype AIHL unit built for lab evaluation, flow rates for sampling, carrier and makeup gas (i.e. that needed to satisfy the pumping rate for the chemiluminescent NO_x analyzer) were regulated with needle valves and flowmeters. These were replaced by mass flow controllers for the atmospheric sampling unit.

C. Theoretical Performance of a Diffusion Denuder

The performance of diffusion denuder tubes having a coating of infinite capacity for the gas to be removed can be approximated by the Gormley-Kennedy equation (23). For viscous, laminar flow, and assuming retention of NH_3 and/or HNO_3 which contact the walls:

$$\frac{C}{C_0} = 0.82 \exp(-15 \Delta) + 0.098 \exp(-89 \Delta) + 0.33 \exp(228 \Delta) \quad (5)$$

Where $\Delta = DL\pi/4Q$ and

D = diffusion coefficient (cm^2/sec), = 0.25 for NH_3 , 0.15 for HNO_3 .

L = total length of tube (cm), excluding portions uncoated with WO_x .

Q = flow rate through tube (cm^3/sec)

C_0 = concentration entering tube

C = average concentration exiting tube

$(1 - C/C_0) \times 100$ = percent removal

This expression is valid if the Reynolds number is kept below 2000 to prevent turbulent flow. The Reynolds number (N_R) is given by the equation:

$$N_R = \rho d v / \eta \quad (6)$$

Where ρ = density. For air, $\rho = 1.29 \times 10^{-3} \text{ g/cm}^3$

d = tube internal diameter, cm

v = average velocity, cm/sec

n = viscosity. For air, $n = 181 \times 10^{-6}$ g/cm-sec

Employing 0.4 cm ID tubing, the Reynolds number equals 378 at 1.0 Lpm, the sampling rate used for the preconcentrator tube, and is < 200 for the carrier gas flow rates ≤ 500 mL/min.

Using a 35 cm coated length of 0.4 cm ID tubing for the preconcentrator tube, a sampling rate of 1 Lpm would provide a calculated efficiency of 99.8% for NH_3 and 98.0% for HNO_3 . An 8.6 cm coated length transfer tube, and carrier air flow rate of 500 mL/min provide a 96.1% calculated efficiency for NH_3 removal. A 10-fold decrease in carrier flow rate increases the expected removal efficiency to 100%. These calculations assume a 100% efficiency of retention of HNO_3 and NH_3 following collision with the WO_x surface.

In the automated TAT, the tungstic acid surface can be saturated with NH_3 and HNO_3 , making equation (5) potentially inaccurate for predicting the efficiency of this system. Braman et al (7) modified equation (5) by considering that the effective length, L , of the TAT tubes changed exponentially with time. At time t , the effective length is:

$$L = L_0 \exp(-kt) \quad (7)$$

Where L_0 = original effective length (35 cm)

k = tube depletion rate constant

The constant, k can be calculated, in turn, from:

$$k = \frac{\text{feed rate (ng/sec)}}{\text{tube capacity (ng)}} \quad (8)$$

Combining equation (7) and (5) and neglecting all except the first term

in equation (5), since subsequent terms are normally negligible, leads to the equation:

$$C/C_0 = 0.82 \exp \left(\frac{-15\pi D}{4 Q} L_0 \exp (-kt) \right) \quad (9)$$

Braman has observed a capacity for HNO_3 of about 600 ng. Assuming a concentration of $20 \mu\text{g}/\text{m}^3$ HNO_3 , at the end of the 10 minute sampling period used in our laboratory studies (at 1 Lpm), the efficiency is calculated as follows:

$$1 \text{ Lpm} = 1.67 \times 10^{-5} \text{ m}^3/\text{sec}$$

$$20 \mu\text{g}/\text{m}^3 = 2.0 \times 10^4 \text{ ng}/\text{m}^3$$

$$(1.67 \times 10^{-5} \text{ m}^3/\text{sec}) \times (2.0 \times 10^4 \text{ ng}/\text{m}^3) = 0.333 \text{ ng}/\text{sec} \text{ HNO}_3$$

$$k = \frac{0.333 \text{ ng}/\text{sec}}{600 \text{ ng}} = 5.55 \times 10^{-5} \text{ sec}^{-1}$$

After 10 min, $kt = 0.0333$. The flow rate Q at 1 Lpm is $16.67 \text{ cm}^3/\text{sec}$. Under these conditions, the calculated percent removal rate after 10 min. sampling is 97.8%. This compares to 98.0% calculated from equation (5). The close agreement in this case is expected since in 10 minutes the HNO_3 loading represents only one third of the expected capacity.

D. Preparation of Tungstic Oxide-Coated Tubes

The coating of tubes with WO_x by vacuum deposition involves substantially more art than science. As devised by Braman et al. (7), Vycor quartz tubes are coated with the device shown in Figure 2. An 0.02 inch diameter tungsten wire is held under spring tension along the center of the Vycor tube. The tube is mounted within a glass pipe, vacuum sealed at

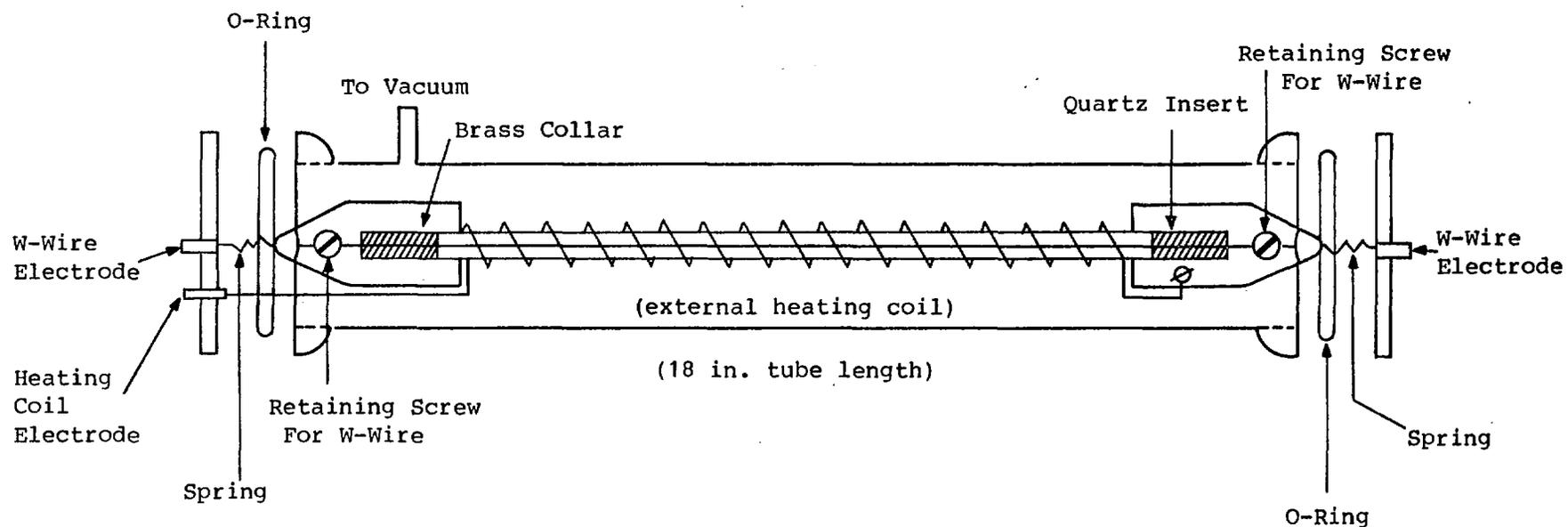


Figure 2. Apparatus for Coating Hollow Tubes with Tungsten Oxide

both ends and evacuated. A nichrome wire heating coil envelopes the Vycor tube and is used for a preliminary bakeout, supposed to remove carbonaceous material from the tungsten wire and wall of the Vycor tube. With power to the nichrome wire off, current is passed through the tungsten wire depositing a blue-black coating of tungsten oxide (believed to be a tungsten (IV) oxide) on the inner surface of the Vycor tube. After coating is completed, the blue-black coating is oxidized to the yellow tungsten VI oxide by passing O_2 through the tube while slowly heating the outside of the Vycor tube with a very short, diffuse natural gas-oxygen flame. The coating technique is detailed in Appendix A. About 20 tungstic acid coated tubes were prepared which exhibited good coating adhesion and uniformity.

Coated tubes were checked for performance with a manual TAT system by briefly sampling relatively high concentrations of HNO_3 or NH_3 , desorption from the heated tube into helium, passage of the products through a gold-coated hollow tube in the presence of oxygen (for conversion of NH_3 and NO_2 to NO) and then into a NO_x analyzer (TECO Model 14 BE). Acceptable tubes displayed a large NO_x signal whereas poor tubes were expected to show little response. None of the coated tubes tested appeared to be defective by this criterion.

E. Response Time of HNO_3 Analyzer

Initial results with the automated TAT suggested that portions of the system upstream from the preconcentrator tube were retaining and then slowly desorbing HNO_3 . To establish if the motor-driven Teflon ball valve (A in Fig. 1) was a source of significant HNO_3 retention, the complete valve unit was removed. With this configuration the atmosphere sampled was changed from dilute HNO_3 to purified air only. In contrast to the previously observed slow response, the first or second cycle following the change showed no measurable HNO_3 . It appeared, therefore, that the all-Teflon (PTFE) ball valve was the source of most, if not all of the HNO_3 retention. Careful cleaning of the ball valve had no effect.

To minimize HNO_3 contact with Teflon, the Teflon ball valve was lined with 0.4 mm I.D. Pyrex glass tubing. The change in behavior of the system was dramatic; re-equilibration within one or two cycles was now observed.

F. Efficiency of the Preconcentrator Denuder Tube for HNO_3 Collection during Automated Analysis

To assess the efficiency of the tungstic oxide denuder tube, a NaCl-impregnated Whatman 41 filter was placed downstream of the denuder tube to retain any HNO_3 penetrating the tube during sampling. Since the capacity of the tube is $< 1 \mu\text{g}$, penetration of the tube during a single sampling cycle would not be measurable by ion chromatography. Accordingly, the system was operated over a total of about 72 hours during which 4.3 m^3 of HNO_3 in air were sampled. The observed nitrate on the NaCl impregnated filter corresponded to an HNO_3 concentration of $2.6 \mu\text{g}/\text{m}^3$. Using the mean HNO_3 sampled, $49 \mu\text{g}/\text{m}^3$, the tungstic acid tube is calculated to be 95% efficient under conditions in which $\leq 700 \text{ ng}$ of HNO_3 was sampled per cycle. Further trials of denuder tube efficiency in manual operation are given in Section IV B, and yield similar results.

G. Measurement of Ammonia

Ammonia is collected together with HNO_3 , at a flow of one Lpm on a 35 cm length WO_x coating in the preconcentrator tube. The transfer tube can be shorter since NH_3 is collected following desorption from the preconcentrator tube at a flow of only 30-100 ml/min. Trials with 8.6 cm and 14.1 cm coating lengths for transfer tubes, demonstrated that the shorter tube provided adequate capacity and sharper peaks in the subsequent bake-out.

A peak occurring during bake-out of the preconcentrator tube loaded with NH_3 is an artifact here termed "apparent HNO_3 ". This error typically corresponded to 0.3% of the NH_3 peak area observed in bake-out of the

transfer tube (i.e. the peak ascribed to NH_3), and should include NH_3 desorbed from the preconcentrator tube but not retained on the transfer tube. Thus, the efficiency of the transfer tube for NH_3 retention is inferred to be $\geq 99.7\%$.

The analyzer was observed to respond rapidly to changes in NH_3 concentration. The first cycle following changes from, for example, $30 \mu\text{g}/\text{m}^3$ NH_3 to synthetic air showed negligible NH_3 peak values. Similar findings were made in returning to such relatively high NH_3 concentrations.

H. Interference Effects With the TAT

1. Introduction

Assessment of interference from NO_2 , HNO_2 and particulate nitrate was severely hampered by the response behavior of the preliminary system, which used the PTFE Teflon ball valve without glass lining. For example, changing from sampling HNO_3 to pure air required about 3 hours to achieve close to background responses. Experiments on interferent effects were designed accordingly.

2. Interference from NO_2

Nitrogen dioxide at 30 or 138 ppb was introduced into the system in air or in air containing about $50 \mu\text{g}/\text{m}^3$ (ca. 20 ppb) of nitric acid. No measurable interference was observed. This is consistent with findings by Braman et al (7). Details are given in Appendix B.

3. Interference from Nitrous Acid (HONO)

Appendix C details the procedures used for preparing the acid and assessment of interference. Because only the sum $\text{NO}_2 + \text{HONO}$ could be directly measured, only a lower limit to the true molar response of HONO was obtainable. This indicated that HONO had at least one third the molar response of nitric acid.

Additional trials with a more reliable, automated TAT configuration, and a manual TAT system are needed to confirm this. Such trials will be included in Phase II of the present study. These will also attempt to assess interference less ambiguously by excluding possible co-generated nitric acid and by measuring HONO concentrations more directly. Manual sampling of HONO with single WO_x coated tubes will also be done to eliminate possible artifacts due to memory or other effects with the automated system.

4. Interference of NH_4NO_3 Particles in Analysis of HNO_3

NH_4NO_3 particles were generated with a nebulizer system from an 0.010%w solution in water. Particle size was measured with a Royco Model 226 optical particle counter, which indicated that > 50% of all particles were $\leq 0.17 \mu m$ in optical diameter. The measurements were made both at the aerosol generator outlet and immediately downstream of the HNO_3 analyzer inlet. Loss in sample lines was found to be < 10%. The concentration of NH_4NO_3 in air was also measured by collection on prefired quartz filters at the generator outlet followed by extraction and NO_3^- determination by ion chromatography.

To insure that the analyzer was responsive, it was operated continuously with NH_3 at $33 \mu g/m^3$ for about 24 hours before switching to NH_4NO_3 . Based on the peak area for NH_3 , the limit of detection for NH_3 (with 20 min. sampling time) is estimated to be $1 \mu g/m^3$.

Trials at $28 \pm 5 \mu g/m^3$ and $69 \pm 4 \mu g/m^3$ NH_4NO_3 (as NO_3^-) showed no measurable response. Based on the estimated limit of detection for NH_3 , the interference from NH_4NO_3 is inferred to be < 7%. This finding is consistent with earlier reports showing negligible loss of NH_4NO_3 aerosol in MgO-coated denuders (1-3). Phase II will confirm these findings with the improved automated system as well as by manual sampling with WO_x -coated tubes.

I. The Influence of Operating Variables with the Automated TAT

1. Introduction

During the evolution of a workable system, laboratory trials were conducted on the influence of such variables as carrier gas type and flow rates, temperature for desorption, and location for introducing makeup air and O₂ needed for catalytic oxidation of NH₃. Because many of the variables appear to be interactive, it is unclear that the results and conclusions of some of these trials are relevant to the design subsequently employed for atmospheric sampling. For purpose of the present report, only evaluations clearly relevant to the atmospheric sampling design are mentioned.

Desorption of HNO₃ from the preconcentrator tube must be accompanied by reduction to NO₂ or NO to avoid capture on the transfer tube and subsequent measurement as apparent NH₃. Such a process should be favored by a high desorption temperature, a relatively slow carrier flow rate, and, possibly, by use of an inert carrier gas. Ammonia desorption must occur as NH₃. Thus chemical transformations should be minimized. The possibility of readsorption of NH₃ in the preconcentrator tube must be minimized, for example, by a high carrier flow rate. However, the carrier flow rate must not be so high as to diminish the efficiency of the transfer tube to trap NH₃. As with HNO₃, an inert carrier might increase the efficiency of transfer of NH₃ to the transfer tube. Since desorption of NH₃ from the transfer tube is followed by oxidation on a gold catalyst at about 625°C, a process which required oxygen, an inert gas cannot be used for the complete analytical cycle.

Substantial effort was devoted to evaluate the automated TAT employing purified ambient air for desorption and to provide the makeup air needed by the NO_x analyzer. The objective was to eliminate reliance on compressed gas cylinders, a marked disadvantage for prolonged atmospheric sampling.

2. Influence of Carrier Gas Type

To maximize the response of the preliminary automated TAT to both HNO₃ and NH₃ a strategy was adopted in which HNO₃ thermal desorption for initial 3 minutes of the preconcentrator tube heating cycle was done at 60 mL/min helium flow rate*. During this 3 minute period the peak due to HNO₃ is observed, and the NO_x response returns to baseline. The remaining 6 minutes of the heating period employed a flow of ca. 500 mL/min carrier air (plus the helium flow at 60 mL/min) initially intended to achieve efficient transfer of NH₃ to the transfer tube.

Helium was compared to air as the carrier gas for desorption of HNO₃ during the initial 3 minutes of the preconcentrator tube heating cycle. As shown in Table 1, helium yielded a 30-40% increase in HNO₃ response.

TABLE 1
Comparison of Helium and Air as Initial Carrier Gases
in Nitric Acid Determination^{a,b}

Date	Time Period	N	Initial Carrier Gas	Preconcentrator Voltage (Variac Setting)	Peak Areas X 10 ⁻⁶	
					HNO ₃	NH ₃ ^c
3/1/84	0800-1030	5	Helium	95	4.88 ± 0.47	0.49 ± 0.10
	1030-1530	10	air	95	3.71 ± 0.30	0.41 ± 0.05
3/2/84	1330-1600	6	Helium	80	3.93 ± 0.08	0.23 ± 0.01
	1630-1730	3	air	80	2.79 ± 0.20	0.33 ± 0.02

- a. Initial flowrate set by flowmeter = 57 mL/min with air. The same flowmeter setting was used with helium, which subsequently was shown to correspond to about 40 mL/min helium.
- b. HNO₃ concentration estimated at 50 ± 10 µg/m³.
- c. Peak area for "apparent NH₃", possibly an artifact.

*Flow rate measured with a rotameter without correction for use of helium. The flow rate measured with mass flow meter was 40 mL/min. The difference between 40 and 60 mL/min is not considered significant.

3. Use of Purified Ambient Air for Makeup and Carrier Gas

Ambient air was purified by passage through a Bendix Model 8833 system utilizing activated charcoal, permanganate-impregnated molecular sieve and an efficient particle filter. Nitric oxide (NO) was not completely removed and yielded a varying baseline. The reproducibility of the automated TAT appeared to be poorer when relying on such air for both makeup and carrier gases compared to the use of bottled gases. Accordingly, this approach was abandoned.

IV. AN IMPROVED, AUTOMATED HNO_3 - NH_3 MONITOR FOR SAMPLING IN RIVERSIDE

A. Introduction

This section describes (1) studies with a manual WO_x technique used to design an improved, automated method, (2) the automated system employed in atmospheric sampling in Riverside, (3) calibration results obtained during atmospheric sampling with the automated TAT, and (4) laboratory studies, principally with NH_3 to elucidate the problems experienced during atmospheric sampling.

B. Preliminary Studies with a Manual Tungstic Oxide Technique

To obtain understanding of the behavior of individual components of an automated TAT system, a manual procedure was employed consisting of a WO_x preconcentrator tube with and without a transfer tube, a gold NO_x catalyst converter, and an NO_x monitor. This was used to evaluate (1) the rate of desorption of NH_3 and HNO_3 from the tubes during heating, (2) the efficiency of a preconcentrator tube for NH_3 and HNO_3 , (3) the extent of artifacts due to various components of the automated system, and (4) desirable changes in the automated system to improve reliability and minimize errors. In addition, following atmospheric sampling, problems encountered with NH_3 sampling and calibration were investigated with a manual TAT.

Denuder tubes sampled HNO_3 or NH_3 from diffusion or permeation tubes after dilution with particle free room air. These were thermally desorbed from the tubes with helium at 50 mL/min and mixed with about 700 mL/min O_2 prior to entry in the gold catalyst. The converter consisted of a 4 mm I.D. tube coated on its interior with metallic gold and heated with a nichrome wire heater at dull red heat.

Both NH_3 and HNO_3 yielded very sharp peaks without tailing (retention times 38 sec for HNO_3 , about 46 sec for NH_3). When NH_3 and HNO_3

were desorbed together, the peaks were not completely resolved regardless of the desorption temperature. To assess efficiency, two tubes in series were used for sampling and the relative amounts of NO_x determined on heating each tube. Table 2 summarizes the data obtained and indicates a single tube efficiency of 93 to 98% at 1 Lpm with 340-1000 ng dosages of HNO_3 and similar values for NH_3 .

TABLE 2

Efficiency of Denuder Sampling for HNO_3 and NH_3 ^{a,b}

Gas	Loading Time (min)	Dosage (ng)	Efficiency, %	Mean Efficiency, %
HNO_3	1.0	342	99.7	97.7 ± 1.6
	1.0	342	97.5	
	1.0	342	97.7	
	1.0	342	95.9	
HNO_3	1.5	513	94.3	95.8 ± 2.0
	1.5	513	97.2	
HNO_3	2.0	684	94.8	93.2 ± 2.8
	2.0	684	95.9	
	2.0	684	89.7	
	2.0	684	92.3	
HNO_3	3.0	1026	91.4	91.4
NH_3	2.0	- ^c	97.1	98.0 ± 1.7
	2.0	-	99.2	
	2.0	-	96.0	
	2.0	-	99.5	

- a. Sampling rate 1.0 Lpm.
- b. HNO_3 conc. $342 \pm 73 \mu\text{g}/\text{m}^3$.
- c. Not determined.

To simulate more closely the automated system used for monitoring NH_3 and HNO_3 simultaneously, a transfer tube was attached to the downstream

end of the preconcentrator tube. The extent of NH_3 penetration to the detector during heating of the preconcentrator tube (i.e. artifact HNO_3) was determined to be $\leq 4\%$. Similarly, with nitric acid, retention and subsequent analysis of HNO_3 during heating of the transfer tube (i.e. artifact NH_3) was measured and found to be $< 3\%$.

The Teflon 3-way solenoid valve used between the preconcentrator tube and transfer tube in the automated system (valve C in Fig. 1) was added to the manual system. The preconcentrator was heated for 2-3 minutes to achieve removal of either NH_3 or HNO_3 . The transfer tube was then heated.

The level of artifact NH_3 was $\leq 5\%$ of the HNO_3 concentration measured. Similarly, with NH_3 the artifact HNO_3 was $< 4\%$ of the NH_3 measured. Thus the solenoid valve did not appear to introduce substantial error under these conditions.

Finally, the motor driven ball valve for the inlet of the automated system (valve A, fig. 1) was attached ahead of the preconcentrator tube and one or two minute samples drawn in through this valve, venting the flow through the 3-way solenoid valve (i.e. by-passing the transfer tube as in the automated method). Again, no significant sampling artifacts were observed in sampling relatively large dosages of either HNO_3 or NH_3 .

C. The Automated TAT Design Used for Atmospheric Sampling

Based on results with the manual system, as well as studies described in Section III I, the automated system was altered as follows:

1. The carrier gas for desorption and transfer of HNO_3 and NH_3 was changed to helium only using a flow rate of 50-70 mL/min. This eliminated the introduction of an air carrier following emergence of the HNO_3 peak since NH_3 could be effectively transferred with helium at ≥ 50 mL/min.

2. The heating times for the preconcentrator and transfer tubes were each reduced to 3 min. This permitted a change from a 30 min cycle to one as short as 15 minute.
3. The 4 mm I.D. tube coated with gold on its interior replaced the strip of gold foil used previously for catalytic conversion of NO_2 and NH_3 to NO^* .
4. A TECO 14BE was used in place of the Monitor Labs NO_x analyzer since the TECO yielded much higher resolution.
5. Zero air, required to aid oxidation over the gold catalyst and to make up the difference between the NO_x analyzer sampling rate and the helium flow rate was altered to be introduced between the transfer tube and gold catalyst rather than ahead of the preconcentrator tube.

An automated TAT unit suitable for field use was constructed in two modules, each in a wooden box for ruggedness and portability. One module contained the Chronrol program module timer, three mass flow controllers and three variable transformers. The second included all solenoid valves, the preconcentrator and transfer tubes, tube heaters, catalytic converter for NH_3 , and glass flowmeters to verify the functioning of the mass flow controllers.

The sample inlet consisted of a 6 mm I.D. inverted U tube, total length about 15 cm, followed by Teflon fittings, and the glass-lined, motor driven ball valve. Beyond the valve, the sample passed through about 15 cm of pyrex or quartz tubing before reaching the WO_x coated section of the quartz tube.

The operating strategy for the automated TAT used in Riverside is summarized in Table 3.

*It was subsequently found that gold in these coated tubes was lost at an excessive rate at the $>600^\circ\text{C}$ temperature required for NH_3 conversion (i.e. the gold foil catalyst was preferable).

TABLE 3
Operating Strategy for the Automated TAT During Automated Sampling

Time From Start of Cycle, min	Function
0 to x where x = 5 to 30	Ambient air sampling
x to (x + 3)	Desorption of HNO ₃ and NH ₃ from preconcentrator tube with He ³ carrier
(x + 3) to (x + 6)	Desorption of NH ₃ from transfer tube with the carrier at 70 mL/min
(x + 6) to (x + 10)	Cool down for next cycle
Heater Voltages:	Preconcentrator - 95V Transfer tube - 45V Au Catalyst tube - 75V
Flow rates:	Helium carrier - 60 mL/min Synthetic air for makeup - 470 mL/min Sampling rate 0.96 Lpm

D. Strategies for Calibration

Two calibration strategies for HNO₃ and NH₃ were considered: (1) HNO₃ (from a diffusion tube) or NH₃ (from a permeation tube) were separately introduced into a ca. 3 cfm volume of dilution air, and the diluted gases sampled simultaneously with the TAT and impregnated filters. TAT sampling times were held constant and the calibration gas concentration altered by changing the degree of dilution or the oven temperature for the diffusion or permeation tube. This strategy most closely resembled ambient air sampling in that the sample was drawn through the Teflon ball valve inlet, and no alteration of the TAT was required. (2) HNO₃ and NH₃ from constant temperature sources were sampled by manually attaching the WO_x preconcentrator tube to the source over which 1 Lpm of filtered room air was passed. Dosage was varied by changing the sampling time.

Comparing these two options, it is strongly preferable to calibrate the TAT without the need to dismantle the system to remove the WO_x -coated preconcentrator tube. However, efforts to employ technique (1) yielded variable and unpredictable results. Memory effects caused by sorption of HNO_3 and NH_3 on glass and Teflon surfaces appeared to contribute to these problems. The alternative of maintaining constant concentration but varying TAT sampling times was not explored but holds promise for work during Phase II. Manual loading of WO_x tubes was adopted for use in atmospheric sampling in Riverside.

E. Reproducibility of the HNO_3 Calibration During Atmospheric Sampling in Riverside

Nitric acid was supplied by a wafer type permeation tube maintained at a temperature of $83 \pm 0.2^\circ C$ in a Metronics Dynacalibrator oven with a flow rate over the wafer of 1 Lpm. Dilution air was supplied by drawing ambient air through a glass fiber filter followed by a NaCl-impregnated filter to remove atmospheric particles and HNO_3 . The output of HNO_3 from the wafer was monitored by sampling with an NaCl-impregnated filter for 8-24 hr periods. Since the entire output of the wafer passed through the filter or WO_x tube, accurate flow measurement was unnecessary; the output was calculated in ng/min. For six filter samples collected throughout the period of atmospheric sampling, the mean output was 96 ± 9 ng/min.

The TAT was calibrated each morning between 0530 and 0830 hrs. Results for nine calibrations, based, with one exception, on 4-8 data points spanning the range expected during atmospheric sampling, are shown in Table 4. To assess the reproducibility of the calibration from day to day at a typical daytime HNO_3 dosage, the HNO_3 corresponding to 2×10^6 area units was calculated by each of the regression equations. From the nine equations the mean HNO_3 was 100.0 ± 10.5 ng for a C.V. of 10.5%.

TABLE 4

Compilation of HNO₃ Calibration Results^a

Date	Time	Intercept	Slope	r	n
9/07/84	evening-2200	-0.0109	0.0186	0.972	7
9/08/84	0600-0800	-0.0297	0.0178	0.993	5
9/15/84	0900-1200	-0.306	0.0257	0.937	8
9/16/84	0600-0900	-0.350	0.0225	0.994	6
9/17/84	0530-0900	+0.136	0.0166	0.992	5
9/18/84	0530-0900	+0.074	0.0203	0.999	4
9/19/84	0530-0700	-0.54	0.0253	0.995	6
9/20/84	0700-0830	-0.209	0.0237	0.996	5
9/21/84	0700-0830	-0.394	0.0236	0.999	3

- a. $y = a + bx$
 $y = \text{Pk Area (Area units } \times 10^{-6})$
 $x = \text{ng HNO}_3 \text{ (as NO}_3^-)$
 $r = \text{Pearson's correlation coefficient}$
 $n = \text{number of data points (generally includes two replicates at each level).}$

F. Calibration for NH₃ During Atmospheric Sampling

During atmospheric sampling, ammonia in air was supplied by a permeation tube maintained at $22.4 \pm 0.2^\circ\text{C}$ in a Wallace-Fisher oven inside an air-conditioned mobile laboratory. The flow over the tube was about 1 Lpm of ambient air which had passed through a glass fiber filter followed by a denuder tube coated with phosphorus acid to remove NH₃. The NH₃ emission rate was measured by sampling the total flow through two tandem oxalic acid-impregnated quartz filters. For seven sampling periods, the mean emission rate was 272 ± 33 ng/min.

Substantial difficulties were encountered in calibrating the TAT for NH₃ including lack of reproducibility and non-linearity of response. Atmospheric sampling results frequently exhibited relatively high NH₃ response or negligible values, implying a loss of system conditioning unless high NH₃ levels were encountered. The following section describes supplementary laboratory studies intended to elucidate and overcome these difficulties.

G. Laboratory Evaluation of the Automated TAT Response to NH₃ Following Atmospheric Sampling

To elucidate the problems encountered with NH₃ calibration and measurements, additional laboratory trials were made. The difference between ambient air temperature (24 hr mean temperature 26-30°C) and laboratory air temperature (estimated 20-24°C) was the only apparent change in condition. No modifications to the automated TAT were made and the system was deliberately not cleaned.

The elevated response observed with low dosages of added NH₃ was apparently due, in part, to contamination of the system during atmospheric sampling. Washing of fittings between the transfer tube and gold coated tube NH₃ converter as well as the solenoid valve (C in fig. 1) between the preconcentrator and transfer tubes diminished the NH₃ response. It is unclear how frequently such cleaning is necessary during atmospheric sampling. Response of the analyzer after such cleaning remained unreproducible, however.

In an effort to improve the reproducibility of the analyzer, the transfer tube was replaced with a fresh one and the gold-coated NH₃ converter tube (about 50% devoid of Au coating) replaced with a tube containing gold foil. The linearity of response was substantially improved. The observed ammonia response was now:

$$y = 1.01 + 0.0256x$$

$$r = 0.96$$

where y = integrator peak area in units 10^6 area units

$$x = \mu\text{g NH}_3 \text{ (as NH}_4^+) \text{ in the range 23 to 204 ng NH}_3.$$

The instrument performance remained erratic, however, with dosages ≤ 45 ng.

A clue to the more fundamental problem with NH_3 sampling was provided by observations of substantial ammonia peaks when helium or other gas scrubbed free of NH_3 was sampled. Furthermore, a clean 50 cm quartz tube (i.e. without WO_x coating) retained NH_3 effectively when dosages of ca. 100 ng were sampled. It appears, therefore, that substantial amounts of NH_3 are retained on glass tubing walls ahead of the tube and/or on the ca. 8 cm uncoated section* of the quartz tube. When the WO_x tube was removed for dosing with NH_3 and then replaced, the heating coil was not repositioned in precisely the same location. Thus a variable amount of the NH_3 collected ahead of the WO_x coating may have desorbed. The ability of the glass and/or quartz tubing ahead of the WO_x coating to retain NH_3 may account for the difficulties in preconditioning the system for NH_3 .

*A clear section ahead of the WO_x coating is intended to insure laminar flow.

V. LABORATORY EVALUATION OF AMMONIA SAMPLING WITH OXALIC ACID-COATED DENUDER TUBES

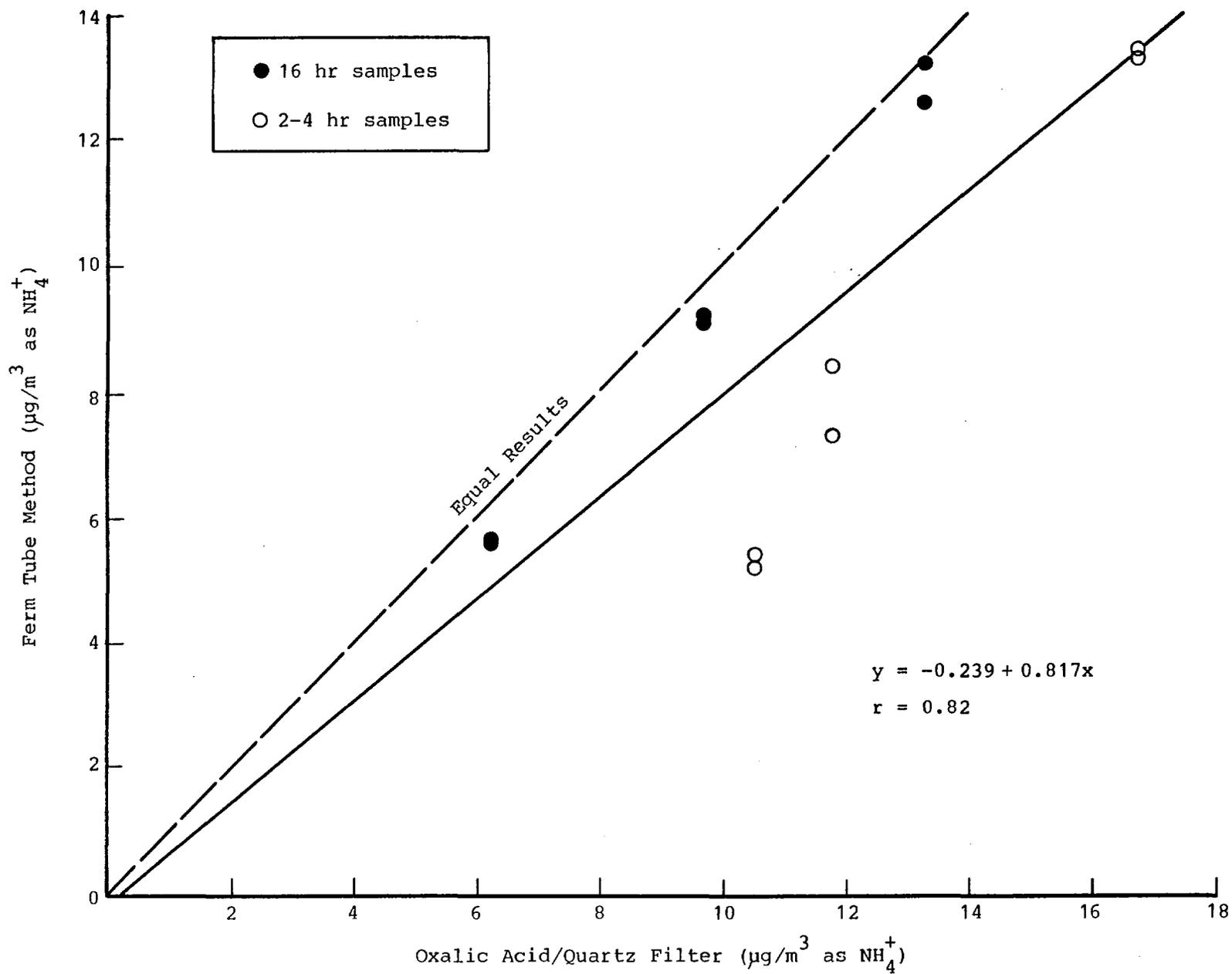
A. Experimental

Oxalic acid-glycerol coated denuder tubes were compared to oxalic acid-glycerol impregnated filters for NH_3 collection. The latter had previously been shown by us to collect $> 99\%$ NH_3 at 100 ppb and 50% R.H. Glass tubes, etched for 3 min in 50% HF, were coated with a methanol solution containing 1.5% oxalic acid and 7.2% glycerol. The solvent was removed by passing N_2 (99.999%) through each tube for 4-5 min. The mean tube blank was $0.24 \pm 0.08 \mu\text{g NH}_4^+$. The Ferm tubes sampling at 1 Lpm were compared to oxalic acid impregnated, 47 mm quartz fiber (PallFlex QAO) filters sampling at 15 Lpm. Identical lengths of pyrex tubing were used ahead of all samplers to equalize losses to inlet surfaces.

B. Results

Figure 3 compares results for 16-hr (solid dots) and 4 ± 1 -hr trials (open dots). The long term samples showed nearly equal results by the two methods, whereas the short term samples differed by about 50%. Including all samples, the regression equation shows about 20% lower values by the Ferm tube method. Since atmospheric sampling for NH_3 was to be done for 12-hr and 24-hour periods with the tubes prepared as described, nearly quantitative collection of atmospheric NH_3 by the denuder tube as well as the filter method, was expected.

Figure 3. Laboratory Comparison of Denuder Tube and Filter NH₃ Determinations



VI. LABORATORY EVALUATION OF HYDROCHLORIC ACID SAMPLING

A. Introduction

A dual filter technique for gaseous HCl was evaluated in which particulate chloride was removed by a Teflon prefilter and the gaseous HCl captured with a cellulose filter impregnated with a mixture of triethanolamine and KOH. The choice of this technique was based largely on the report of its high efficiency at hi-vol sampler face velocity (14). If confirmed, such sampling would permit relatively short-term (e.g., 4-hr) HCl sampling and, therefore, assessment of diurnal concentration changes.

The objectives of the laboratory experiments were (1) to measure single triethanolamine-KOH filter efficiency, (2) to measure loss of HCl by sorption-desorption on clean Teflon prefilters and on the filter holder, and (3) to evaluate alternative filter configurations for ambient air sampling.

When applied to atmospheric sampling, the chloride measured on the impregnated filter was taken to be the upper limit concentration for atmospheric HCl.

B. Experimental

Gaseous HCl in N₂ was introduced into an airstream purified by passage through charcoal, Purafil, triethanolamine/diatomaceous earth and a HEPA filter. The temperature of the airstream and relative humidity were held constant within 0.5°C and 1% R.H., respectively. After vortex mixing, the diluted HCl was sampled simultaneously with five samplers:

- A. A 47 mm diameter, 2 µm pore size Teflon (Zefluor) pre-filter and a 47 mm triethanolamine-KOH impregnated Whatman 41 (T-K) after-filter contained in separate sections of a Nuclepore dual filter holder (Figure 4). The filters were extracted and analyzed separately.

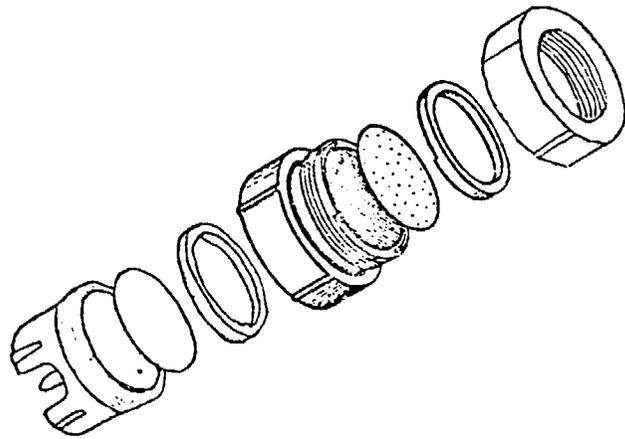


Figure 4. Nuclepore Multiple Holder Adapter for Collection on Several Filters in Series

- B. The same filters as in A contained in a single-stage Nuclepore filter holder without a spacer between the filters. The filters were extracted and analyzed together.
- C. The same filters and filter holder as in (B) but with a 1000 μm hole size Teflon mesh separating the filters. To achieve an airtight seal it was necessary to use an anodized aluminum filter holder in place of the plastic Nuclepore holder. The filters were extracted and analyzed separately.
- D. Two T-K filters contained in the same Nuclepore filter holder without a spacer between filters. The filters were extracted and analyzed together.
- E. Two T-K filters each contained in separate sections of a Nuclepore dual filter holder. The filters were extracted and analyzed separately.

All samplers operated at 37.4 Lpm to provide a face velocity approximately equal to that of a hi-vol sampler with 8" x 10" filter at 40 cfm.

Storage of samples prior to extraction was at $\leq 5^{\circ}\text{C}$. The filters were extracted in 10 ml of 0.002 M NaHCO_3 by mechanical shaking for 1 hour at room temperature, in plastic screw-capped test tubes. The Teflon filters and Teflon plus T-K filter were agitated for an additional 30-60 min. with a Fisher RotoRack, also at room temperature. Chloride analysis was by ion chromatography. Experiments were conducted at two HCl concentration levels, 4-5 $\mu\text{g}/\text{m}^3$ and 20-25 $\mu\text{g}/\text{m}^3$ with 3 replications at each level. Samples were collected for four hours at low concentrations and for two hours at the higher concentrations.

C. Results

Chloride recovered from sampler D was used as a measure of the true HCl concentration. Results are expressed as a percent of the sampler D concentration. This strategy is supported by (1) the high single T-K

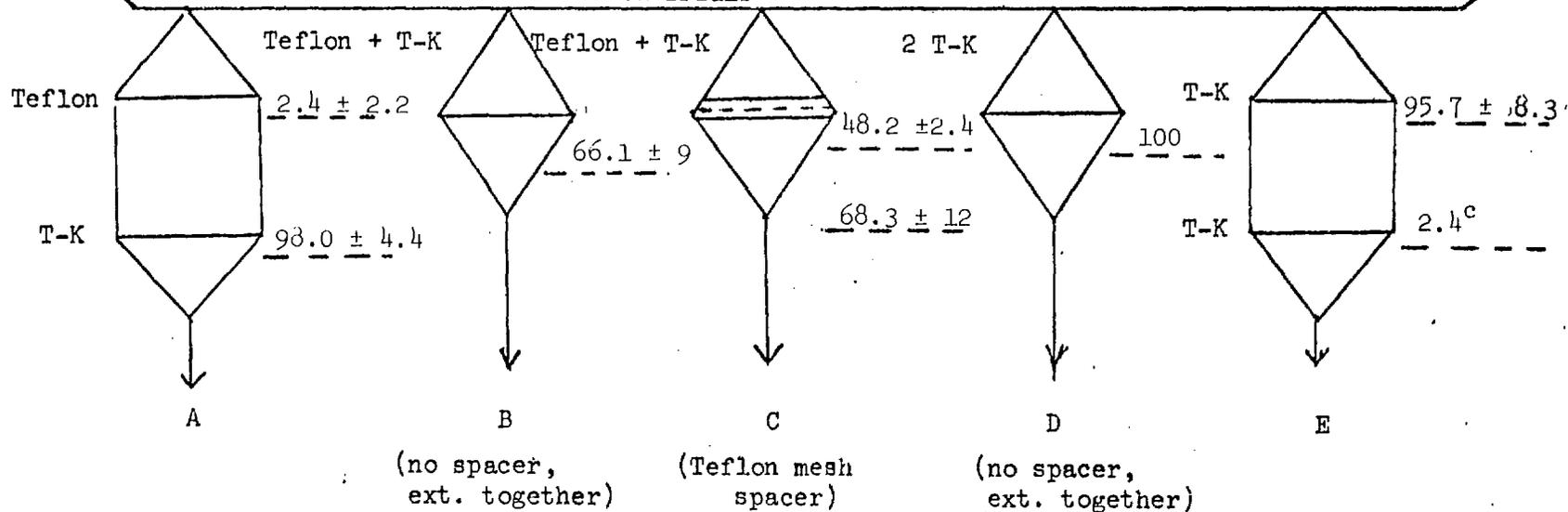
filter efficiency demonstrated below, and (2) the minimal filter holder surfaces exposed to HCl in this configuration, minimizing possible losses.

Figures 5a and 5b show schematically the experimental design as well as mean results for the low and high concentration trials, respectively. Single T-K filter efficiency can be inferred from the results for sampler E and A. Sampler E indicates a mean efficiency of 96% for one T-K filter at both concentrations. The mean Cl^- on the T-K after-filter of sampler E, 0.5 and 2.4%, suggests that the T-K prefilter was > 97% efficient. Because of possible loss to the filter holder, this is an upper limit value. The sampler A results indicate a loss of about 8% HCl at high concentration and complete recovery at low concentration. Because of HCl retention on Teflon and loss to filter holder surfaces, the value 89.3% for sampler A (Figure 5b) is a lower limit to the single filter efficiency for T-K filters.

Recovery of HCl from atmospheric particle-free Teflon filters reflects the net result of sorption and desorption. Results with sampler A suggest only a small degree of retention, if any (mean 2.4%). Eight percent of the HCl is unaccounted for and may have been lost by desorption from the prefilter prior to extraction in spite of refrigerated storage. Sorption on the prefilter support and walls of the sampler probably contribute to the 8% loss, as well. Lower and upper limit measurements for HCl retention on Teflon filters are $2.4 \pm 4.2\%$ and $8.4 \pm 7.2\%$, respectively.

Loss of HCl to the prefilter support and/or walls of the Nuclepore filter holder is best measured by sampler A. Consistent with the preceding discussion, this could range from 0 to 8.4%. The results for sampler B show loss of 24-34% of the HCl sampled. The reason for the greater loss compared to sampler A was not firmly established. Interference by

Figure 5a. Efficiency of HCl Collection on Teflon Plus Triethanolamine-KOH (T-K) Impregnated Filters (% Relative to Sampler D)^a
 Low Concentration Trials^b

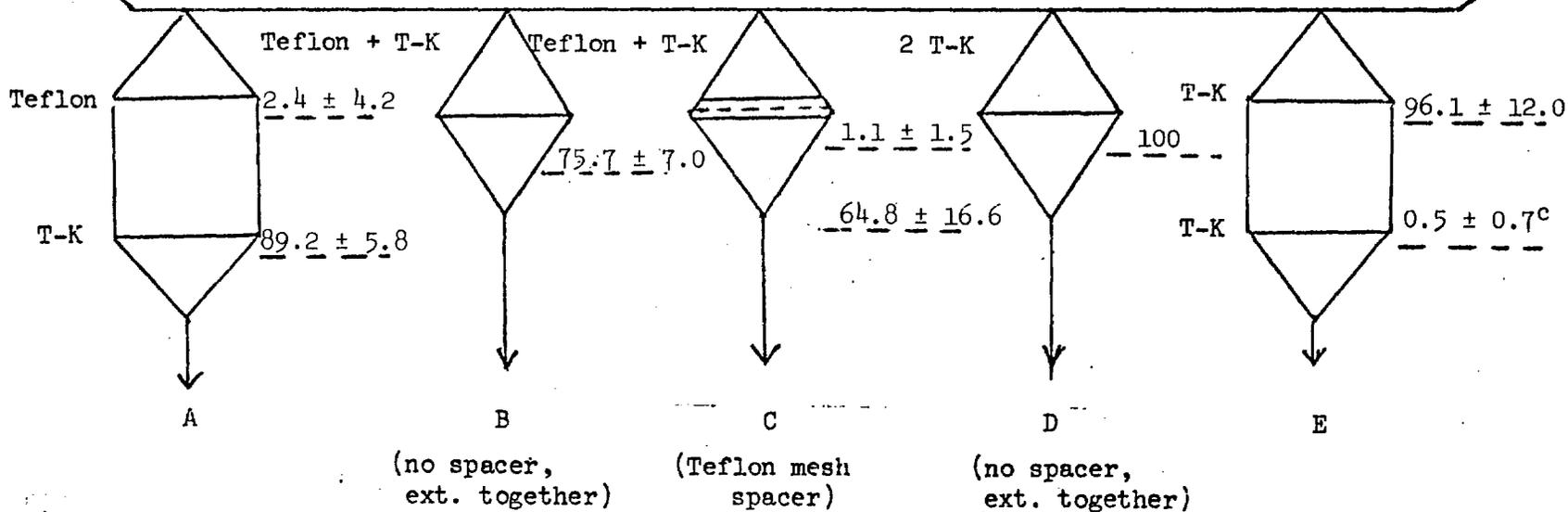


a. Experimental conditions: 50% R.H.
 Flow rates 37.4 LPM
 Temp. 20 °C
 Sampling time 5 hr

b. Concentrations for 3 trials: 3.7, 4.8 and 4.5 µg/m³, respectively.

c. Single trial. Two values discarded as unreliable.

Figure 5b. Efficiency of HCl Collection on Teflon Plus Triethanolamine-KOH (T-K) Impregnated Filters (% Relative to Sampler D)^a
High Concentration Trials^b



- 37 -

a. Experimental conditions: 50% R.H.
Flow rates 37.4 LPM
Temp. 20 °C
Sampling time 2 hr

b. Concentrations for 3 trials: 19.6, 22.8 and 25.7 µg/m³, respectively.

c. Two values averaged. Outlier discarded.

the Teflon filter extraction of the T-K filter was not the problem since, in water, the filters pieces separated due to the density difference. However, it was subsequently demonstrated that with a Teflon and T-K filter in the same Nuclepore holder, a vacuum tight seal was not readily achieved. Sampler leakage is the most likely explanation for the greater loss of sampler B.

Regarding possible atmospheric sampling options, samplers A and C, permitting separate analysis of particulate and gaseous chloride (presumed to be mainly HCl in the atmosphere), were the two techniques considered. The consistently low recovery of gaseous chloride with sampler C (65-68%) compared to 89-98% with Sampler A may reflect HCl loss to the anodized aluminum filter holder, and/or to the Teflon mesh, as well as poor sealing of the dual filter plus spacer sandwiched in the holder. The latter is less likely, however, since the loaded filter holder was checked for vacuum tightness before starting HCl collection.

We conclude from this work that for HCl dosages of 36-112 μg sampled at a face velocity of 47 cm/sec:

1. Single T-K filter efficiency for HCl is at least 96%.
2. Retention of gaseous HCl on Teflon filters is at least 2.4%.
3. The configuration shown as Sampler C (Figures 5a and 5b) should not be used for atmospheric sampling because of HCl loss to the analyzed aluminum filter holder and/or the Teflon mesh spacer.
4. Atmospheric sampling should be done with a system analogous to sampler A. By using 88 mm diameter filters* at a flow rate of 4 cfm (face velocity 34.9 cm/sec), relatively short term (e.g., 4-hr) sample collection can be used.

*Two dual filter samplers designed to minimize filter support surface area to minimize losses of reactive gases were furnished by B. Huebert.

VII. ATMOSPHERIC SAMPLING

A. Introduction

Atmospheric sampling was done on the campus of the University of California (Riverside) in collaboration with the Statewide Air Pollution Research Center. The samplers and sampling strategy employed are detailed in Table 5.

The principal objectives of this sampling were:

- (1) to evaluate the performance of the automated TAT for HNO_3 and NH_3 measurement.
- (2) to obtain HNO_3 measurements by the denuder difference technique (i.e. sampler 3 NO_3^- -sampler 2 NO_3^-) for comparison with the automated TAT.
- (3) to obtain measurements of NH_3 by oxalic acid-coated denuder tube and filter collection methods for comparison with one another and with NH_3 by the automated TAT.
- (4) to measure upper limit values for atmospheric HCl by a dual filter technique.

These measurements were supplemented by those for O_3 , NO , NO_2 , dewpoint and temperature to aid in data interpretation.

Simultaneous measurements with these samplers were performed for the period 1600 hr 9/7 to 0800 hr, 9/9 and, again, from 1200 hr 9/15 to 1200 hr 9/21/84. The first period was characterized by exceptionally low pollution levels. Accordingly, sampling was suspended. The second period included days of moderate-to-heavy photochemical smog (O_3 maxima > 0.3 ppm).

TABLE 5.
Sampling Strategy - Riverside, September 1984

Sampler Number	Sampler	Collection Medium	Samples/day	Sampling Rate, Lpm	Species Measurement
1	TAT	WO _x	Semi-continuous	1.0	HNO ₃ , NH ₃
2	total fine NO ₃ ⁻	Nylon ^a filter (following MgO-coated denuder)	5 ^b	20	fine NO ₃ ⁻ , SO ₄ ⁼
3	fine particle NO ₃ ⁻	Nylon filter	5	20	fine NO ₃ ⁻ , SO ₄ ⁼ + HNO ₃
4	Ferm tube	oxalic acid	2	1.0	NH ₃
5	Ferm tube	oxalic acid	1	1.0	NH ₃
6	dual filter NH ₃	Teflon ^c prefilter 2 oxalic acid/quartz ^d filters	5 5	25 25	NH ₄ ⁺ (particle phase) NH ₃ (gas phase)
7	dual filter HCl	Teflon ^e prefilter KOH-TEA/Whatman 41 filters	3 5	4.0 cfm 4.0 cfm	Cl ⁻ (particle phase) Cl ⁻ (gas phase)
8	Hi-Vol	glass fiber ^f filter	1	40 cfm	NO ₃ ⁻ , SO ₄ ⁼
	chemiluminescent NO _x (Monitor Labs)	-----	Continuous	0.75	NO, NO ₂
	dew point	-----	Continuous		dew point
	Dasibi O ₃ monitor	-----	Continuous		O ₃
	Resistance thermometer device	-----	Continuous		temperature

- a. Nylasorb (47 mm dia.) filters, Membrana Corp.
b. 0800-2400 hr, 4 hour samples. 0000-0800 hr, one sample.
c. Two μm pore size Zeflour (47 mm dia.), Membrana Corp.
d. Pallflex 2500 QAO (47 mm dia.) quartz fiber filters.
e. Three μm pore size Zefluor (88 mm dia.), Membrana Corp.
f. Schleicher and Schuell, 1HV filters (1981 EPA-Grade).

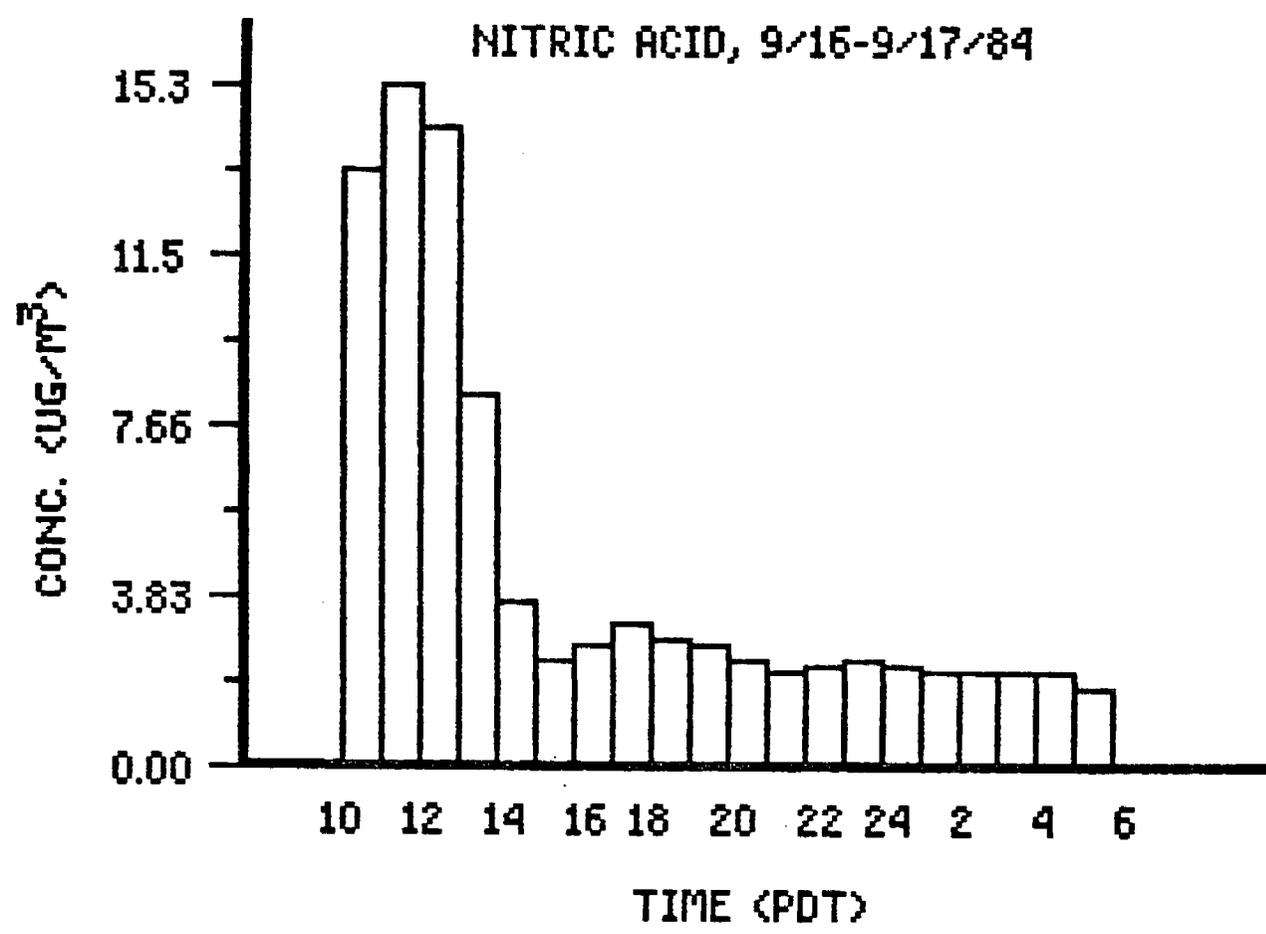
B. Semi-Real Time Nitric Acid Results

For the period 2200 hours, 9/7 - 0700 9/8, the HNO_3 concentration, measured with the automated TAT, ranged from 0.6 to 0.8 $\mu\text{g}/\text{m}^3$. During the daytime period, 0800 - 1700 hr 9/8, the concentration ranged from 0.6 to 1.6 $\mu\text{g}/\text{m}^3$ with maxima at 0900 - 0930 and 1330 - 1400 hours. These relatively low values were consistent with ozone concentration < 0.05 ppm.

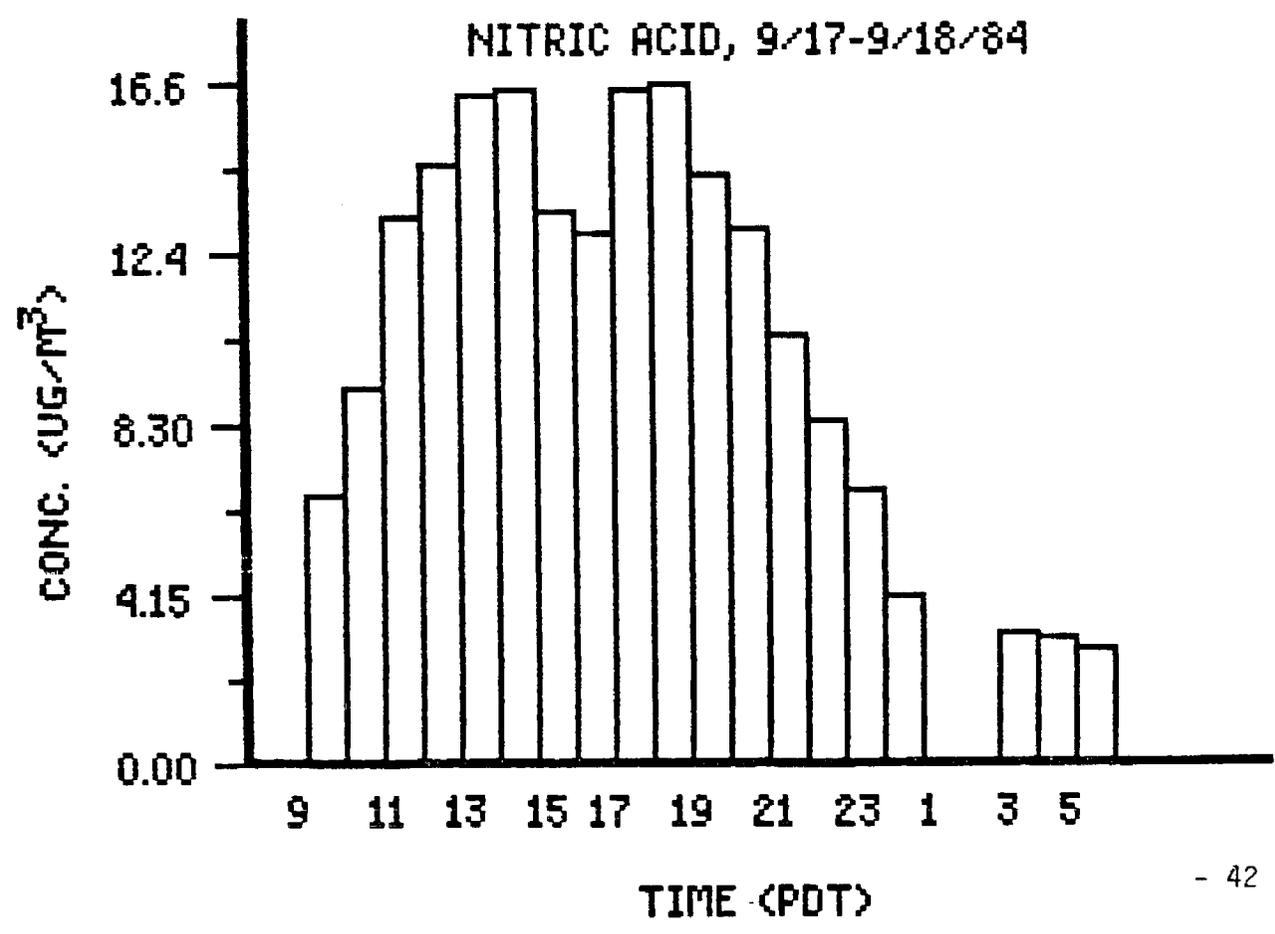
Nitric acid measurements resumed at noon, 9/15/84 with concentrations ranging from 3 to 6 $\mu\text{g}/\text{m}^3$. However equipment failure prevented measurements after 2200 hr. Nitric acid concentrations for five successive 24-hour periods beginning 9/16/84 are shown in Figures 6-10. Concentrations are shown as one hour average values. For periods beginning 9/16 and 9/17, hourly averages are based upon two, 20 minute samples per hour. For the remaining days, hourly averages are based on four, 5 minute samples per hour. Such short sampling times were needed to prevent saturation of the preconcentrator tube.

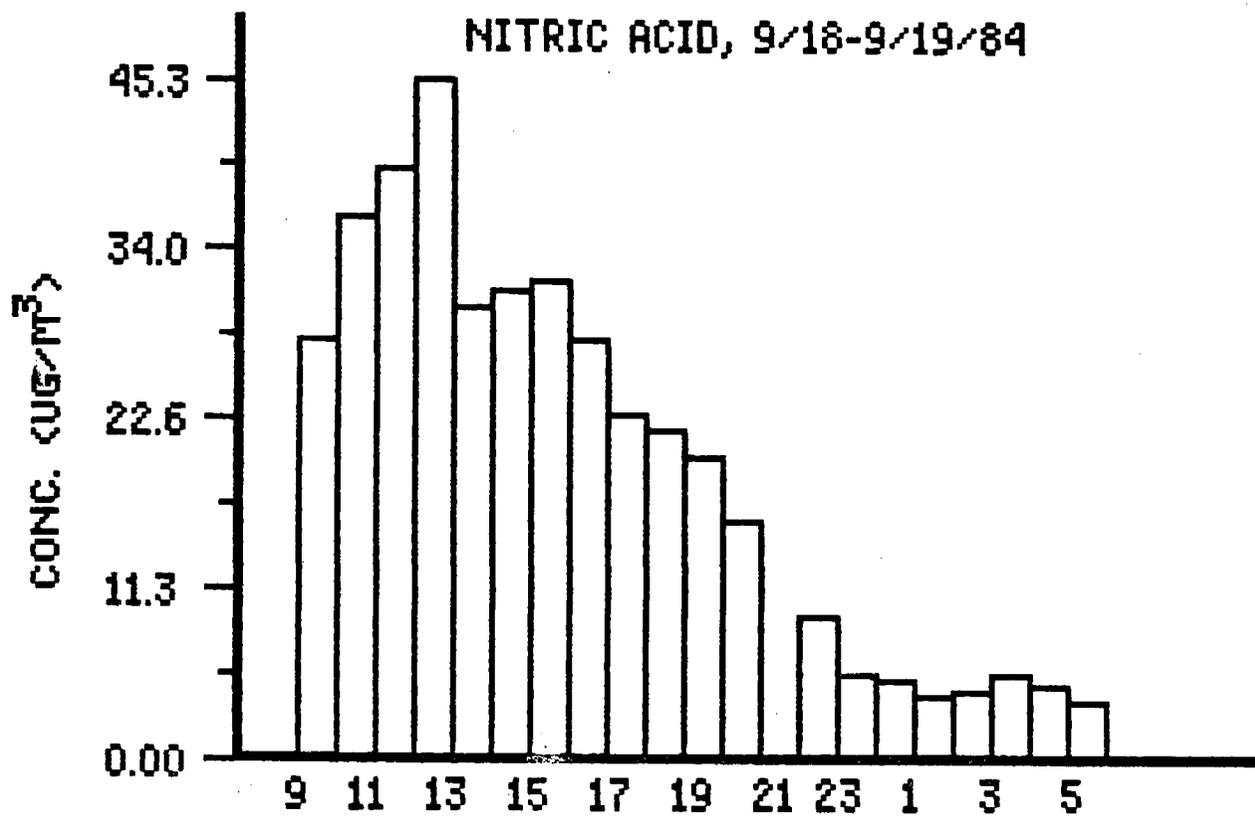
Short term nitric acid levels, as measured with the TAT, exceeded 40 $\mu\text{g}/\text{m}^3$ at their maximum. Maxima were observed during midday. The sharp decrease on 9/16 coincided with rain which persisted in the area from 1400-1800 hours. Figure 11 shows the moderately high ($r = 0.78$) correlation between HNO_3 by the TAT and hourly average O_3 values.

Figure 12 is a scatter diagram of NO_2 against HNO_3 concentrations and reveals little or no correlation. Thus, although NO_2 may be the principal, relatively stable HNO_3 precursor, other factors (e.g., the concentration of OH radicals and relative humidity) may be more significant in determining HNO_3 concentrations.

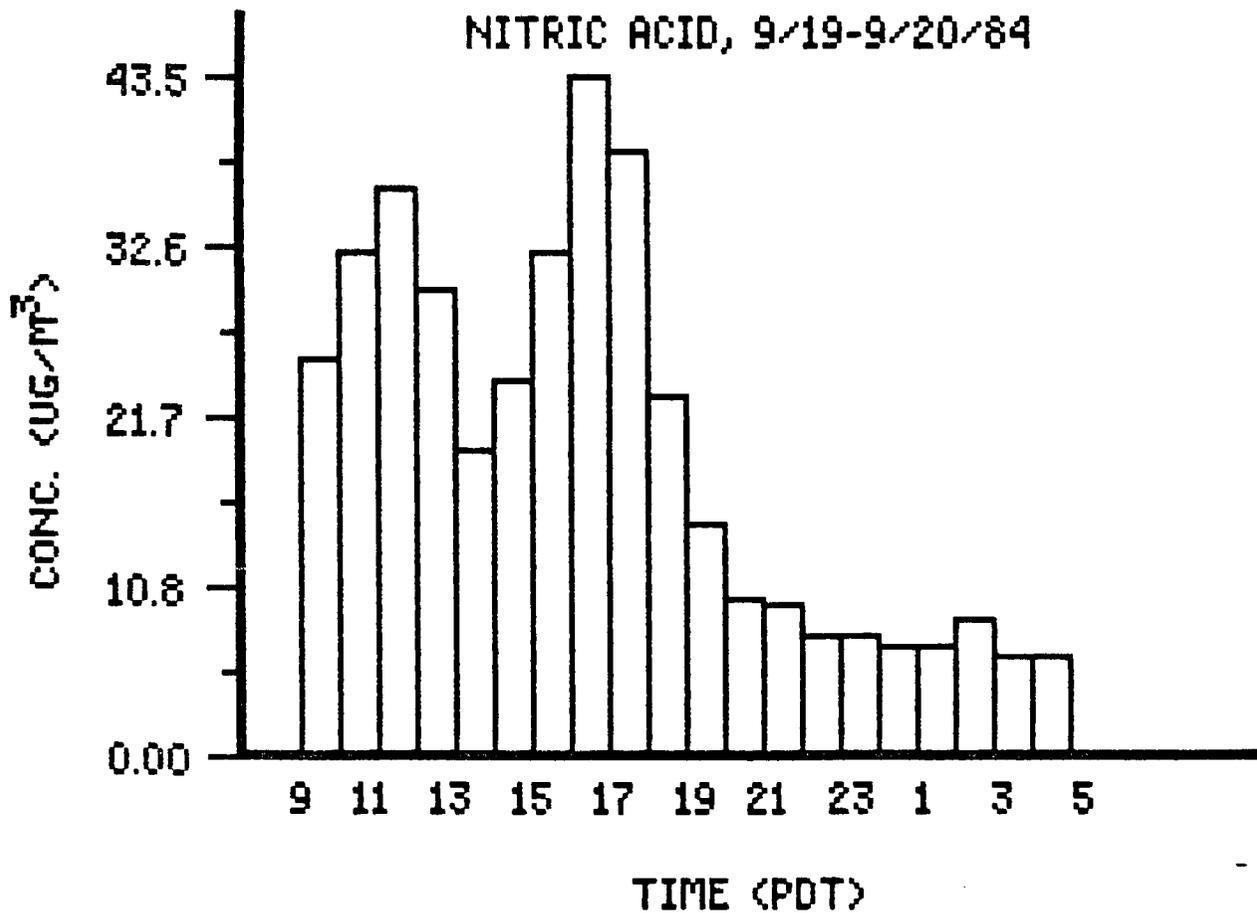


Figures 6 and 7. Diurnal Variation of Nitric Acid at Riverside, CA





Figures 8 and 9. Diurnal Variation of Nitric Acid at Riverside, CA



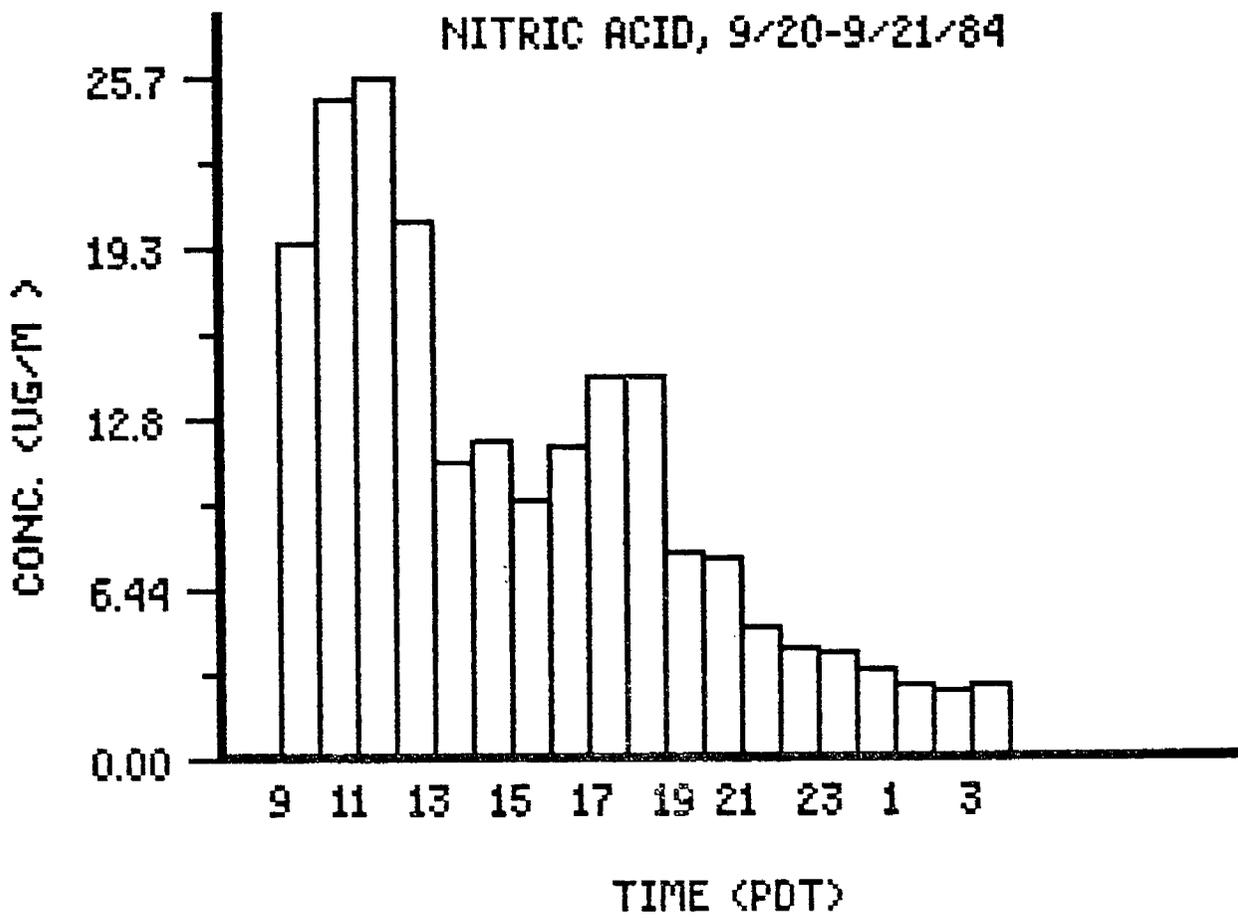


Figure 10. Diurnal Variation of Nitric Acid at Riverside, CA

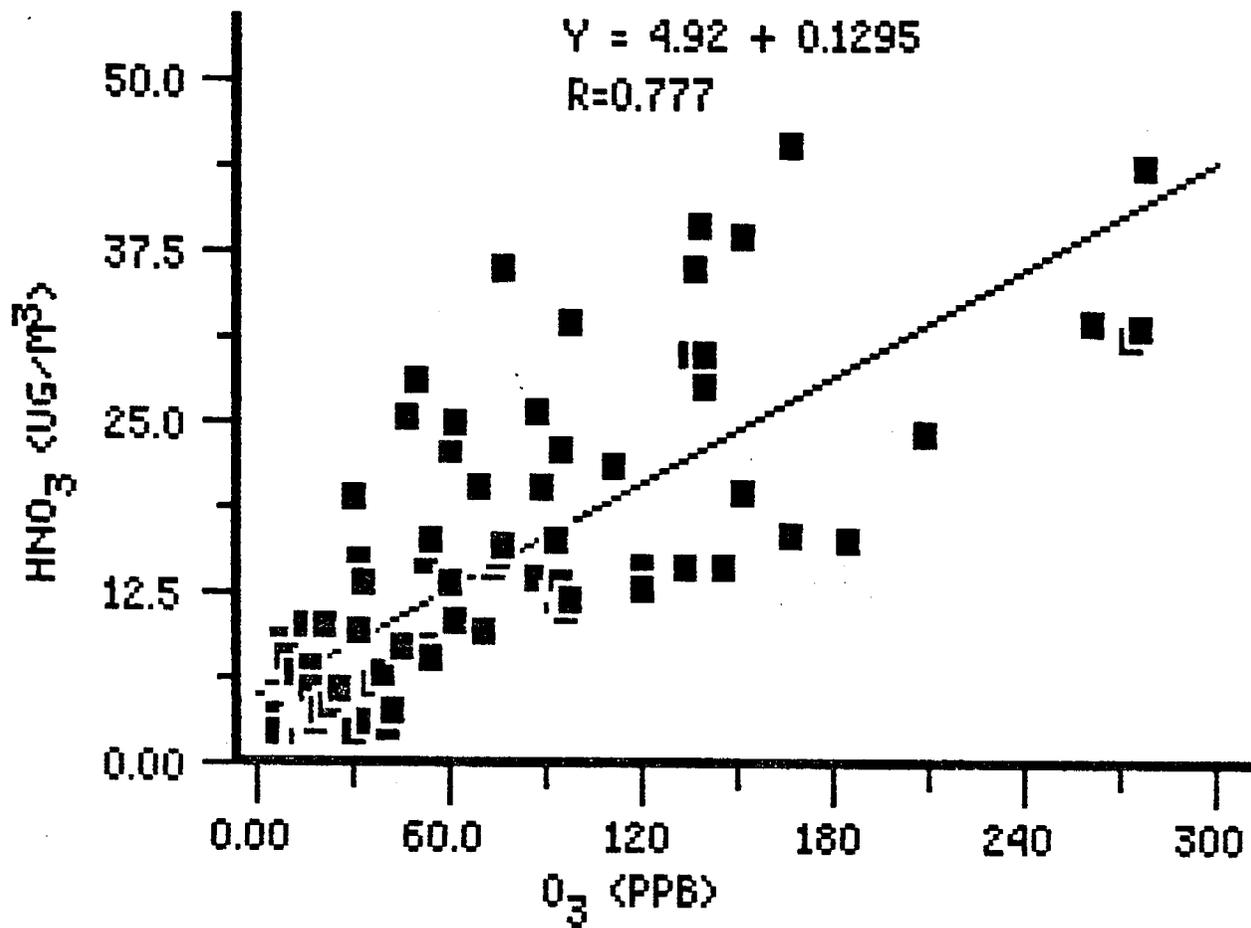


Figure 11. Scatterdiagram of Atmospheric Ozone vs HNO₃ Concentrations Measured with the Automated TAT

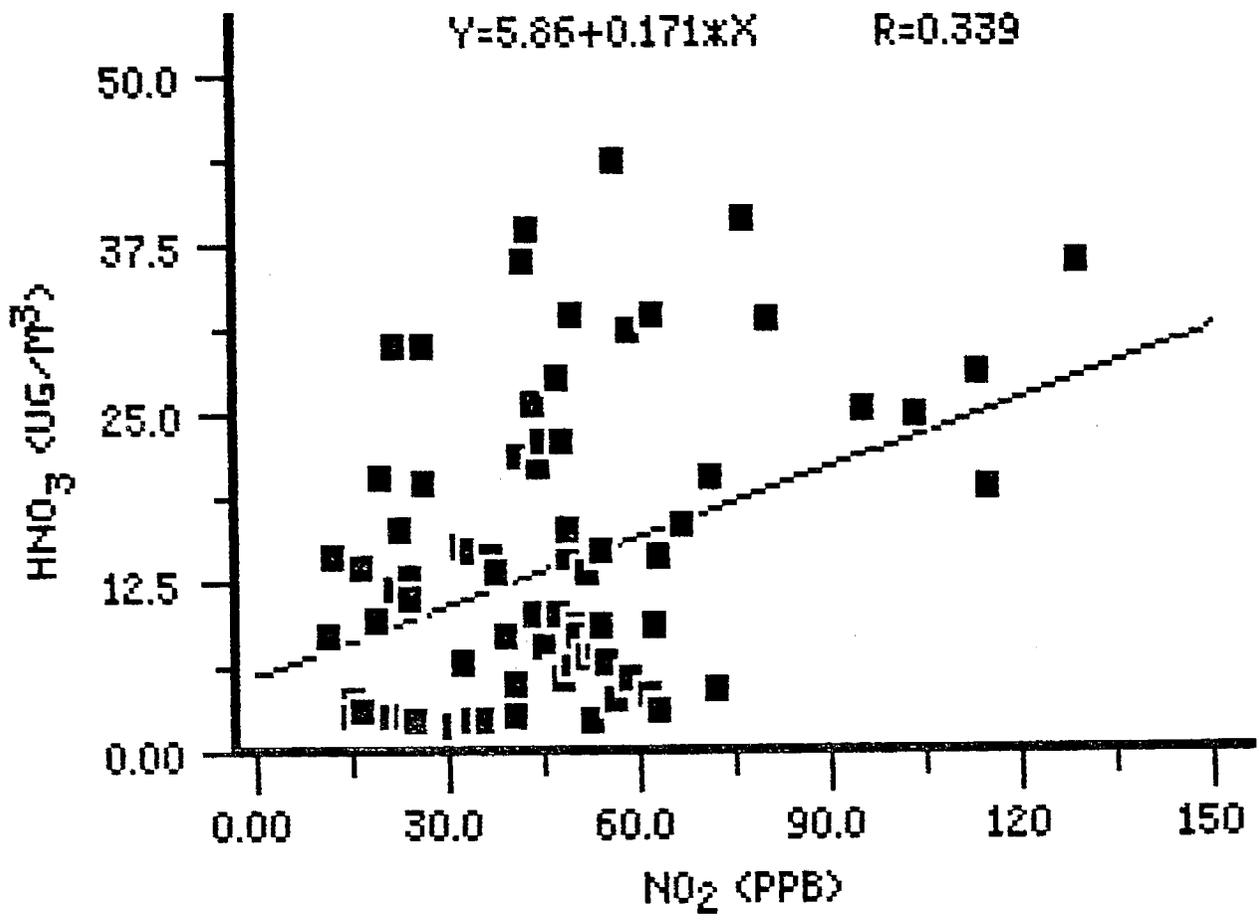


Figure 12. Scatterdiagram of Atmospheric NO₂ vs HNO₃ Concentrations Measured With the Automated TAT

C. Fine Particle Nitrate and Sulfate Plus Nitric Acid Results by the Denuder Difference Method

1. Methodology

Sampler 3 nitrate results are taken to represent the sum of fine (i.e. $< 2.2 \mu\text{m}$) particle nitrate plus nitric acid. Sampler 2, which used a MgO-coated denuder to remove HNO_3 , measured fine particulate nitrate, only. The difference (Sampler 3 NO_3^-) - (Sampler 2 NO_3^-) measured atmospheric HNO_3 .

The accuracy of the procedure requires:

- a. The efficient retention of both particulate nitrate and nitric acid on the nylon filters.
- b. The efficient removal of HNO_3 by the denuder.
- c. The absence of fine particulate nitrate loss in passing through the denuder.
- d. The absence of retention on nylon filters of gaseous NO_x species other than nitric acid.
- e. Accurate and precise control of flow rates.
- f. Negligible loss of HNO_3 within the teflon-coated cyclone of sampler 3.

Aside from flow rates, only one of these can be readily checked during atmospheric sampling. If fine particulate sulfate is assumed to be similar to fine particle nitrate regarding loss within the denuder, and assuming equivalent sulfate sampling errors, then comparison of sulfate concentrations on sampler 2 and 3 provides an estimate of such loss. Figure 13 compares sulfate on the two

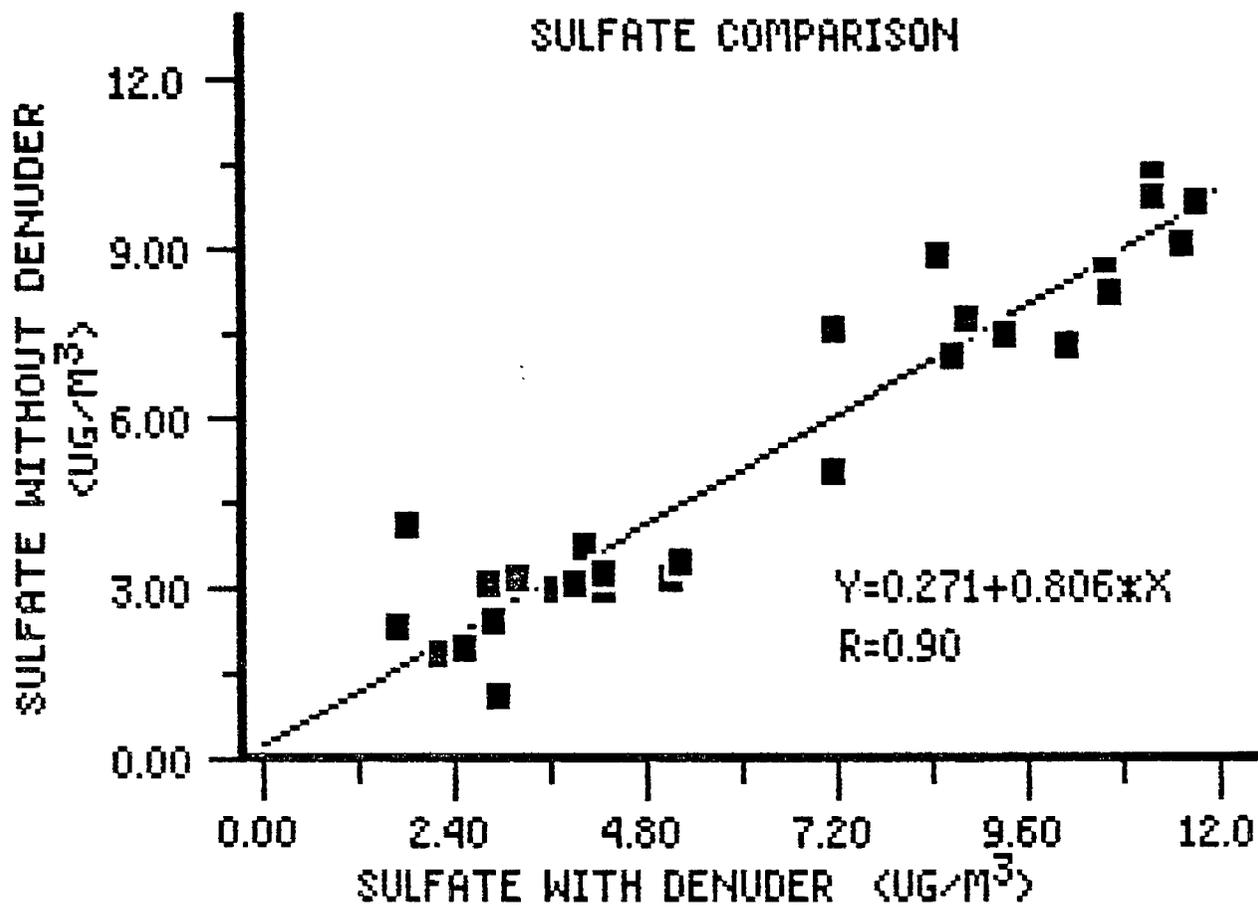


Figure 13. Comparison of Atmospheric Sulfate Collection With and Without a MgO-Coated Denuder

samplers. Results are generally higher on the sampler with denuder (ratio of means 1.17) which might indicate appreciable loss of fine particles. If true, this would result in HNO_3 values which are too high using the denuder difference method. Prior studies (19) comparing such sulfate measurements on Teflon filters showed differences of $< 1\%$. We infer that the present sulfate results on nylon filters without the denuder, rather than indicating particle loss in the denuder, are too high because of partial retention of SO_2 or other species later analyzed as $\text{SO}_4^{=}$ (22).

Flow rates on both samplers were regulated by mass flow controllers and remained constant within about 3%. Factors a-d have been dealt with in prior studies (3,4 and references cited therein) and were not re-investigated here. Factor f will be checked during Phase II of this study.

2. Results

Table 6 lists nitrate and sulfate results together with HNO_3 concentrations by the denuder difference method and other measurements. These are discussed in relation to TAT measurements in the following sections.

D. Comparison of HNO_3 Measurements by the TAT and Denuder Difference Method

To permit comparison of the TAT and denuder difference method (DDM) results, 1 hour average TAT HNO_3 values were averaged for the time periods of filter collection. The results are compared in Figure 14 and indicate high correlation ($n = 0.94$) between methods for concentrations $> 5 \mu\text{g}/\text{m}^3$, but about 50% higher values by the TAT.

Possible sources of such difference include:

TABLE 6

Filter Sampling Results Plus Mean Temperatures at Riverside^a

Date	Time (PDT)	Fine ^b SO ₄ ⁼	Fine ⁻ NO ₃ ⁻	HNO ₃ ^c	NH ₄ ^{+d}	NH ₃ ^{as} NH ₄ ⁺	T(°C)
9/7/84	1600-2200	- ^e	1.29	3.83	-	16.0	26.1
	2200-0800	-	1.61	0.89	-	7.69	22.2
9/8	0800-1200	-	1.39	4.79	-	9.29	26.5
	1200-1600	-	0.50	3.57	0.52	3.66	30.0
	1600-2000	-	0.40	1.87	0.54	4.12	29.7
	2000-0800	-	2.22	-0.90	0.46	11.8	23.9
	1200-1700	2.95	12.5	-6.21	-	16.2	-
9/15	1700-2000	2.12	0.70	2.33	0.92	12.8	24.1
	2000-2400	2.29	1.07	1.27	1.20	13.4	22.8
	0000-0800	2.99	4.44	-2.30	3.53	17.0	22.9
9/16	0800-1200	3.90	3.71	10.7	1.68	18.2	26.2
	1200-1600	3.20	1.37	4.53	1.15	11.8	27.7
	1600-2000	2.05	1.11	0.60	0.80	15.9	26.0
	2000-2400	2.67	1.23	-0.56	0.89	20.0	26.2
	0000-0800	2.05	0.69	0.91	1.16	20.0	26.0
9/17	0800-1200	3.78	6.79	3.41	3.22	27.6	27.0
	1200-1600	3.65	7.81	8.58	2.98	39.8	29.0
	1600-2000	10.3	16.9	9.22	9.57	60.7	28.8
	2000-2400	8.29	6.68	4.26	5.23	15.5	26.2
	0000-0800	9.58	23.1	4.58	13.4	16.2	26.1
9/18	0800-1200	10.57	33.6	20.8	16.9	21.6	28.0
	1200-1600	10.75	36.3	22.9	12.8	56.8	31.1
	1600-2000	10.8	2.77	4.16	4.77	16.7	27.1
	2000-2400	9.46	3.35	3.18	3.82	13.5	26.0
	0000-0800	8.42	14.0	2.71	9.21	11.3	25.9
9/19	0800-1200	8.69	15.8	18.0	6.98	15.7	28.2
	1200-1600	7.39	26.8	19.9	9.64	59.3	30.6
	1600-2000	7.92	4.64	17.6	2.95	16.7	28.6
	2000-2400	3.51	1.51	0.37	1.09	12.3	26.2
	0000-0800	4.37	2.74	0.99	2.72	13.4	26.0
9/20	0800-1200	6.11	12.2	13.4	6.18	20.8	27.2
	1200-1600	3.34	8.23	8.65	2.99	49.8	29.1
	1600-2000	8.70	12.3	-7.6	8.79	21.3	27.5
	2000-2400	4.17	4.25	1.05	3.96	20.8	-
	0000-0800	-	0.81	1.83	3.95	17.6	25.9
9/21	0800-1200	-	9.03	0.20	1.41	3.57	26.2

- a. Except as noted, values are in $\mu\text{g}/\text{m}^3$.
b. Mean result for sampler 2 and 3.
c. By the denuder difference method.
d. Particulate NH₄⁺ collected without size segregation.
e. Not determined.

- (1) Positive interference in the TAT by nitrogen oxides, including NO_2 , nitrous acid (HONO), particulate nitrate (in spite of the absence of measureable interference from NO_2 and particulate nitrate under laboratory conditions), and possibly by organic nitrates. In addition to the interference studies in the present program, PAN, propyl-nitrate, HCN and NO_2 have been shown not to interfere with the TAT (7,20).
- (2) Penetration of HNO_3 through the nylon filters employed.

To assess the source of the difference in HNO_3 measured by the TAT and denuder difference method (DDM), Figure 15 plots the difference in results by the two methods against NO_2 . The results are positively correlated ($r = 0.62$) in contrast to the TAT HNO_3 vs. NO_2 (see Figure 12). Since NO_2 is probably not retained on WO_x tubes, these data suggest that species whose concentration correlate with NO_2 (e.g. organic nitrates) may be retained. Figure 16 is a scatterdiagram of the TAT-DDM difference against relative humidity over the same averaging periods (4-8 hr). No correlation was observed. Since R.H. was highest at night and since HONO concentrations can build up at night, greatest differences might be expected at high R.H. However, Hoell has observed (21) decreasing collection efficiency for HNO_3 with WO_x tubes at increasing R.H., a factor tending to give low TAT results.

Although prior studies (3) have demonstrated the high efficiency of nylon filters for nitric acid, recent unpublished studies (17) suggest that this may not always be the case. It is argued that in the presence of atmospheric moisture, nitric acid forms a gas phase hydrate with a diffusion coefficient substantially below that for HNO_3 . The reduced diffusion coefficient would reduce the efficiency of trapping nitric acid during passage through a Nylon filter.

In the present study this was re-investigated using nitric acid diluted with both dry gas (O_2) and filtered room air at 56% R.H. Tungstic oxide-coated tubes sampled ahead and, subsequently, downstream of test filters. The

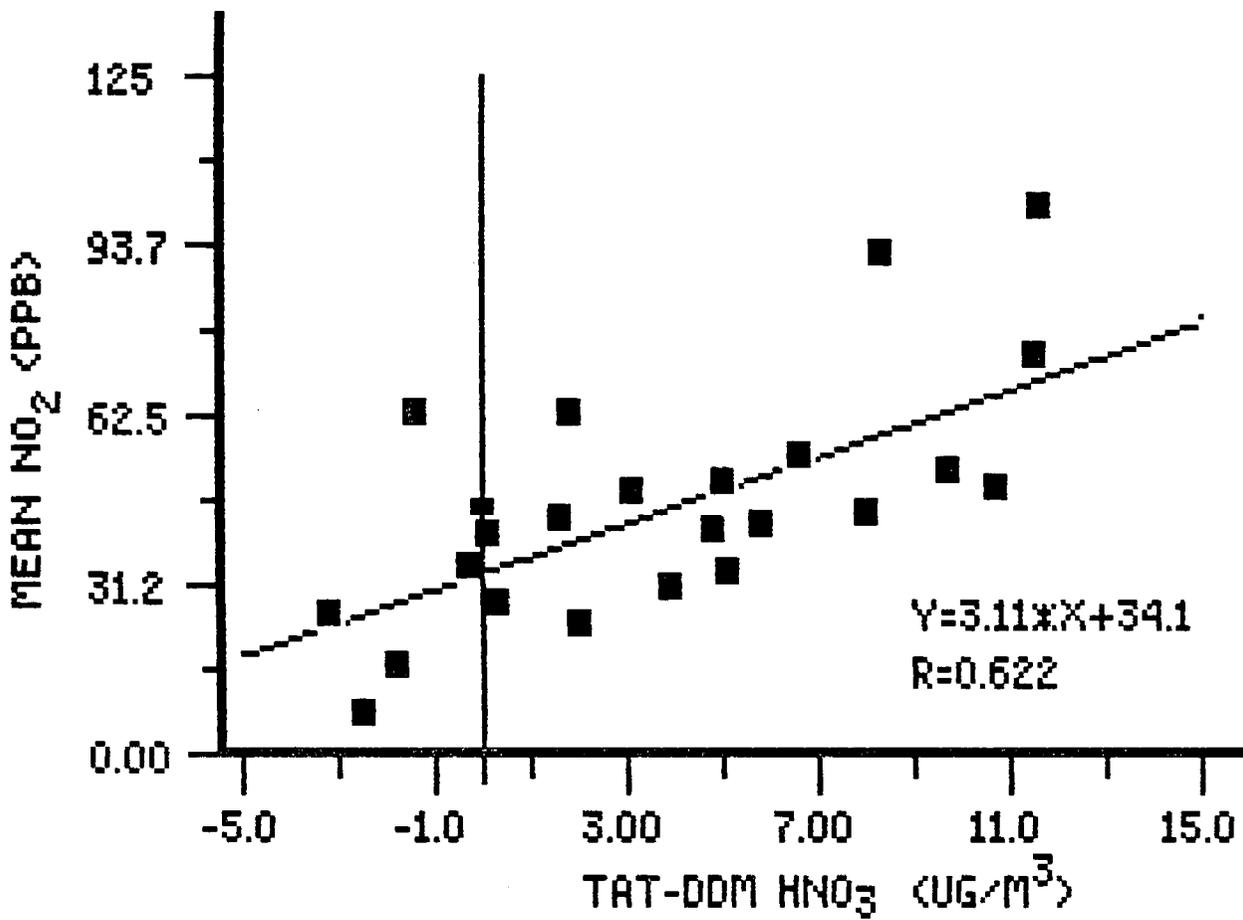


Figure 15. Scatterdiagram of the Difference in Atmospheric HNO₃ by the TAT and DDM vs NO₂ Concentrations

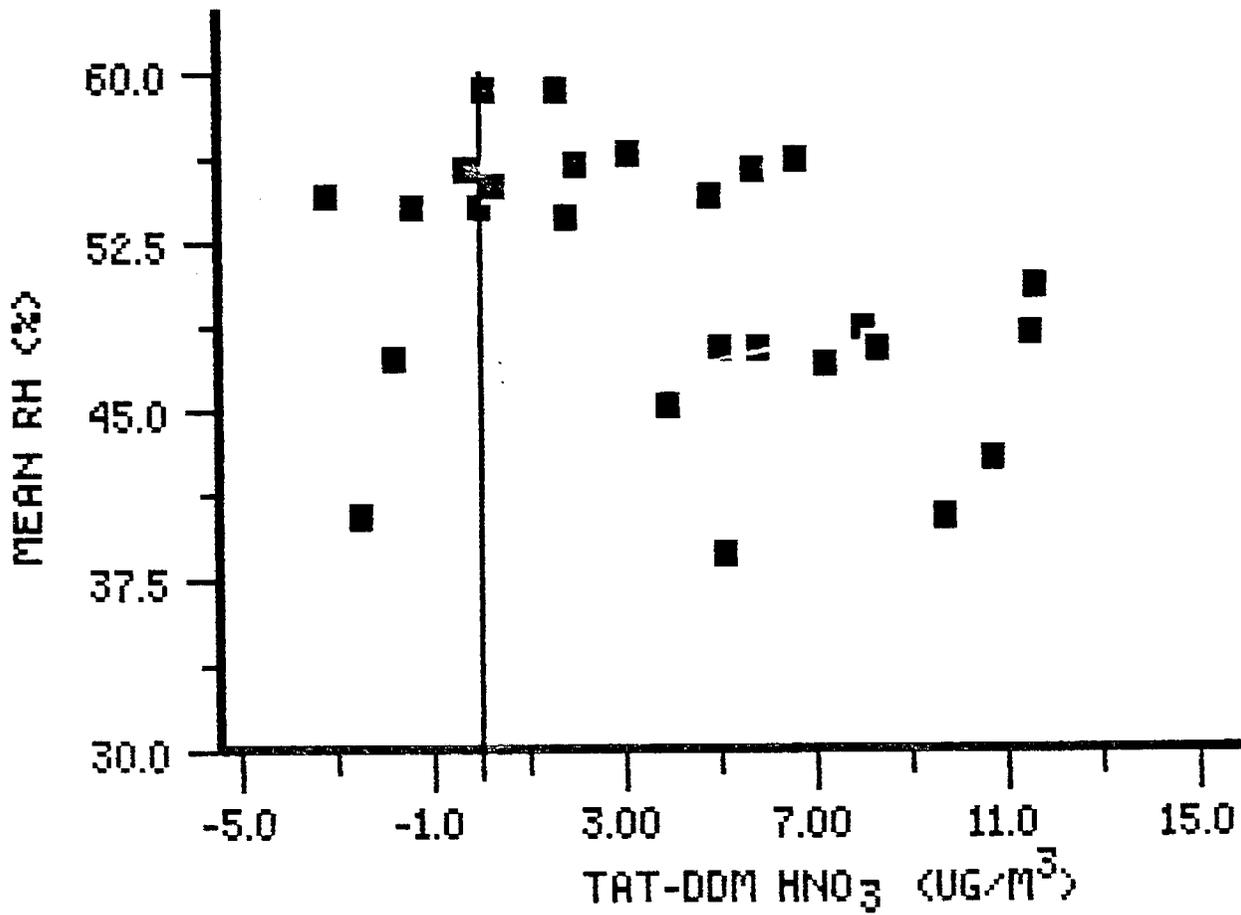


Figure 16. Scatterdiagram of the Difference in Atmospheric HNO₃ by the TAT and DDM vs Relative Humidity

collected acid was then determined by the usual thermal conversion and chemiluminescence detection. Nylon filters sampling at 10 Lpm showed < 6% penetration. With NaCl/Whatman 41 filters at 20 Lpm, the apparent penetration was 3.1%. These results are similar to those we previously observed (3). We conclude that Braman's observations possibly resulted from artifacts in his experimental procedure. The high efficiency of nylon filters for nitric acid was also observed recently by Roberts (18) using a tunable diode laser technique.

The present findings showing about 50% higher HNO_3 by the automated TAT are similar to those reported by Roberts et al. (20) at a site about 50 km west of Boulder, Colorado (Niwot Ridge). Using the nitrate collected on nylon filters by the dual filter technique as a measure of nitric acid, an automated TAT yielded values about a factor of three higher. They concluded that unidentified, probably carbonaceous nitrogen oxides were being retained on WO_x tubes and analyzed together with HNO_3 . Nitrous acid was not considered a likely source of interference because of the high daytime photolysis rate for this material. The present results contrast with those of McClenny et al. which showed agreement within 20% between the DDM and automated TAT in sampling near Research Triangle Park, N.C. (9).

E. Ammonia Measurements with the TAT, Oxalic Acid-Coated Filters and Denuder Tubes

It was previously noted that problems with the TAT prevented its calibration for NH_3 measurement. The responsiveness of the TAT to atmospheric NH_3 is indicated by Figure 17. This plots NH_3 values obtained with oxalic acid impregnated filters against integrator areas for the peak ascribed to NH_3 . Data points enclosed in the box are believed to reflect the loss of conditioning of the TAT when air relatively free of NH_3 was sampled. The remaining points exhibited relatively good linear correlation. At higher NH_3 levels, the TAT appeared to be responding approximately linearly to NH_3 . Phase II studies with the TAT will attempt to overcome the problems indicated by these results.

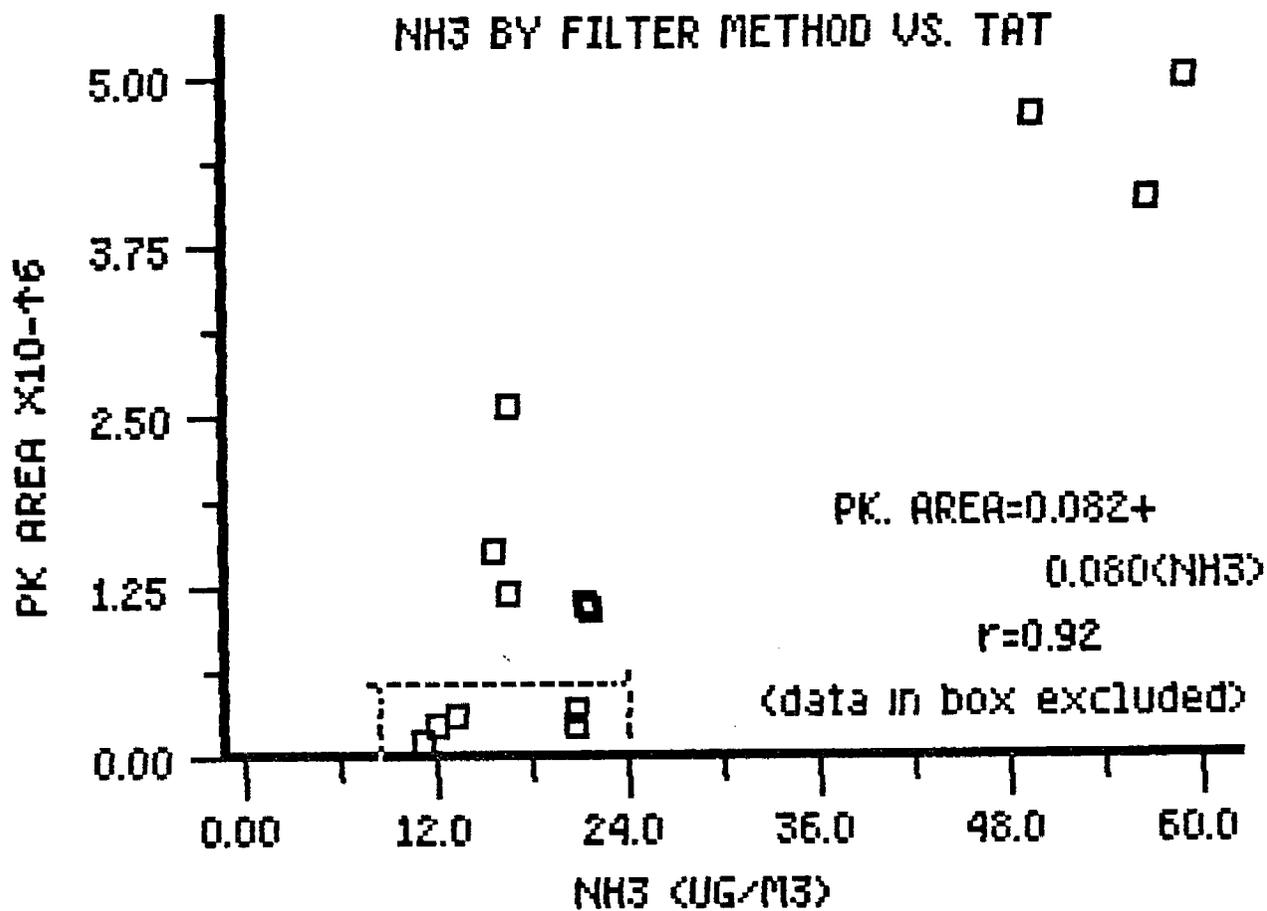


Figure 17. Scatterdiagram of Atmospheric NH₃ Concentrations (by Filter Method) vs NH₃ Peak Area with the Automated TAT

In addition to NH_3 measurements by the dual filter technique, NH_3 was collected with oxalic acid-coated denuder tubes with both 12 hr and 24 hr collection times. Filter results for 4 and 8 hr samples were averaged to permit comparison to denuder NH_3 results.

Figure 18 compares filter results to the 12 hr denuder tube NH_3 values and indicates excellent correlation, but somewhat higher values by the filter method. The ratio of mean values, (Filter NH_3)/(Denuder NH_3) was 1.12. Higher NH_3 results by the filter method are expected because of dissociation of ammonium salts (especially NH_4NO_3) on relatively inert Teflon prefilters.

The limited duration of sampling hampers adequate comparison of 12 hr and 24 hr NH_3 denuder results. For five, 24 hour periods, the ratio of means, (24-hr NH_3 calculated from 12 hr samples)/(observed 24-hr NH_3) was 1.23 indicating higher average results for 12 hr samples. These findings are consistent with diminished collection efficiency after prolonged sampling at the relatively high NH_3 levels existing in Riverside. The capacity of the tubes for NH_3 was not established by laboratory trials.

F. Particulate NH_4^+ Results

Particulate NH_4^+ concentrations were measured without size segregation using a 47 mm Teflon (Zefluor) filter ahead of the oxalic acid filters intended to retain NH_3 . The results given in Table 6 range from 0.5 to 17 $\mu\text{g}/\text{m}^3$. These values may be compared to those calculated from fine particle $\text{SO}_4^{=}$ and NO_3^- with the assumptions that (1) all NH_4^+ exists on particles $< 2.5 \mu\text{m}$, and (2) $\text{SO}_4^{=}$ and NO_3^- are present as $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , respectively. The comparison is given in Figure 19 and indicates moderate correlation ($r = 0.87$) with somewhat higher calculated values compared to those observed. Such findings are consistent with the contributions of cations other than NH_4^+ .

The fraction of NH_4^+ in the particle phase may reflect, in part, the dissociation of NH_4NO_3 . Figure 20 is a scatter diagram of the fraction (partic. NH_4^+)/(partic. NH_4^+ + NH_3 as NH_4^+) against temperature. Clearly, the proportion of particle phase NH_4^+ is not principally governed by temperature.

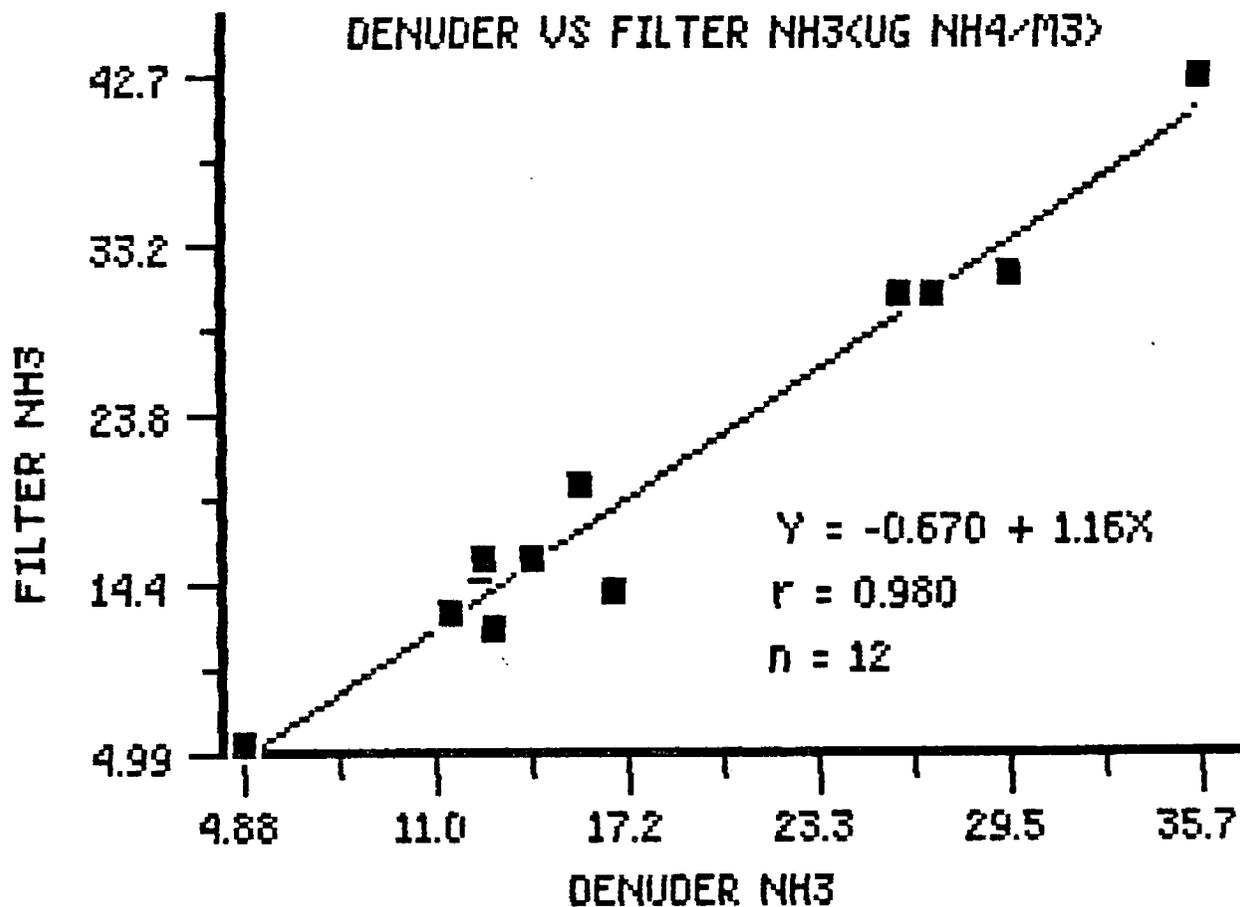


Figure 18. Scatterdiagram of Atmospheric NH₃ by Oxalic Acid-Coated Denuder Collection vs Oxalic Acid-Impregnated Filter Collection

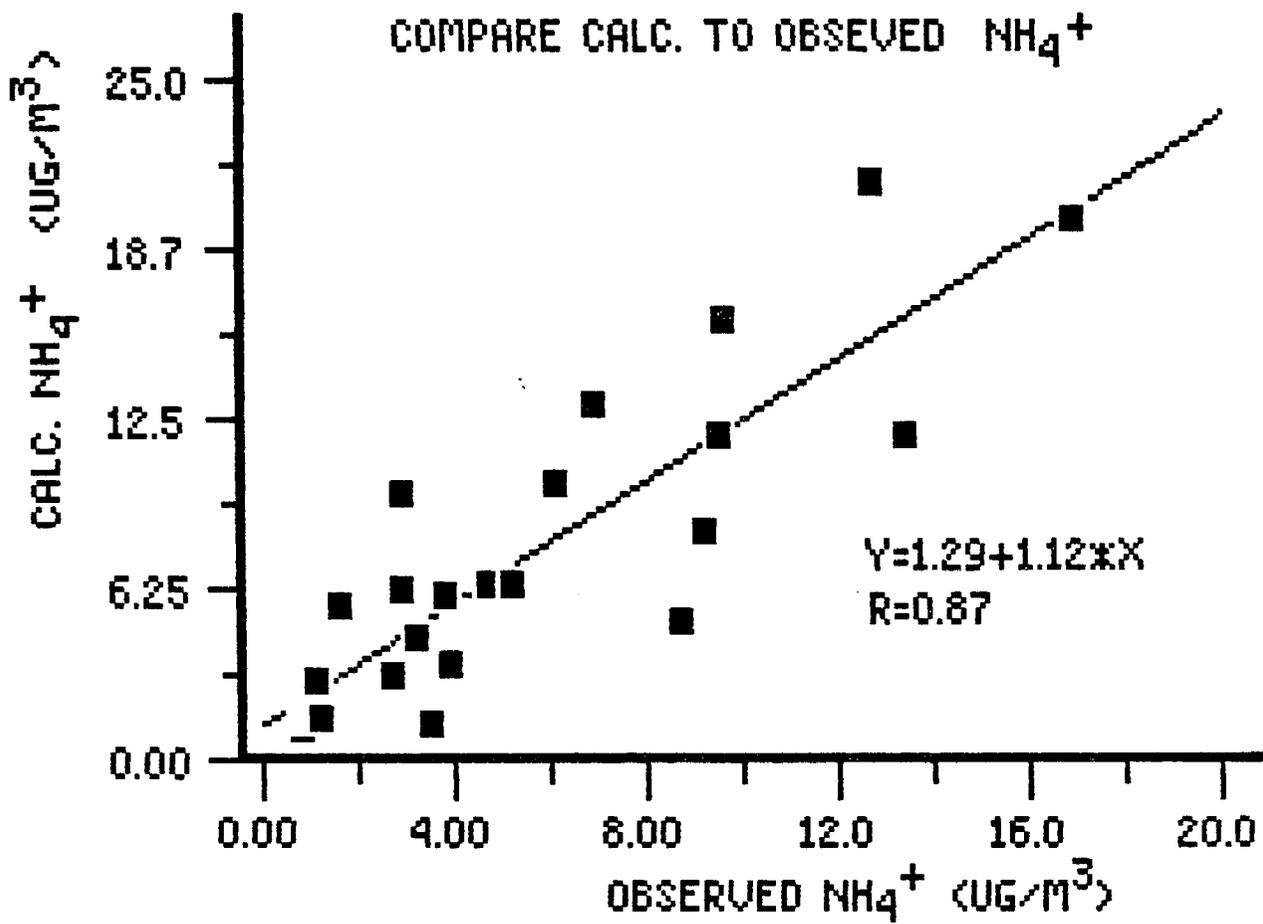


Figure 19. Comparison of Observed and Calculated Atmospheric Particulate NH_4^+ Concentrations

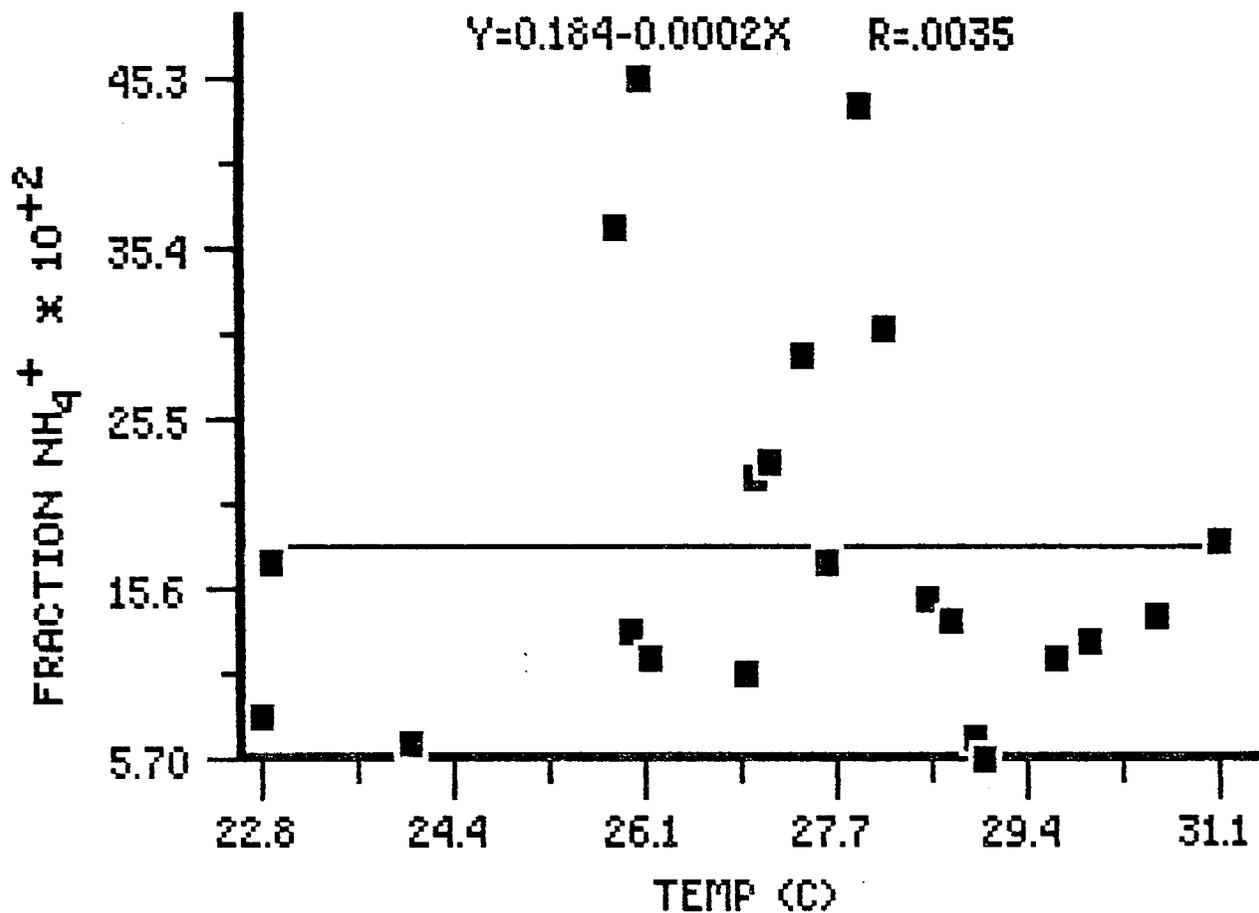


Figure 20. Scatterdiagram of Mean Ambient Temperature vs the Fraction of NH₄⁺ plus NH₃ in the Particle State

G. HCl and Particulate Chloride

Table 7 summarizes results for gaseous chloride determination taken as upper limit estimates of the concentrations of HCl at the site. Levels ranged from below detection to $3.1 \mu\text{g}/\text{m}^3$ as Cl^- (or 2.0 ppb). A pronounced diurnal pattern was observed with maxima usually in the daytime periods 0800-1200 or 1200-1600 hr.

In the next phase of this study HCl measurements will be made in the western part of the Los Angeles basin where much higher levels are expected. Correlations between the concentrations of gaseous acids (i.e. HCl and HNO_3) and atmospheric particulate strong acidity will be sought.

TABLE 7
Concentration of Gaseous Chloride as a Measure of HCl
at Riverside ($\mu\text{g}/\text{m}^3$ as Cl^-)

Date	0000-0800 hr	0800-1200 hr	1200-1600 hr	1600-2000 hr	2000-2400 hr
9/8/84	0.33	0.93	0.40	<0.2	N.D. ^a
9/15/84	N.D.	N.D.	0.46	<0.3	<0.3
9/16/84	0.25	N.D.	0.17	0.25	<0.26
9/17/84	0.38	1.76	2.77	1.50	0.28
9/18/84	0.48	3.08	1.46	0.47	0.43
9/19/84	0.93	1.91	1.13	0.94	0.3
9/20/84	0.12	1.12	0.76	1.32	0.3
9/21/84	0.83	1.09	N.D.	N.D.	N.D.

a. Not determined.

Sea salt is probably the most significant source of particulate chloride in California samples. Because relatively low levels of particulate chloride were anticipated in Riverside, Teflon prefilters (from which such chloride was determined) were run consistently for 8-hr periods. Table 8 summarize the data obtained. Throughout the period 9/8 - 9/19/84, particulate Cl^- concentrations remained $< 0.8 \mu\text{g}/\text{m}^3$. Substantially higher values were found on 9/20 - 9/21. No linear correlation was observed between particulate chloride and gaseous chloride ($r = -0.16$).

TABLE 8
Concentration of Particulate Chloride at Riverside ($\mu\text{g}/\text{m}^3$)

Date	0000-0800 hr	0800-1600 hr	1600-2400 hr
9/15/84	N.D. ^a	N.D.	0.11
9/16/84	0.76	0.13	0.21
9/17/84	0.10	0.16	0.21
9/18/84	0.71	0.21	0.15
9/19/84	0.39	<0.15	0.27
9/20/84	0.47	N.D.	2.22
9/21/84	4.67	1.38 ^b	N.D.

- a. Not determined.
b. For 0800-1200 hr only.

H. Hi-Vol (Glass Fiber) Filter Results and Comparison of Nitrate Values

Twenty four-hour Hi-Vol filter samples were collected employing glass fiber filters. The filter batch (Schleicher and Schuell 1HV, 1981 EPA Grade) had been previously shown to retain efficiently both particle phase nitrate and nitric acid at TIN levels up to $32 \mu\text{g}/\text{cm}^2$ of filter area (19). Hi-Vol SO_4^- and NO_3^- concentrations are shown in Table 9 together with fine total inorganic nitrate (FTIN) values for four 24 hr periods. Equipment malfunction prevented obtaining two additional Hi-Vol samples. FTIN results shown were 24 hr averages calculated from short term samples obtained with Sampler 3.

Hi-Vol NO_3^- and FTIN are strongly correlated with consistently higher values being obtained with the Hi-Vol. The differences may reflect retention of coarse NO_3^- as well as more efficient retention of such materials as organic nitrates on the glass fiber filters.

Hi-Vol NO_3^- as well as FTIN are notable for the substantial day-to-day variability in contrast to SO_4^- ; the range in 24-h average SO_4^- concentration was < 25%.

TABLE 9

Hi-Vol Sampler Results and Comparison of Hi-Vol NO_3^- and FTIN ($\mu\text{g}/\text{m}^3$)

Date ^a	Hi-Vol $\text{SO}_4^{=}$	Hi-Vol NO_3^-	FTIN ^b
9/8-9/9	11.1	3.58	2.73
9/17-9/18	11.0	23.0	19.8
9/18-9/19	11.7	28.3	26.8
9/20-9/21	9.09	16.6	9.62
		$\text{Hi-Vol NO}_3^- = 3.63 + 0.966 (\text{FTIN})$ $r = 0.967$ $n = 4$	

- a. Hi-Vol sampler employed Schleicher & Schuell 1HV glass fiber filters (1981 EPA Grade) and sampled from 0800-0800 hr.
- b. Fine total inorganic nitrate as measured by sampler 3.

VIII. REFERENCES

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APPENDIX A

PREPARATION OF TUNGSTIC ACID DENUDER TUBES

A. INTRODUCTION

Hollow tubes are coated by vacuum deposition of polymeric blue tungsten oxide then thermally oxidized to tungstic acid.

B. MATERIALS

1. HF - 50% solution.
2. NaOH - 50% solution.
3. Vycor (quartz) tubing, 4 mm I.D., 45 cm length.
4. Metal inserts (short sections of tubing < 4 mm O.D. inserted at each end of tube to be coated to prevent coating the ends of the Vycor tubes).

C. TUBE PREPARATION - New Tubes

1. Supporting the tube vertically, apply suction through a short section of plastic tubing and draw HF solution to above the level of the quartz tube and hold for about two min.
2. Allow HF to drain and rinse thoroughly with distilled water.
3. Similarly treat the tube with 50% NaOH.
4. Rinse well with distilled water.
5. Allow tube to air dry. Do not oven dry tube to avoid contamination of HF cleaned surface.

D. TUBE PREPARATION - Previously Coated Tubes

1. Follow steps 1 and 2 above.
2. Repeat process two or three times. Most of the tungstic acid should begin to flake off quickly. Although not obvious, portions still adhering will also be loosened.
3. Remove tube from HF solution and rinse both inside and outside of tube with running tap water. Flush for 2-3 min. until all traces of tungstic acid are gone. Scrape stubborn spots out with a piece of stiff "bare" copper wire.
4. Finish rinsing with distilled water.

E. COATING TUBES

1. Install tube inserts and tungsten wire in coating apparatus (Figure 2 in text). Make sure the inserts are properly in place and the tungsten wire is centered and straight.
2. Support the apparatus vertically, start the pump and vacuum dry the tube. Increase voltage of external heating coil until it is a barely visible dull red heat (about 110 V with AIHL system).
3. Continue to pump until vacuum is < 100 Torr.
4. Turn heater off and increase tungsten wire voltage setting, while monitoring current flow, until wire is a very bright orange heat (9.2 amps, AC, with AIHL system). For a new wire, note the powerstat setting at the bright orange heat and rapidly decrease then increase the current to that setting several times. Check that the wire is straight and centered in tube.

5. A blue-black coating will be visible in about 5 min., with a heavier coating on the ends. Check the system about every five min. to track coating progress. After 15 to 20 min. the tungsten filament will no longer be visible on the ends and barely visible in the middle.
6. When the glow of the wire is no longer visible in the center, turn off the tungsten powerstat (too thick a coat will result in a granular appearance which may flake when oxidized). When coating chamber is cool, disassemble coating apparatus and remove tube.

F. OXIDATION OF COATING

1. Turn gas-oxygen torch on using burner tip No. 5. Adjust the fuel-oxygen mixture to provide a cool flame (yellow-orange center).
2. Connect coated tube to oxygen feed through swivel, rotate the tube, and begin heating one end of the blue-black coating to a dull red glow.
3. Continually rotate the tube to avoid local overheating. Overheating will vaporize and create holes in the coating. Following oxidation, properly heated sections on cooling will be bright, translucent, uniform yellow in appearance. Advance the burner tip slowly along the entire coated section of the tube. Transparency (always most apparent in the center section) is indicative of a thin coat but does not necessarily mean poor collection efficiency.
4. When all the coating has been satisfactorily oxidized, increase the oxygen flow to the torch to provide a hotter, blue flame and heat the uncoated ends of the tube to red heat to burn off all traces of tungsten from these sections.
5. When cool, disconnect tube and immediately seal tube ends with Parafilm to avoid contamination of coating.

APPENDIX B

INTERFERENCE OF NO₂ IN HNO₃ MEASUREMENTS WITH THE TAT

Efforts to detect interference effects were hampered by the response behavior of the preliminary version of the TAT system. Since changing from HNO₃ to purified air required ca. 3 hours to achieve close to background HNO₃ response, the apparent instrument response to NO₂ was expected to vary with time and the prior history of the analyzer. The first trials with NO₂ employed the analyzer well conditioned for HNO₃, changing test atmospheres from HNO₃ in air to NO₂ in air. Table B-1 gives the results. The initial cycles following the change to NO₂ showed a large increase (ca. 50%) in apparent HNO₃ peak area. Over a 3 hour period this decreased to about half the initial value with NO₂ added, but the peak area remained high ($7.6 \pm 0.6 \times 10^5$). Changing from NO₂ to synthetic air or 80/20 He-O₂ caused no measurable decrease in response (mean $6.6 \pm 0.9 \times 10^5$). Thus NO₂ appears to have no long-term interference capability. It remains unclear why the blank was so high on this day.

To minimize the uncertainty in interpreting instrument response to interferents, NO₂ was added in mixture with dilute HNO₃ following about 3 hours of conditioning with HNO₃. The addition was done in such a way as to keep the HNO₃ concentration unchanged (within 2%), at about 50 $\mu\text{g}/\text{m}^3$ or 20 ppb (est. from prior calibration). The final NO₂ level was 57 $\mu\text{g}/\text{m}^3$ (30 ppb). Following addition of NO₂ the apparent HNO₃ peak remained unchanged in area [$(8.66 \pm 0.54) \times 10^5$ vs. $(8.69 \pm 0.27) \times 10^5$], indicating no measurable interference. The change from NO₂-HNO₃ to synthetic air only caused an immediate sharp drop in measured HNO₃.

TABLE B-1

INTERFERENCE OF NITROGEN DIOXIDE IN THE AUTOMATED HNO₃ ANALYZER

Atmosphere Sampled	Cycle ^a	TAT Response (Area X 10 ⁻⁵)
0.138 ppm NO ₂ in synthetic air	1	15.2
	2	12.1
	3	10.1
	4	9.54
	5	8.13
	6	7.65
	7	7.56
Synthetic air	8	5.92
	9	5.65
80:20 He:O ₂	10	7.04
	11	6.20
	12	7.65
	13	7.92 ^b
	14	5.97 ^b

- a. Each cycle is 30 minutes including a 10 minute sample collection. Cycles 1-14 are consecutive cycles on the same day.
- b. An NaCl-impregnated filter was placed in the sampling line just ahead of the inlet to the TAT to remove HNO₃ possibly present as a contaminant from tubing walls.

APPENDIX C

INTERFERENCE OF NITROUS ACID IN HNO_3 MEASUREMENT WITH THE TAT

A. EXPERIMENTAL

Nitrous acid was prepared following a procedure (1) developed at the University of California (Riverside) Statewide Air Pollution Research Center (SAPRC). In this procedure 0.012 M NaNO_3 was added dropwise to a slowly stirred, 5%w H_2SO_4 solution at room temperature, while flowing N_2 through the all glass and Teflon system. Further dilution with N_2 yielded HONO concentrations < 150 ppb. Nitrous acid preparation is made difficult by the co-generation of NO_2 and NO. The studies at SAPRC found molar ratios of $\text{HONO}/(\text{NO} + \text{NO}_2 + \text{HONO})$ of up to 0.5.

In the present study, an NO_x analyzer provided measurement of the NO formed and of the sum $\text{NO}_2 + \text{HONO}$. With this sum and the reported maximum mole fraction of HONO, an upper limit to the HONO concentration could be calculated.

The procedure used for HONO trials included:

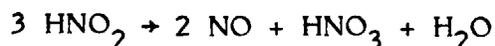
1. Conditioning of the TAT system with HNO_3 .
2. Calibration of the NO_x monitor for NO and NO_x using a known concentration of NO in air.
3. Measurement with the NO_x monitor the NO and $\text{NO} + \text{NO}_2 + \text{HONO}$ (NO_x) in the diluted nitrous acid in N_2 immediately before and after the 10 minute sampling by the TAT system. Measurements before and after sampling were needed because the NO_x from the HONO generator decreased with time. The averages of the NO_x and NO measurements together with the maximum mole fraction of HONO, were used to determine the upper limit HONO concentration being sampled by the TAT.

4. Measuring the TAT response to HONO as apparent HNO₃.
5. Measuring the TAT response to HNO₃ while simultaneously measuring the HNO₃ concentration by filter collection using NaCl-impregnated Whatman 41 filters.

B. RESULTS

Table C-1 summarizes results for trials with nitrous acid. Earlier work (Appendix B) demonstrated that NO₂ does not interfere. Since interference from NO is much less probable, the present results clearly suggest that HONO does interfere significantly. The results appear to show that HONO is up to 1/3 as responsive as HNO₃ in the TAT. However, determining the efficiency of HONO for interference is made difficult by the use of generally higher levels of HONO compared to HNO₃. Relatively high HONO concentrations were needed to permit real-time measurement of the HONO with the NO_x analyzer. During some of these trials the WO_x preconcentrator column may have been saturated by HONO. As a result peak area responses would have been too low for HONO making the calculated response per ppb too low. In addition, since HONO values are upper limit concentrations, response factors should be lower limit values only. Thus it cannot be concluded from the current data that HONO is substantially less responsive than HNO₃ in the TAT.

As an alternative hypothesis to direct interference by HONO, nitrous acid can decompose via the reaction:



The generation of nitric acid by decomposition via this route would, of course, produce an interference with a response about 1/3 of that for HNO₃. If such decomposition occurs within the TAT it would represent a source of interference to be expected in atmospheric sampling. If, however, it occurred within the HONO generation system or the Teflon lines transporting the diluted HONO to the TAT, this would be an experimental artifact. The present data do not discriminate between the possible pathways to interference by HONO. Use of

a nylon filter to remove HNO_3 ahead of the TAT will eliminate this ambiguity in trials to be done in Phase II.

Quantitative retention of nitrous acid on nylon wool has recently been demonstrated (R. Atkinson, personal communication, 1984). Thus HONO can be measured by a difference method.

$$(\text{HONO}) = (\text{NO}_x)_{\text{total}} - (\text{NO}_x)_{\text{Nylon}}$$

where: $(\text{NO}_x)_{\text{Nylon}}$ is the total NO_x (with HNO_3 previously removed by nylon filter) penetrating a tube pack with Nylon wool.

Reference

1. R. Atkinson. Preparation of Nitrous Acid, unpublished manuscript (1983).

TABLE C-1

INTERFERENCE OF NITROUS ACID IN NITRIC ACID MEASUREMENT

Date	Time	Maximum HONO (ppb) ^a	HNO ₃ (ppb)	TAT Response 6 (Area Units X 10 ⁻⁷)	Response per ppb ^b (Area Units X 10 ⁻⁷)
11/30/83	1000	95	-	0.65	6.88
	1030	88	-	0.55	6.22
	1100	132	-	0.63	4.75
	1130	114	-	0.71	6.18
	1200	-	11.4	0.56	49.8
12/6/83	0900	-	7.4	0.53	71.4
	1100	128	-	0.887 ^c	6.93
	1130	44	-	0.714 ^c	16.2
	1200	24	-	0.610 ^c	25.8

a. Estimated assuming mole fraction of HONO is ≤ 0.5 .

b. Since HONO concentrations are upper limit values, response factors for HONO are lower limit values.

c. Corrected for blank with synthetic air.

APPENDIX D

ANALYSIS OF HCl AND PARTICULATE CHLORIDE IN ATMOSPHERIC SAMPLES

Teflon prefilter samples were extracted in 0.0018 NaHCO₃ solution and analyzed by ion chromatography for chloride. Filter blanks for 88 mm diameter filters were low (3.2 ± 4.2 µg/filter). The triethanolamine-KOH impregnated Whatman 41 (T-K) filters were extracted as above. However, ion chromatographic analysis proved unfeasible because of interfering peaks. While such peaks had been observed in laboratory studies as well, their relative magnitude had been much lower, permitting chloride measurement. T-K filter extracts were successfully analyzed by potentiometric titration with AgNO₃.

Potentiometric titration of chloride was done in 15 ml 0.5 M HNO₃, to make the sample extract acidic. This HNO₃ solution was saturated with AgCl by adding 2 µg Cl⁻ and titrating to the potentiometric endpoint with AgNO₃ using a Model ABU 12 autoburette (Radiometer). An 0.8 ml aliquot of the sample extract was then added and the solution again titrated to the endpoint (i.e. the point of maximum rate of change of potential).

The recovery of chloride was assessed with one and two µg samples and ranged from 65-80% with these samples. Precision was assessed with standards and ranged from about 5% with 10 µg samples to about 20% with 1 µg samples. No corrections were applied to the resulting atmospheric data. Further work is needed to assess more completely the precision and accuracy of this method with the atmospheric samples.

During Phase II of this study, alternative sampling media (e.g. Na₂CO₃ impregnated filters) will be evaluated to permit improved quantitation of HCl (as Cl⁻) by ion chromatography.

