

EVALUATION AND DEVELOPMENT OF PROCEDURES  
FOR DETERMINATION OF SULFURIC ACID, TOTAL PARTICLE-  
PHASE ACIDITY AND NITRIC ACID IN AMBIENT AIR-PHASE II

(Contract No. ARB A8-111-31)

Final Report

October 1980

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1980

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## ABSTRACT

Methods for measurement of sulfuric acid, strong acids and nitrate in atmospheric particulate matter, and for gaseous nitric acid were evaluated. Selective extraction with benzaldehyde and titrimetry for strong acids were compared in atmospheric trials. Gaseous nitric acid was determined by 1) measuring the nitrate collected on nylon or NaCl-impregnated cellulose filters after removal of particulate matter with Teflon prefilters, and 2) the difference between total inorganic nitrate (TIN) and particulate nitrate (PN). TIN was measured by the sum of the nitrate collected with a Teflon prefilter and nylon or NaCl-impregnated after-filter. PN was measured by the nitrate able to penetrate a diffusion denuder coated to remove acidic gases including  $\text{HNO}_3$ . Losses of nitrate from Teflon prefilters were determined by comparing the nitrate retained by these filters to the nitrate penetrating the acid gas denuder. TIN was compared with the nitrate collected on glass fiber filters to assess the origin of the artifact particulate nitrate on the latter. A modified chemiluminescent  $\text{NO}_x$  monitor converted to measure nitric acid continuously, was compared to the filter techniques.

Levels of  $\text{H}_2\text{SO}_4$  up to  $11 \mu\text{g}/\text{m}^3$  were observed in California's South Coast Air Basin (SCAB) using selective extraction with benzaldehyde. Strong particulate acid measurements by titrimetry generally supported the  $\text{H}_2\text{SO}_4$  determinations. However,  $\text{HNO}_3$  appeared to contribute to the particulate acidity together with the  $\text{H}_2\text{SO}_4$ . Gaseous nitric acid measurements in the SCAB using nylon or NaCl-impregnated after-filters were substantially higher than those by the difference technique. This correlated with losses of nitrate from the Teflon prefilters, which exceeded 50% at high ambient temperature and low relative humidity. Heating the filter samplers was shown to increase sampling errors. Atmospheric nitrate results obtained in short-term, low volume sampling with Gelman A glass fiber filters approximated those with the TIN samplers. Accordingly, these glass fiber filters retained essentially all the gaseous nitric acid sampled.

## TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
List of Figures	vi
List of Tables	viii
Acknowledgements	x
I. Introduction	1
II. Technical Summary and Conclusions	3
III. Laboratory Evaluations of Techniques for HNO <sub>3</sub> and Particulate Nitrate Measurement	8
A. Nitric Acid Sampling with Filters	8
B. Negative Errors in Particulate Nitrate Filter Sampling	20
C. A Potential Reference Method for HNO <sub>3</sub> and Particulate Nitrate Sampling	24
D. Modified Chemiluminescent NO <sub>x</sub> Analyzer Method	30
E. Intermethod Comparison of Techniques for HNO <sub>3</sub> Measurement	35
IV. Laboratory Evaluation of Sampling Techniques for Atmospheric H <sub>2</sub> SO <sub>4</sub>	45
A. Introduction	45
B. Experimental Procedure	45
C. Results	45
V. Atmospheric Sampling Studies	48
A. Sampling Strategy	48
B. Experimental Procedures	48

	<u>Page</u>
C. Summary of Data	52
D. Particulate Acid Results	52
E. Measurement of Nitric Acid	63
F. Negative Errors in Particulate Nitrate Sampling	68
G. Positive Errors in Particulate Nitrate Sampling with Glass Fiber Filters	71
H. Atmospheric Nitrate and HNO <sub>3</sub> Levels at Claremont, California	75
I. Intermethod Comparison of Techniques for Atmospheric Ammonia Determination	75
J. The Role of Ammonia in Nitrate Chemistry	75
K. The Composition of Atmospheric Particulate Nitrate	79
L. Conclusions	83
VI. References	87

LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Retention of HNO <sub>3</sub> on Atmospheric Particulate Matter (300-500 µg/m <sup>3</sup> HNO <sub>3</sub> )	15
2	HNO <sub>3</sub> Collection Efficiency of Nylon and NaCl-Impregnated Filters (50-80% R.H.)	18
3	Schematic Diagram of Nitric Acid Measurement by a Difference Technique	27
4A	Schematic of Unmodified Monitor Labs NO <sub>x</sub> Analyzer	34
4B	Schematic of Monitor Labs Analyzer Modified for HNO <sub>3</sub> Analysis	34
5	Monitor Labs Response to Nitric Oxide on 100 ppb Range	36
6	Monitor Labs Response to HNO <sub>3</sub> on 100 ppb Range	37
7	Schematic Compilation of HNO <sub>3</sub> Filter Collection Results, Trial 16C (µg/m <sup>3</sup> )	39
8	Schematic Compilation of HNO <sub>3</sub> Filter Collection Results, Trial 16D (µg/m <sup>3</sup> )	40
9	Schematic Compilation of HNO <sub>3</sub> Filter Collection Results, Trial 16E (µg/m <sup>3</sup> )	41
10	Schematic Compilation of HNO <sub>3</sub> Filter Collection Results, Trial 16F (µg/m <sup>3</sup> )	42
11	SO <sub>2</sub> Emissions and Prevailing Wind Patterns	50
12	Diurnal Variations of Particulate Acids, Ammonia, Wind Speed and Direction at Lennox, California	59
13	Diurnal Variations of Particulate Acids, Ammonia and Nitric Acid at Claremont, California	64
14	Atmospheric HNO <sub>3</sub> Collection on Nylon vs NaCl/Whatman 41 Filters	65
15	Comparison of HNO <sub>3</sub> by Filter Collection and "by Difference" Using Heated Samplers	66
16	Comparison of HNO <sub>3</sub> by Filter Collection and "by Difference" Heated Samplers	67

LIST OF FIGURES (continued)

<u>Number</u>	<u>Title</u>	<u>Page</u>
17	Comparison of $\text{HNO}_3$ by Long Path Fourier Transform Infrared (FTIR) and "by Difference"	69
18	Scatter Diagram of Nitrate Against Strong Acid Concentrations for Hi-Vol Samples Collected on Quartz Fiber Filters	70
19	Scatter Diagram of the Proportion of Particulate Nitrate Retained by a Teflon Filter Against the Particulate Strong Acid Concentration at Lennox, California	72
20	Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Unheated)	73
21	Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Heated)	74
22	Glass Fiber Filters as Total Inorganic Nitrate Samplers	76
23	Diurnal Variations of $\text{HNO}_3$ , Particulate Nitrate and Ozone at Claremont, California	77
24	Comparison of $\text{NH}_3$ by Long Path Fourier Transform Infrared (FTIR) and by Oxalic Acid-Impregnated Filters	78
25	Atmospheric Nitric Acid Against Ammonia Concentrations at Claremont	80
26	Relative Humidity Dependence of the Calculated $\text{NH}_4\text{NO}_3$ Dissociation Constant	81
27	Temperature Dependence of the Calculated $\text{NH}_4\text{NO}_3$ Dissociation Constant	82
28	The Percent of Nitrate on the Prefilter of the Particulate Nitrate Sampler vs $\text{HNO}_3$ Concentration	84
29	The Percent of Nitrate on the Prefilter of the Particulate Nitrate Sampler vs Temperature	85

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Recovery of HNO <sub>3</sub> by Various Extraction Procedures from Unheated Samplers (μg NO <sub>3</sub> <sup>-</sup> per Filter)	9
2	Recovery of HNO <sub>3</sub> with and without Teflon Prefilters Using Unheated NaCl/W41 Samplers	11
3	Loss of HNO <sub>3</sub> on Prefilters, Particulate Matter and Sampler Walls	12
4	The Effects of Heating on HNO <sub>3</sub> Recovery with Clean and Particulate Loaded Prefilters	13
5	Efficiency of Post-Heated Filters for HNO <sub>3</sub> Collection	16
6	Comparison of Duralon and Ghia Nylon Filters for HNO <sub>3</sub> Collection	19
7	Loss of < 0.5 μm NH <sub>4</sub> NO <sub>3</sub> Particles from Teflon Filters into a Clean Air Stream (μg NO <sub>3</sub> <sup>-</sup> /filter)	21
8	Percent Loss of NH <sub>4</sub> NO <sub>3</sub> from Teflon Filters by Reaction with HCl in Air at 50% R.H.	23
9	Loss of NH <sub>4</sub> NO <sub>3</sub> from Inert Filters Due to Reaction with H <sub>2</sub> SO <sub>4</sub> Aerosol	25
10	Efficiency Values of Diffusion Denuder for 220-345 μg/m <sup>3</sup> (85-135 ppb) Nitric Acid	29
11	Conditions Studied for Loss of 0.1-0.4 μm NH <sub>4</sub> NO <sub>3</sub> Particles in the Acid Gas Denuder	31
12	Loss of 2 ± 1 μm NH <sub>4</sub> NO <sub>3</sub> Particles in Acid Gas Denuder Based on Particulate Nitrate Collection	32
13	Intermethod Comparison of HNO <sub>3</sub> Sampling Techniques under Laboratory Conditions (μg/m <sup>3</sup> )	43
14	Assessment of Artifact H <sup>+</sup> Formation Caused by Use of An Ammonia Denuder at 20°C	46
15	Sampling Strategy at Lennox and Claremont, California	49
16	Summary of Analytical Methods and Their Precision, Accuracy and Limits of Detection	51
17	Analysis of Respirable Particulate Hi-Vol and NH <sub>3</sub> Sampler Results from Lennox, California (μg/m <sup>3</sup> )	53

## LIST OF TABLES (continued)

<u>Number</u>	<u>Title</u>	<u>Page</u>
18	Analysis of Respirable Particulate Hi-Vol and NH <sub>3</sub> Sampler Results from Claremont, California ( $\mu\text{g}/\text{m}^3$ )	54
19	Analysis of Lo-Vol Respirable Particulate Samples (with NH <sub>3</sub> Denuder) from Lennox, California ( $\mu\text{g}/\text{m}^3$ )	55
20	Analysis of Lo-Vol Respirable Particulate Samples (with NH <sub>3</sub> Denuder) from Claremont, California ( $\mu\text{g}/\text{m}^3$ )	56
21	Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Lennox, California ( $\mu\text{g}/\text{m}^3$ as NO <sub>3</sub> <sup>-</sup> )	57
22	Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Claremont, California ( $\mu\text{g}/\text{m}^3$ as NO <sub>3</sub> <sup>-</sup> )	58
23	Correlation Coefficients Between Aerosol and Gaseous Pollutants Sampled At Lennox, California	61
24	Linear Regression Analysis of Aerosol and Gaseous Pollutants Sampled at Lennox, California	62

#### ACKNOWLEDGEMENTS

FTIR measurements were made by E. C. Tuazon, Statewide Air Pollution Research Center, University of California (Riverside). The concept of measuring nitric acid as the difference between total inorganic nitrate and particulate nitrate determined using an acid gas denuder was devised by R. Shaw and co-workers, U. S. Environmental Protection Agency. The authors also express their appreciation to Professor G. Kok, Harvey Mudd College, and to the staff and management of the South Coast Air Quality Management District for providing facilities for atmospheric sampling. S. Twiss assisted with the data reduction and display.

J. Suder served as project officer for this program. His helpfulness throughout this work is sincerely appreciated.

This report was submitted in fulfillment of ARB Contract Number A8-111-31, Evaluation and Development of Procedures for Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air--Phase II, by the Air and Industrial Hygiene Laboratory, Laboratory Services Branch, California Department of Health Services. Work was completed as of October 1, 1980.

## I. INTRODUCTION

Phase I of this program investigated methods for the determination of sulfuric acid and strong acids in atmospheric particulates as well as nitric acid in ambient air. The procedures for particulate acids employed sampling with inert filters, processing the samples under conditions designed to preserve strong acids followed by analytical techniques appropriate for sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and strong acids. These techniques were evaluated and compared using laboratory-generated mixtures of  $\leq 0.3 \mu\text{m}$  diameter  $\text{H}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{HSO}_4$  aerosols on clean and atmospheric particulate-loaded filters. Based on filtration efficiencies and recovery studies with submicron sulfuric acid aerosol, acid-washed quartz fiber and one or two micron pore size Teflon membrane filters were employed.  $\text{H}_2\text{SO}_4$  was determined by selective extraction with benzaldehyde followed by quantitation as sulfate by the AIHL microsulfate method. Strong acid was measured by microtitration with exclusion of carbon dioxide. Nitric acid was sampled by collection on nylon, and on sodium chloride-impregnated cellulose filters after removal of atmospheric particles with an inert prefilter. Following aqueous extraction, nitric acid was determined as nitrate by the automated copper-cadmium reduction, diazotization procedure.

The applicability and utility of these procedures were assessed by atmospheric sampling in Pittsburg, California. To stabilize strong acids on filters,  $> 3 \mu\text{m}$  particles, which can contain alkaline soil components, were excluded. In addition, with one sampler atmospheric ammonia was removed ahead of the filter by means of a diffusion denuder. Simultaneous gas phase ammonia measurements were made to assist in interpreting the particulate sample results.

The Phase I results showed that the presence of atmospheric particulate matter sharply reduced recoveries of laboratory-generated  $\text{H}_2\text{SO}_4$  but recoveries of total strong acid usually remained  $\geq 60\%$ . Anhydrous benzaldehyde was found to extract  $\text{NH}_4\text{HSO}_4$  to a substantial degree. Laboratory-generated nitric acid was collected with high efficiency by both nylon and  $\text{NaCl}$ -impregnated filters while nitrogen dioxide was not retained by these filters at 90% R.H. The ammonia denuder was shown to remove ammonia with  $> 99\%$  efficiency.

The field sampling in Pittsburg, California showed good correlation between sulfuric acid and particulate strong acid measurements. As much as  $0.6 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  and  $1.6 \mu\text{g}/\text{m}^3$  acidity, expressed as  $\text{H}_2\text{SO}_4$ , was found.

However, based on recovery studies we believe these represent lower limit values. Excellent agreement was found between nitric acid measurement by nylon and NaCl on cellulose filter collection with concentrations up to  $4 \mu\text{g}/\text{m}^3$ . Glass fiber filters were shown to collect, quantitatively, both particulate nitrate and gas phase nitric acid at the relatively low concentrations observed at Pittsburgh.

The present phase of this study was designed to evaluate these sampling and analysis techniques at two locations in California's South Coast Air Basin (SCAB). One of the sites, Lennox, was expected to exhibit relatively high  $\text{H}_2\text{SO}_4$  levels based on its proximity to sulfur oxide emission sources. The second site, Claremont, was in an area where high ( $> 50 \mu\text{g}/\text{m}^3$ )  $\text{HNO}_3$  and particulate nitrate levels were expected. Improved procedures were employed to minimize losses of the particulate acids during sample storage and handling, and the analytical procedure was modified to reduce the limit of detection for  $\text{H}_2\text{SO}_4$  with hi-vol filter samples. In addition to the nitrate and  $\text{HNO}_3$  sampling techniques previously employed, the present study included a potential reference technique for particulate nitrate and  $\text{HNO}_3$  measurement. This technique measures  $\text{HNO}_3$  as the difference between total inorganic nitrate (gaseous plus particulate nitrate) and true particulate nitrate.  $\text{HNO}_3$  and  $\text{NH}_3$  results at Claremont were compared to those of the Statewide Air Pollution Research Center's Fourier transform, long path infra-red analysis method. The effect of atmospheric  $\text{NH}_3$  on both nitrate and sulfate chemistry was also assessed.

Laboratory evaluations in the present phase included measurement of sampling errors for  $\text{HNO}_3$  with filter techniques, and an evaluation of the potential reference technique for particulate nitrate and nitric acid. In addition, a continuous  $\text{HNO}_3$  analyzer was constructed from a chemiluminescent  $\text{NO}_x$  monitor, and evaluated. Since the use of the  $\text{NH}_3$  denuder in acid sulfate sampling may cause increased acid formation in particulate matter by loss of  $\text{NH}_3$  from  $\text{NH}_4^+$  salts, laboratory trials evaluated this possibility.

## II. TECHNICAL SUMMARY AND CONCLUSIONS

A combined laboratory and field study has continued investigations of methods for monitoring atmospheric sulfuric acid, nitric acid and strong acids in atmospheric particulates. A potential reference technique for atmospheric  $\text{HNO}_3$  and particulate nitrate was also investigated. Sulfuric acid was measured by selective extraction with benzaldehyde followed by quantitation as sulfate using the ATHL microchemical sulfate method. Nitric acid was measured by sampling with nylon or sodium chloride-impregnated cellulose filters following removal of particulate nitrates with a Teflon prefilter (1 or 2  $\mu\text{m}$  pore size Zefluor, Ghia Corp.). Following aqueous extraction, nitric acid was measured as nitrate by the automated, copper-cadmium reduction diazotization procedure. Nitric acid was also measured continuously by a modified Monitor Labs chemiluminescent  $\text{NO}_x$  analyzer and by a newly proposed difference technique. The latter uses the sum of the nitrate retained by a Teflon prefilter and nylon or NaCl-impregnated after-filter to measure total inorganic nitrate (TIN). Particulate nitrate (PN) was measured with a Teflon prefilter plus after-filter following passage of the sample stream through a diffusion denuder coated with powdered MgO to remove acidic gases (e.g.,  $\text{HNO}_3$ ). TIN less PN provided a measure of the  $\text{HNO}_3$  concentration. The TIN and PN samplers were evaluated as potential reference methods for  $\text{HNO}_3$  and particulate nitrate. Particulate strong acid was measured by a microtitration procedure in which an amount of strong acid sufficient to produce  $\text{pH} = 4.0$  in distilled water was added to each sample followed by potentiometric titration with base to this pH.

The laboratory phase of the  $\text{H}_2\text{SO}_4$  and particulate acid method evaluation included an assessment of errors induced by use of an ammonia diffusion denuder. The latter was used in atmospheric sampling to minimize losses of the acid by neutralization with  $\text{NH}_3$  and other gaseous bases following collection on a filter. In principle such a denuder could cause errors in measured  $\text{H}_2\text{SO}_4$  and  $\text{H}^+$  values by inducing loss of  $\text{NH}_3$  from  $(\text{NH}_4)_2\text{SO}_4$  and other ammonium salts. In addition any transfer to the filter of the  $\text{NH}_3$ -trapping reagent, phosphorous acid, would produce positive errors in the  $\text{H}^+$  measurements. However, passage of clean air through the denuder followed by blank Teflon filters or filters loaded with  $(\text{NH}_4)_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$ - $\text{NH}_4\text{NO}_3$  mixtures caused no increase in acidity on the filters. Thus use of the ammonia denuder does not produce positive errors of this type.

Nitric acid sampling with filters was evaluated with and without filter heating (e.g., passing heated air through the sample for three minutes

following sampling) to desorb  $\text{HNO}_3$  from sampler surfaces. The efficiency of NaCl-impregnated Whatman 41 cellulose filters (NaCl/W41) for  $\text{HNO}_3$  collection remained about 97% under all conditions. However, with heated nylon filters the efficiency was low at high  $\text{HNO}_3$  loadings (e.g., 30% for sampling of 2350  $\mu\text{g HNO}_3$ , as  $\text{NO}_3^-$ ). Unheated nylon filters provided  $95 \pm 11\%$  collection efficiency at up to 3000  $\mu\text{g HNO}_3$ . Nylon filters from Millipore Corp. and Ghia Corp. were shown to be equal for  $\text{HNO}_3$  sampling.

Clean Teflon prefilters retained negligible amounts of  $\text{HNO}_3$  with or without heating. However, prefilters loaded with atmospheric particulate matter retained up to 25% of  $\text{HNO}_3$  at 300 to 500  $\mu\text{g}/\text{m}^3$  concentration, the retention increasing with the particulate matter loading. Heating decreased but did not eliminate the observed retention. The  $\text{HNO}_3$  retained on the prefilter represents a positive error in particulate nitrate measurement by filter collection. However, a loss of atmospheric  $\text{HNO}_3$  by collection on the prefilter may not be observable in atmospheric sampling because of a compensating error; dissociation of  $\text{NH}_4\text{NO}_3$  on inert prefilters and loss as  $\text{HNO}_3$  might more than compensate for atmospheric  $\text{HNO}_3$  retention. Such dissociation is probably repressed in laboratory trials with constant, elevated levels of  $\text{HNO}_3$ .

Loss of  $\text{NH}_4\text{NO}_3$  from Teflon filters by volatilization into a stream of clean air (with collection of  $\text{HNO}_3$  on a reactive after-filter) was shown to be important. At 21°C, an average of 45% nitrate loss was observed in six hours at 20 Lpm with filters initially loaded with about 200  $\mu\text{g NO}_3^-$ . A lower limit dissociation constant value of 22 (ppb)<sup>2</sup> was determined. Such loss yields positive errors in  $\text{HNO}_3$  sampling by the Okita and Spicer procedures but negative errors in particulate nitrate. Loss of  $\text{NH}_4\text{NO}_3$  from Teflon filters was also demonstrated by reaction with  $\text{H}_2\text{SO}_4$  aerosol and with gaseous HCl. With  $\text{H}_2\text{SO}_4$  at an  $\text{H}^+/\text{NO}_3^-$  equivalents ratio of 1.4, nitrate loss of about 95% was observed in six hours in a stream of clean air at 90% R.H.

Loss of nitrate by  $\text{NH}_4\text{NO}_3$ -HCl reaction has not been previously reported. Two hour exposures of  $100 \pm 20 \mu\text{g NH}_4\text{NO}_3$  to air containing about 20 ppb HCl at 50% R.H. caused ca. 90% loss of nitrate compared to 18% by volatilization under these conditions. Atmospheric levels of HCl in U.S. cities have not been reported but may be similar to values found in coastal cities in Japan ( $\leq 8$  ppb). Thus nitrate reaction with HCl may be another source of negative error in particulate nitrate and positive error in  $\text{HNO}_3$  measurement by dual filter methods.

Laboratory evaluation of the potential nitrate reference sampler included measurement of the efficiency of the denuder for  $\text{HNO}_3$  removal and the extent of particulate nitrate loss in the denuder. The denuder was shown to remove, on average, 88% of gaseous  $\text{HNO}_3$ . No loss of 0.1 to 0.4  $\mu\text{m}$  or  $2 \pm 1 \mu\text{m}$  particles of  $\text{NH}_4\text{NO}_3$  was measurable in the denuder. However, loss of  $\geq 3 \mu\text{m}$  nitrate particles by impaction might still be a significant source of error. This could not be directly evaluated.

A dual channel Monitor Labs model 8840 E chemiluminescent  $\text{NO}_x$  analyzer was converted to measure  $\text{HNO}_3$  by difference between  $\text{NO} + \text{NO}_2 + \text{HNO}_3$  on one channel and  $\text{NO} + \text{NO}_2$  on the second. Response of the sampler to pure  $\text{HNO}_3$  was about 10% below that with  $\text{NO}$ . The limit of detection was estimated to be 6 ppb. A substantial lag time was observed in response to variation in the  $\text{HNO}_3$  levels apparently due to conditioning of the tubing. Further improvements are needed to decrease the limit of detection and improve the response rate before its routine use can be recommended.

Nitric acid measurements by the modified chemiluminescent  $\text{NO}_x$  analyzer were compared to those by filter collection (Okita Method) and to nitric acid by the difference method, TIN-PN, using laboratory-generated  $\text{HNO}_3$ . When corrected for the 12%  $\text{HNO}_3$  penetration through the denuder, results for the three methods agreed within 11%. Without correction, agreement was within 17%. The presence of particulate matter on the prefilter caused the Okita method results to be 13 to 18% below those of the other methods, reflecting  $\text{HNO}_3$  retention on the particulate matter.

Atmospheric sampling was done at Lennox and Claremont, California in the South Coast Air Basin. Lennox was chosen because of its expected elevated  $\text{H}_2\text{SO}_4$  levels while high nitrate levels were expected at Claremont. Sampling techniques included all described above except the chemiluminescent  $\text{HNO}_3$  analyzer which was not then available. In addition, sampling for  $\text{NH}_3$  was done using a lo-vol filter sampler with a glass fiber prefilter (pH = 7.6) and an oxalic acid-impregnated after-filter. Sampling for  $\text{H}_2\text{SO}_4$ ,  $\text{H}^+$  and other aerosol constituents employed short term respirable hi-vol filter samples on acid-washed quartz filters (without  $\text{NH}_3$  denuder) in addition to the lo-vol sampler previously described.

At Lennox  $\text{H}_2\text{SO}_4$  concentrations up to  $11 \mu\text{g}/\text{m}^3$  were observed with the hi-vol sampler, the first report of substantial  $\text{H}_2\text{SO}_4$  levels in California ambient air. This compares to California's 24-hour standard of  $25 \mu\text{g}/\text{m}^3$  for total water-soluble  $\text{SO}_4^{2-}$ . Particulate acidity values appeared to represent  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and adsorbed (or dissolved)  $\text{HNO}_3$ . Eight-hour lo-vol filter samples had low  $\text{H}_2\text{SO}_4$  recoveries but  $\text{H}^+$  values up to nearly  $11 \mu\text{g}/\text{m}^3$  (expressed as  $\text{SO}_4^{2-}$ ), consistent with the conversion of  $\text{H}_2\text{SO}_4$  to  $\text{NH}_4\text{HSO}_4$ , a strong acid, on the filter. Short term sampling and low temperature sample storage appeared to be useful in maximizing  $\text{H}_2\text{SO}_4$  recovery. The dependence of  $\text{H}_2\text{SO}_4$  levels on wind direction at Lennox suggested stationary emissions as the source of the observed  $\text{H}_2\text{SO}_4$ .

Glass fiber 47 mm diameter filters sampling 2 to 8 hours at 25 Lpm were shown to approximate total inorganic nitrate (TIN) samplers, collecting both atmospheric particulate nitrates and nitric acid. The latter represented, on average, about half of the TIN. Nitric acid was the only observable contributor to artifact particulate nitrate with glass fiber filters.

Heating of filter samplers for atmospheric particulate nitrate and  $\text{HNO}_3$  caused increased error and is not recommended. Even without artificial heating, > 50% loss of PN from Teflon prefilters occurred under warm and

dry ambient conditions with corresponding positive error in  $\text{HNO}_3$  measurement. Such loss and positive error appear to dominate over  $\text{HNO}_3$  retention on the prefilters, which were changed at 2 to 8 hour intervals to minimize particulate loadings. Under conditions of high particulate acidity, evidence of acid-induced nitrate loss was also found.

Atmospheric nitric acid values were compared to those by simultaneous Fourier transform infra-red measurements. Results by the difference method were, on average, high by 20%, but were substantially more accurate than those by simple filter collection techniques. The 12% penetration of  $\text{HNO}_3$  through the acid gas denuder was more than offset by an opposing source of error, possibly loss of  $> 3 \mu\text{m}$  PN in the denuder. Nevertheless, sampling of PN with an acid-gas denuder led to improved sampling accuracy, especially at high ambient temperature, relative to nitrate sampling with a Teflon filter.

Aside from volatilization of nitrate from the prefilters, simultaneous  $\text{HNO}_3$  and  $\text{NH}_3$  measurements and the temperature dependence of the calculated dissociation constant support the significance of an equilibrium of these gases with solid  $\text{NH}_4\text{NO}_3$  in the atmosphere. Observed diurnal variations of particulate nitrate (e.g., morning maxima) and  $\text{HNO}_3$  may be more influenced by the effects of changing temperature and  $\text{NH}_3$  levels than on the kinetics of  $\text{NO}_x$  to  $\text{HNO}_3$  conversion.

Principal conclusions from the current study are as follows:

1. Atmospheric  $\text{H}_2\text{SO}_4$  in California's South Coast Air Basin can be determined by short term (2 to 8 hour) sampling with acid-washed quartz fiber filters, low temperature storage of samples in air-tight containers, selective extraction with benzaldehyde and quantitation as  $\text{SO}_4^{2-}$  by the AIHL microsulfate method.
2. Levels of  $\text{H}_2\text{SO}_4$  up to  $11 \mu\text{g}/\text{m}^3$  were observed at Lennox probably due to nearby emissions of  $\text{H}_2\text{SO}_4$  and/or  $\text{SO}_3$ . Adsorbed or dissolved  $\text{HNO}_3$  probably contributes to the particulate acidity measured by titration.
3. An  $\text{NH}_3$  denuder is not essential for sampling atmospheric  $\text{H}_2\text{SO}_4$ .
4. Particulate nitrate sampling with inert filters yields results which are frequently only a small fraction of the true value because of dissociation of  $\text{NH}_4\text{NO}_3$  and loss of the resulting  $\text{HNO}_3$ . In addition, other strong acids (e.g.,  $\text{H}_2\text{SO}_4$ ) can cause substantial nitrate loss. If present, gaseous strong acids (e.g.,  $\text{HCl}$ ) will also cause negative errors in particulate nitrate.
5. Nitric acid values obtained by dual filter techniques (e.g., the Okita and Spicer procedures) are typically too high because of particulate nitrate loss from the prefilter.
6. Particulate nitrate (PN) results obtained with an acid gas denuder which removes  $\text{HNO}_3$  are substantially more accurate than those obtained

by sampling with inert filters under conditions of high ambient temperature and low R.H.

7. Nitric acid results obtained as the difference between total inorganic nitrate (TIN) and PN are more accurate than these by the dual filter procedures, but average about 20% too high relative to a long path infra-red technique. Loss of  $> 3 \mu\text{m}$  nitrate particles in the denuder may be the cause of the positive error.
8. Artifact nitrate formation on glass fiber filters corresponded to the collection of essentially all of the atmospheric  $\text{HNO}_3$  even at high levels of the acid. Thus it is likely that the nitrate values obtained by the present ARB hi-vol network represent the sum of the particulate nitrate and nitric acid rather than particulate nitrate alone. For samples in the South Coast Air Basin,  $\text{HNO}_3$  represented about half of the total inorganic nitrate.
9. Further modifications of the Monitor Labs  $\text{NO}_x$  analyzer are needed to reduce the limit of detection for  $\text{HNO}_3$  as well as the response time.

### III. LABORATORY EVALUATION OF TECHNIQUES FOR $\text{HNO}_3$ AND PARTICULATE NITRATE MEASUREMENTS

#### A. Nitric Acid Sampling with Filters

##### 1. Introduction

The Okita procedure<sup>2</sup> for  $\text{HNO}_3$  collection employs a Teflon pre-filter to remove particulate matter and an NaCl-impregnated cellulose after-filter to collect the  $\text{HNO}_3$ , later measured as nitrate. The Spicer procedure<sup>3</sup> differs only in the use of nylon in place of the NaCl-impregnated filter. Filter collection of gaseous  $\text{HNO}_3$  is, in principle, subject to error from losses by sorption on the inner walls of the sampler, on the inert pre-filter and on the atmospheric particulate matter on the prefilter. Since such sorption might be rapidly reversible, desorption could occur after sampling but before  $\text{HNO}_3$  on the prefilter or sampler walls could be recovered by extraction. The effects of heating the sampler to drive any weakly bound  $\text{HNO}_3$  to the after-filter was, therefore, evaluated using both clean and atmospheric particulate-loaded Teflon prefilters.

Both Duralon (Millipore Corp.) and Ghia Corp. nylon filters were evaluated. The former are no longer commercially available. Nylon and NaCl-impregnated, Whatman 41 cellulose filters (NaCl/W41) were compared for efficiency with and without filter heating at varying  $\text{HNO}_3$  loadings. The influence of extraction conditions was evaluated since any differences observed may relate to the ease of extraction of  $\text{HNO}_3$  (as  $\text{NO}_3^-$ ) following collection. As in the preliminary studies<sup>1</sup>, nylon filters were extracted in 0.1N NaOH based on findings by Lazrus<sup>4</sup>, and NaCl/W41 and Teflon prefilters, in double distilled water.

##### 2. Extraction of $\text{HNO}_3$ from Filters

To evaluate the effectiveness of different extraction procedures,  $\text{HNO}_3$  at two levels was collected simultaneously with up to seven filters without using prefilters. Extraction conditions and results are given in Table 1 from which we conclude that, 1) extraction using an Eberbach platform shaker recovers, on average, 35% more nitrate compared to ultrasonic extraction, and 2) no difference is observable between 30 and 60 minutes ultrasonic extraction or between 30 and 60 minutes mechanical shaking.

Table 1

RECOVERY OF  $\text{HNO}_3$  BY VARIOUS EXTRACTION PROCEDURES FROM UNHEATED SAMPLERS ( $\mu\text{g NO}_3^-$  PER FILTER)<sup>a, b</sup>

<u>Trial</u>	<u>Filter Type</u>	<u>Solvent</u>	<u>Extraction Device</u>	<u>Time, min</u>	<u>HNO<sub>3</sub> Recovered</u>
A	Duralon (nylon)	0.1N NaOH	ultrasonic bath <sup>c</sup>	30	2198 ± 184
	Duralon (nylon)	0.1N NaOH	ultrasonic bath	60	2160 <sup>e</sup>
	Duralon (nylon)	0.1N NaOH	platform shaker <sup>d</sup>	60	2994 ± 161
	NaCl/W41	H <sub>2</sub> O	platform shaker	30	2880 <sup>e</sup>
<hr/>					
B	Duralon (nylon)	0.1N NaOH	platform shaker	30	171 ± 125
	Duralon (nylon)	0.1N NaOH	platform shaker	60	146 ± 23
	Duralon (nylon)	0.1N NaOH	ultrasonic bath	30	118 <sup>e</sup>
	NaCl/W41	H <sub>2</sub> O	platform shaker	60	131 ± 74

- a. Two hour sampling at 20 Lpm and 50% R.H. No prefilters were employed. Based on nitrate recovered from NaCl/W41 filters the  $\text{HNO}_3$  concentrations were  $1200 \mu\text{g}/\text{m}^3$  and  $55 \pm 31 \mu\text{g}/\text{m}^3$  for trials A and B, respectively. Except as noted, results are mean values for two filters in parallel.
- b. Nylon filters are extracted in 5.0 mL 0.1M NaOH and neutralized with 5 mL 0.1N HCl prior to analysis. NaCl/W41 filters are extracted in 10 mL H<sub>2</sub>O.
- c. Bransonic Model 42.
- d. Eberbach Model 6000.
- e. Single trial.

Based on these results as well as independent studies of nitrate extraction in water,<sup>5</sup> 60-minute mechanical shaking was employed for subsequent laboratory and atmospheric samples.

### 3. Loss of HNO<sub>3</sub> on Prefilters, Particulate Matter and Sampler Walls

If HNO<sub>3</sub> loss by desorption from Teflon prefilters is significant, then samplers lacking prefilters should yield higher HNO<sub>3</sub> recoveries. Indeed preliminary results suggested this to be the case.<sup>1</sup> Additional trials comparing HNO<sub>3</sub> collection with clean and atmospheric particulate-loaded prefilters, with and without a Teflon prefilter, are given in Table 2. Two types of samplers without prefilters were evaluated; one type employed a two-stage, stacked Nuclepore filter holder with the first-stage empty. The second used only a Nuclepore single-stage filter holder. No filter heating was employed. Comparison of results with these samplers permitted assessment of the significance of air leakage with the two-stage sampler as well as the additional wall losses encountered when a prefilter is used. Results are corrected for the atmospheric particulate nitrate if present (assuming no volatilization of this nitrate from the prefilter during these trials).

Based on ratios of means, average results by the three samplers differed by only  $\pm 3\%$ . Relative to the samplers with prefilters, the ratios of mean results were 0.97 for the two-stage and 1.03 for the single-stage samplers without prefilters. Thus these results do not support the significance of HNO<sub>3</sub> loss by desorption. The retention of HNO<sub>3</sub> on particulate matter observed in these trials will be discussed below.

Okita et al.<sup>2</sup> and Forrest et al.<sup>6</sup> have employed sampler heating to decrease error in HNO<sub>3</sub> sampling. To evaluate the effects of such heating, Teflon prefilters and NaCl/W41 or nylon after-filters were subjected to either continuous heating during sampling at 40°C, or to three minutes sampling clean air at ca. 50°C following HNO<sub>3</sub> collection. Both clean and atmospheric-particulate loaded pre-filters were employed. The filter holder inner walls and filter support grid were rinsed to assess HNO<sub>3</sub> losses on these surfaces.

Tables 3 and 4 detail experiments to assess the effects of filter heating, use of a clean or soiled prefilter and extent of wall losses. We conclude from these experiments that 1) as in Table 2, the use of a clean prefilter does not reduce the HNO<sub>3</sub> recovered on the after-filter with or without filter heating, 2) HNO<sub>3</sub> losses to the sampler walls are not significant, 3) particulate matter on the prefilter caused  $5.6 \pm 0.4\%$  retention of HNO<sub>3</sub> at 50% R.H. and about 30% retention at 80% R.H. in spite of filter heating. (Since the atmospheric nitrate level on the prefilter was only about  $3 \mu\text{g}/\text{m}^3$ , volatilization of this NO<sub>3</sub><sup>-</sup> from the pre-filter would cause a relatively minor error in the observed HNO<sub>3</sub>

Table 2 RECOVERY OF HNO<sub>3</sub> WITH AND WITHOUT TEFLON PREFILTERS USING UNHEATED NaCl/W41 SAMPLERS<sup>a</sup>.

Trial	Temp °C	R.H. (%)	Prefilter	Prefilter Loading, µg	HNO <sub>3</sub> Recovered, µg/m <sup>3</sup> as NO <sub>3</sub> <sup>-</sup>		
					Prefilter	After-Filter	Σ <sup>b</sup>
16C	32	30	None <sup>c</sup>	None	-	300	300
	32	30	None <sup>d</sup>	None	-	244	244
	32	30	Zefluor <sup>e</sup>	None	1.3 ± 0.1	240 ± 14	244 ± 14
16D	32	30	None <sup>c</sup>	None	-	193	193
	32	30	None <sup>d</sup>	None	-	256	256
	32	30	Zefluor <sup>e</sup>	271 ± 87	7.0 ± 4.4 <sup>f</sup>	235.0 ± 0.5	242 ± 4.4
16E	21	50	None <sup>c</sup>	None	-	211	211
	21	50	None <sup>d</sup>	None	-	255	255
	21	50	Zefluor <sup>e</sup>	None	2.2 ± 0.1	236 ± 14	238 ± 14
16F	21	50	None <sup>c</sup>	None	-	207	207
	21	50	None <sup>d</sup>	None	-	210	210
	21	50	Zefluor <sup>e</sup>	768 ± 5	39.6 ± 1.5 <sup>g</sup>	174 ± 1	214 ± 2

- a. All trials are approximately four hours at 20 Lpm.
- b. Based on the recoveries in preceding trials, washing of filter holders was omitted.
- c. A two stage Nuclepore stacked filter holder was used with the first stage empty.
- d. A single-stage Nuclepore filter holder was used.
- e. 2.0 µm pore size Ghia Corporation Teflon filters.
- f. Corrected for the 1.0 µg/m<sup>3</sup> NO<sub>3</sub><sup>-</sup> contributed by the atmospheric particulate matter.
- g. Corrected for the 6.1 µg/m<sup>3</sup> NO<sub>3</sub><sup>-</sup> contributed by the atmospheric particulate matter.

Table 3

Loss of HNO<sub>3</sub> on Prefilters, Particulate Matter and Sampler Walls<sup>a</sup>

Exp. No.	Relative Humidity %	Teflon Prefilter Loading	After-Filter	Heating Technique	HNO <sub>3</sub> Recovered, $\mu\text{g}/\text{m}^3$ as NO <sub>3</sub> <sup>-</sup>			
					Prefilter	After-Filter	Holder	$\Sigma$
2	50	clean	NaCl/W41	post <sup>b</sup>	< 4.0	253 ± 53	10 ± 6.2	265 ± 53
	50	atm. particulate <sup>c</sup>	NaCl/W41	post	15 ± 1.2 <sup>d</sup>	254 ± 4	4.7 ± 0.4	274 ± 4
	50	clean	NaCl/W41	contiruous <sup>e</sup>	< 3.6	262 ± 2	12 ± 15	276 ± 15
	50	clean	NaCl/W41	none	< 3.6	274	7.3	283
3	50	clean	Duralon <sup>f</sup>	post	< 4.0	214 ± 4	5.5 ± 2	222 ± 4
	50	clean	Duralon	contiruous	< 4.0	220	5.7	228
	50	clean	NaCl/W41	post	< 3.7	238 ± 42	33 ± 17	273 ± 45
	50	atm. particulate <sup>c</sup>	Duralon	contiruous	12 <sup>d</sup>	222	3.3	237
4	80	clean	Duralon	contiruous	< 3.8	190 ± 8	2.9 ± 0.3	195 ± 8
	80	atm. particulate <sup>g</sup>	Duralon	contiruous	29 ± 4 <sup>d</sup>	177 ± 8	3.3 ± 0.4	209 ± 17
	80	atm. particulate <sup>g</sup>	Duralon	post	32 <sup>d</sup>	157	9.9	200
	80	clean	NaCl/W41	post	< 3.7	229 ± 8	9.6 ± 1	240 ± 8
5a	50 <sup>h</sup>	clean	NaCl/W41	post	0.4 ± 0	308 ± 42	4.2 ± 1.0	313 ± 42
	50 <sup>h</sup>	no filter	NaCl/W41	post	---	343	3.5	347
5b	80 <sup>h</sup>	clean	NaCl/W41	post	0.7 ± 0.4	236 ± 2	5.1 ± 1	242 ± 2
	80 <sup>h</sup>	no filter	NaCl/W41	post	---	237	3.7	241

a. Except as noted, two-hour sampling at 20 Lpm with 47 mm filters. Prefilters are 1  $\mu\text{m}$  pore size Zefluor filters (Ghia Corp.).

b. Ambient air heated to ca. 50°C passed through sampler at 20 Lpm for 3 minutes.

c. Filters pre-loaded with 10 m<sup>3</sup> air samples in Berkeley containing 3.3 ± 0.4  $\mu\text{g}/\text{m}^3$  NO<sub>3</sub><sup>-</sup>.

d. Corrected for atmospheric NO<sub>3</sub><sup>-</sup>.

e. Sampler heated continuously at 40°C during sampling.

f. Nylon filters supplied by Millipore Corp.

g. Filters pre-loaded with 10 m<sup>3</sup> air samples in Berkeley containing 2.8 ± 0.4  $\mu\text{g}/\text{m}^3$  NO<sub>3</sub><sup>-</sup>.

h. Six-hour sampling.

Table 4

The Effects of Heating on HNO<sub>3</sub> Recovery with Clean and Particulate Loaded Prefilters<sup>a</sup>

<u>Prefilter</u>	<u>After-Filter</u>	<u>Heating Procedure</u>	<u>Nitric Acid Recovered <math>\mu\text{g}/\text{m}^3</math> as <math>\text{NO}_3^-</math></u>			
			<u>Prefilter<sup>b</sup></u>	<u>After-Filter</u>	<u>Holder</u>	<u><math>\Sigma</math></u>
Atm. particulate on 2 $\mu\text{m}$ Zefluor	Duralon	none	86.6	226	7.1	320
"	Duralon	post	83.1	140	7.1	230
Atm. particulate on 1 $\mu\text{m}$ Zefluor	Duralon	none	50.4	231	9.8	291
"	Duralon	continuous	41.4	174	4.7	220
"	Duralon	post	50.2	158	8.9	217
<hr/>						
Clean 2 $\mu\text{m}$ Zefluor	NaCl/W41	none	< 2.1	62.3 $\pm$ 7.2	8.4 $\pm$ 5.7	73 $\pm$ 9.2 <sup>c</sup>
"	NaCl/W41	post	< 2.1	66.4 $\pm$ 0.1	7.2 $\pm$ 0.1	75.2 $\pm$ 0.1 <sup>c</sup>
"	Duralon	none	< 2.1	53.1	9.0	63.2

a. Two-hour sampling at 50% R.H., 20 Lpm.

b. Results corrected for atmospheric nitrate with particulate loaded filters.

c. In these trials an additional NaCl/W41 filter behind the after-filter was used which collected ca. 1  $\mu\text{g}/\text{m}^3$  HNO<sub>3</sub> as NO<sub>3</sub><sup>-</sup>. The summations include these values.

retention), and 4) with heated samplers using nylon after-filters, recovery of  $\text{HNO}_3$  was reduced in some cases by up to 25%. The source of this loss and its variability will be discussed in Section 4 below.

In Tables 2 through 4, the level of  $\text{HNO}_3$  retained by the particulate matter on the prefilters varied depending on particulate loadings and exposure conditions. The relationship between TSP loadings on the prefilter and  $\text{HNO}_3$  retention with heated and unheated samplers is shown in Figure 1. With high TSP, > 20% retention is observed. It should be noted that with prefilters bearing relatively high particulate nitrate levels, volatilization of ammonium nitrate by dissociation to  $\text{HNO}_3$  may more than offset  $\text{HNO}_3$  retention. Under such conditions heating the samplers may aggravate this source of positive error in  $\text{HNO}_3$  measurement. However, such sources of positive error in  $\text{HNO}_3$  are probably repressed during these laboratory trials since the presence of a continuous, relatively high  $\text{HNO}_3$  level should hinder dissociation of  $\text{NH}_4\text{NO}_3$ . Positive errors in  $\text{HNO}_3$  measurement are more likely to be observed in atmospheric sampling. Frequent filter changes are desirable to minimize both positive and negative error in  $\text{HNO}_3$  measurement.

The nitrate values on nylon and NaCl/W41 filters in Tables 2, 3, 4 permit assessment of the precision of sampling  $\text{HNO}_3$  in the concentration range 60 to 300  $\mu\text{g}/\text{m}^3$ . The median C.V. for trials in which two or more values were averaged was 3.5% for NaCl/W41 ( $n = 13$ , range 0.1 to 21%) and 4.4% for Duralon nylon ( $n = 4$ , range 1.9 to 6.8%).

#### 4. The Efficiency of Nylon and NaCl-Impregnated Filters for $\text{HNO}_3$ Collection

The efficiency of post-heated nylon and NaCl/W41 for  $\text{HNO}_3$  collection at high  $\text{HNO}_3$  loadings was determined by sampling with two filters of the same type in series, and with nylon followed by NaCl/W41, as shown in Table 5. All trials were for six hours during which 1700-2600  $\mu\text{g}$  of  $\text{HNO}_3$  was sampled. Based on the proportion of  $\text{HNO}_3$  retained on the initial filter, NaCl/W41 filters were  $97 \pm 1\%$  efficient at 50 and 80% R.H. With a Duralon front filter and NaCl/W41 after-filter, the total recovered  $\text{HNO}_3$  was reduced by 16 to 40% suggesting unidentified losses in spite of post-heating the sampler. With two nylon filters in series, 30-50% of the  $\text{HNO}_3$  was on the after-filter. This implies relatively low efficiency for these filters, consistent with the low total recovered  $\text{HNO}_3$  in these samplers. To obtain efficiencies for nylon filters, the  $\text{HNO}_3$  retained on nylon front filters was compared to the  $\text{HNO}_3$  retained by the NaCl/W41 front filter sampling in parallel. The latter was corrected for the 3% penetration.

The results indicate that at high  $\text{HNO}_3$  loadings, post-heated nylon filters are only about 33% efficient at 50% R.H. and about

Figure 1

RETENTION OF  $\text{HNO}_3$  ON ATMOSPHERIC PARTICULATE MATTER  
( $300\text{-}500\mu\text{g}/\text{m}^3$   $\text{HNO}_3$ )

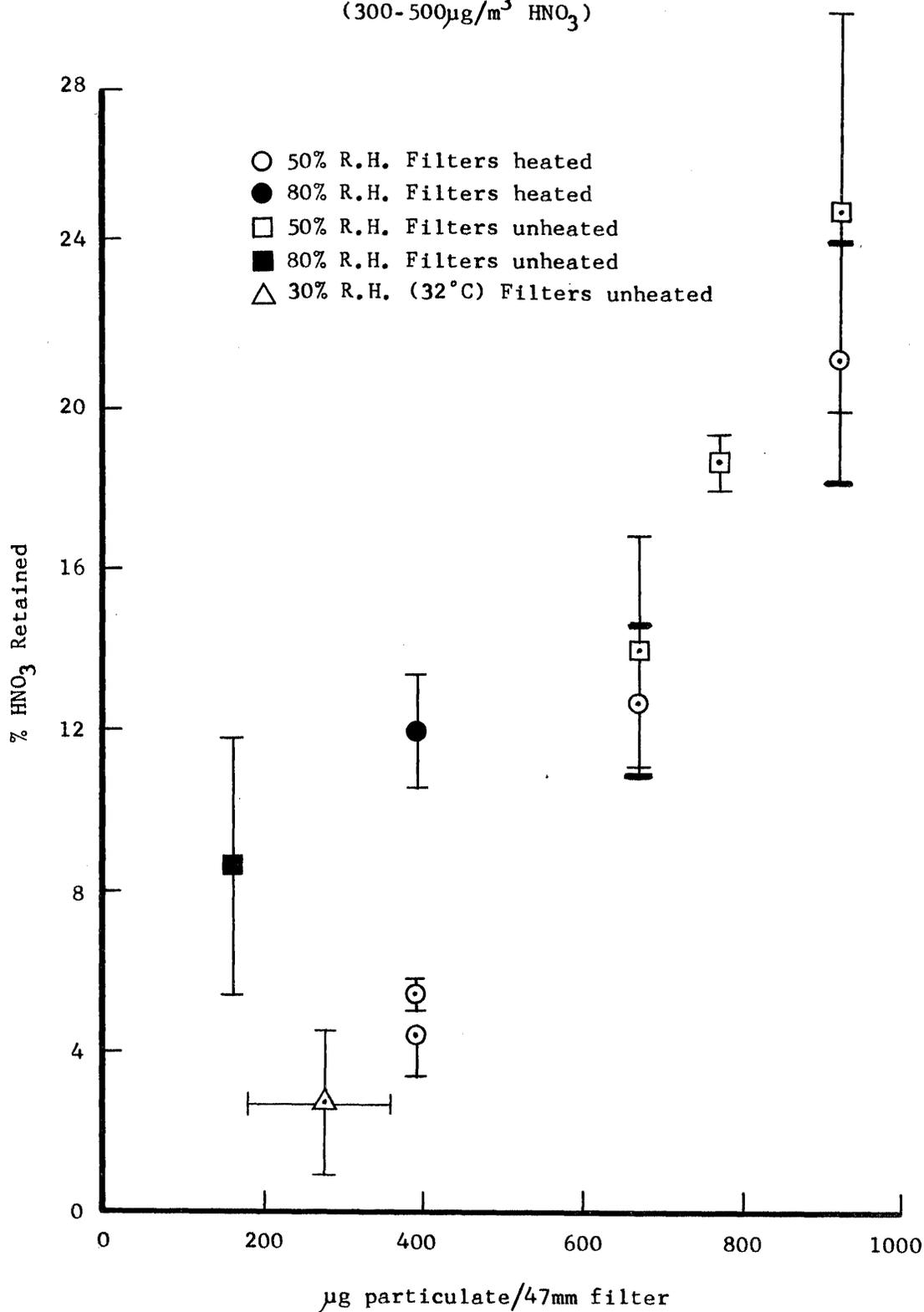


Table 5

Efficiency of Post-Heated<sup>a</sup> Filters for HNO<sub>3</sub> Collection<sup>b</sup>

R.H.(%)	Front Filter	After-Filter	HNO <sub>3</sub> Recovered, µg/m <sup>3</sup> as NO <sub>3</sub> <sup>-</sup>			Σ	Front Filter Efficiency, %
			Front Filter	After-Filter	Holder		
50	NaCl/W41	NaCl/W41	341	3.6	1.9	347	98.3 <sup>c</sup>
50	Duralon	NaCl/W41	109	95.4	4.5	209	31.0 <sup>d</sup>
50	none	NaCl/W41	---	343	3.5	347	---
50	Duralon	Duralon	119	119	3.1	241	33.9 <sup>d,e</sup>
-----							
80	NaCl/W41	NaCl/W41	210	5.1	2.6	218	96.3 <sup>c</sup>
80	Duralon	NaCl/W41	120	60.6	3.4	184	55.5 <sup>d</sup>
80	none	NaCl/W41	---	237	3.7	241	---
80	Duralon	Duralon	95.4	46.3	3.6	145	44.1 <sup>d,f</sup>

91

a. See footnote b, Table 3.

b. Six-hour sampling at 20 Lpm with 47 mm filters.

c. The % of the total recovered NO<sub>3</sub><sup>-</sup> on the front filter. The mean efficiency at 50 and 80% R.H. is 97.2 ± 1.7%.

d.  $\frac{\text{NO}_3^- \text{ on Front Filter (Duralon)}}{\text{NO}_3^- \text{ on Front NaCl/W41 Filter}} \times \frac{1}{.972} \times 100$

e. Using the technique of Smith<sup>12</sup>, the overall efficiency for the two filters in series is about zero.

f. Using the technique of Smith<sup>12</sup>, the overall efficiency for the two filters in series is about 78%.

50% efficient at 80% R.H. These results contrast with those shown in Tables 3 and 4 implying that the efficiency of nylon filters for  $\text{HNO}_3$  varies with the total amount collected, at least when heated samplers are employed. Figure 2 summarized calculated efficiencies observed for Duralon nylon and NaCl/W41 filters at varying  $\text{HNO}_3$  loadings and 50-80% R.H.

Efficiencies for heated nylon filters decreased sharply with increased  $\text{HNO}_3$  loadings. However at loadings likely to be encountered in ambient air samples,  $\leq 500 \mu\text{g HNO}_3$  as  $\text{NO}_3^-$ , efficiencies for nylon are  $\leq 10\%$  below those for NaCl/W41. With unheated nylon filters the mean collection efficiency was  $95 \pm 11\%$ .

Forrest et al. have noted the decrease in efficiency of NaCl impregnated filters at low R.H., finding about 50% efficiency at 25% R.H.<sup>13</sup> To assess the effect of humidity, unheated NaCl/W41 filters were evaluated for efficiency at  $< 2\%$  R.H. With three trials at  $285 \mu\text{g}/\text{m}^3$ , on average, only 55% of the  $\text{HNO}_3$  retained by two NaCl/W41 filters in series was on the front filter. Using the technique of Smith,<sup>12</sup> the overall sampler efficiency for the two filters in series is about 40%. In general, these results are not significant for atmospheric sampling but may influence laboratory applications of these filters as  $\text{HNO}_3$  samplers.

Since Duralon filters are no longer commercially available, an alternative nylon filter supplied by Ghia Corp. was compared to Duralon as shown in Table 6. The results indicate no significant difference in efficiency between the two filter types.

## 5. Summary and Conclusions

- a.  $\text{HNO}_3$  sampling with heated nylon filters yields low results because of reduced efficiency especially for high  $\text{HNO}_3$  loadings. Unheated nylon and NaCl/W41 filters with or without heating are  $\geq 95\%$  efficient independent of  $\text{HNO}_3$  levels. These results are consistent with  $\text{HNO}_3$  retention on nylon by physical adsorption and on NaCl/W41, by chemical reaction (e.g.,  $\text{NaNO}_3$  formation with liberation of HCl).
- b. Ghia and Duralon nylon filters are not significantly different for  $\text{HNO}_3$  sampling.
- c. Losses of  $\text{HNO}_3$  up to 25% were found on particulate matter on the prefilter. The losses were highest with unheated samples at high R.H.
- d. Heating filter samplers reduced loss of  $\text{HNO}_3$  on soiled Teflon prefilters significantly. Heating may, however, aggravate positive errors in atmospheric  $\text{HNO}_3$  measurement by volatilization of  $\text{NH}_4\text{NO}_3$  from the prefilter.

Figure 2

HNO<sub>3</sub> COLLECTION EFFICIENCY OF NYLON AND NaCl-IMPREGNATED FILTERS  
(50-80 % R.H.)

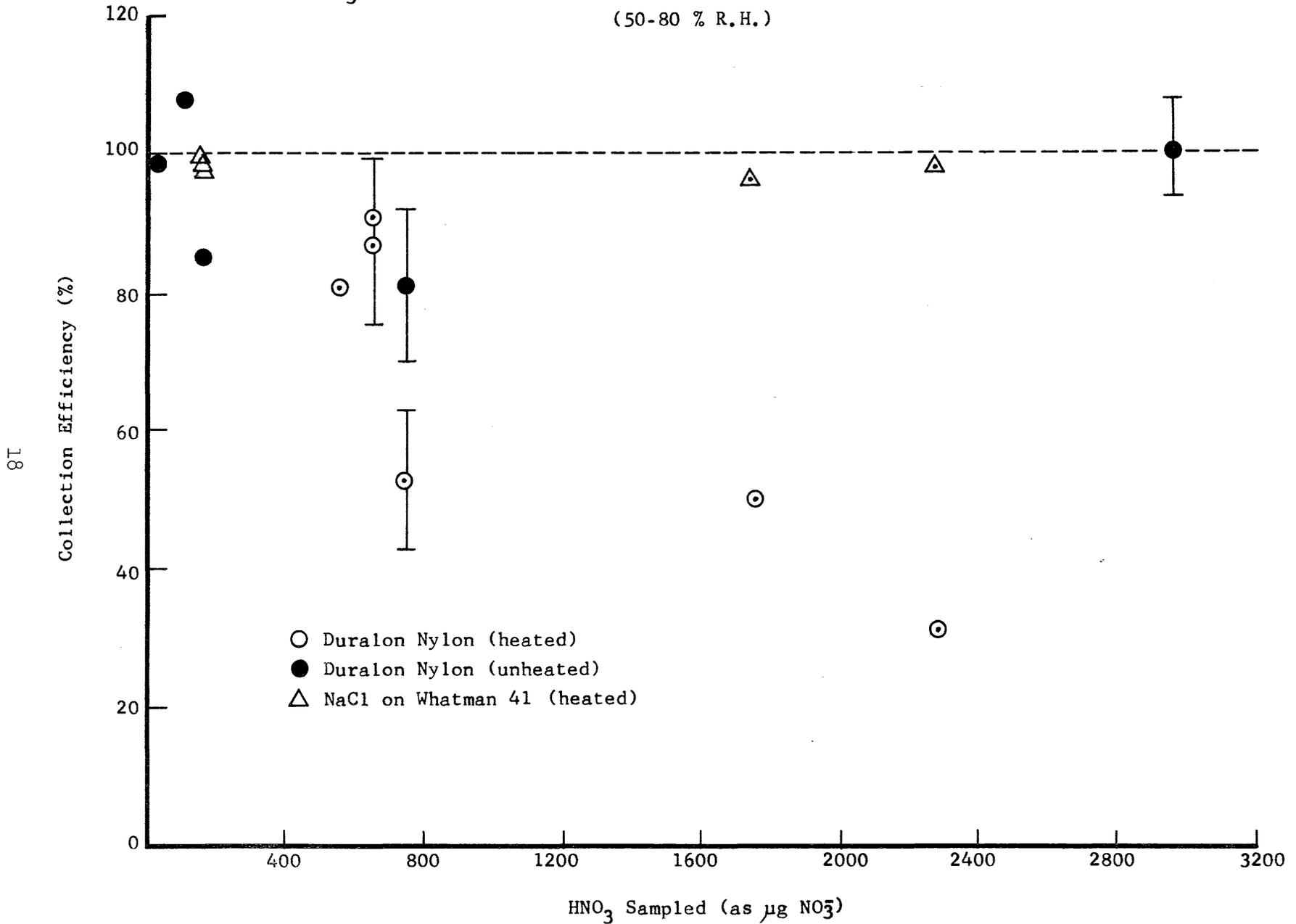


Table 6

Comparison of Duralon and Ghia<sup>a</sup> Nylon Filters for HNO<sub>3</sub> Collection

<u>HNO<sub>3</sub> Sampled (as <math>\mu\text{g NO}_3^-</math>)</u>	<u>Ghia Nylon/ Duralon</u>
684 <sup>b,c</sup>	1.13
1368 <sup>c,d</sup>	0.96
1699 <sup>b,e</sup>	1.00
3398 <sup>d,e</sup>	0.99

Mean: 1.0  $\pm$  0.1

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a. Ghia Corp., Pleasanton, California.

b. 10 Lpm.

c. 50% R.H.

d. 20 Lpm.

e. 80% R.H.

- e. Since volatilization of  $\text{NH}_4\text{NO}_3$  from the prefilter will yield lower apparent  $\text{HNO}_3$  loss, the observed loss of  $\text{HNO}_3$  to particulate matter is expected to vary with the nitrate content of the particulate matter.

## B. Negative Errors in Particulate Nitrate Filter Sampling

### 1. Introduction

As discussed in the preceding section,  $\text{HNO}_3$  is retained by particulate matter on inert prefilters representing a source of positive error in determining particulate nitrate by conventional filter collection. Such error may, however, be more than offset by losses of particulate nitrate from the prefilter producing a corresponding positive error in  $\text{HNO}_3$  measurement by collection on an after-filter. Such loss of particulate nitrate can result from volatilization of nitrate salts or by reaction of such salts with gaseous or particulate strong acids.

### 2. Volatilization of Ammonium Nitrate

To evaluate losses due to volatilization, air free of particulate nitrate and  $\text{HNO}_3$  was passed through filters loaded with about  $200 \mu\text{g} < 0.5 \mu\text{m}$  particle size  $\text{NH}_4\text{NO}_3$  at 20 Lpm for six hours. Both the decrease in nitrate on the loaded filter and the increase in nitrate on NaCl/W41 after-filters downstream of the loaded filter were measured. The results of trials at 50% and 80% R.H. are shown in Table 7. At 50% R.H. excellent agreement was observed between the techniques; both indicated close to 60% loss of nitrate to the air stream. At 80% R.H., the 50%  $\text{NO}_3^-$  loss, by difference, compares to 33% based on the  $\text{NO}_3^-$  collected on the after-filter. Nitrate losses to the inner surfaces of the filter holder may account for some of this difference. Such losses were not measured, however. On average, the loss of  $\text{NH}_4\text{NO}_3$  appears to decrease at higher R.H.

These results suggest that volatilization of  $\text{NH}_4\text{NO}_3$  can be a major source of negative error in sampling particulate  $\text{NO}_3^-$  with Teflon filters. This must result in a corresponding positive error in  $\text{HNO}_3$  measurements by the nitrate collected on after-filters. However, the presence of relatively high  $\text{NH}_3$  and  $\text{HNO}_3$  levels in ambient air may decrease this error relative to that in Table 6, while elevated temperatures should increase it.

These data permit estimation of the equilibrium constant for  $\text{NH}_4\text{NO}_3$  dissociation:



Based on a mean loss of  $45 \pm 11\%$ ,  $K$  is  $\geq 22$  (ppb)<sup>2</sup>. Since the air

Table 7

Loss of  $< 0.5 \mu\text{m}$   $\text{NH}_4\text{NO}_3$  Particles from Teflon Filters into a Clean Air Stream ( $\mu\text{g NO}_3^-/\text{filter}$ )<sup>a,b</sup>

<u>Relative Humidity, %</u>	<u>Initial <math>\text{NH}_4\text{NO}_3</math> Loading</u>	<u>Final <math>\text{NH}_4\text{NO}_3</math> Loading</u>	<u>Calculated Nitrate Loss</u>	<u><math>\text{NO}_3^-</math> on After-Filter<sup>c</sup></u>	<u>Mean % Loss<sup>e</sup></u>
50	$190 \pm 8^d$	$76.5 \pm 4.1$	$113.5 \pm 9$	$109 \pm 10.2$	$58.6 \pm 1.7$
80	$180 \pm 7^d$	$90.0 \pm 5.7$	$90.0 \pm 11$	$59.9 \pm 5.3$	$42 \pm 12$

a. Contaminant particulate nitrate and  $\text{HNO}_3$  were removed from the air stream by two  $\text{NaCl/W41}$  filters in series ahead of the  $\text{NH}_4\text{NO}_3$ -loaded  $1 \mu\text{m}$  Fluoropore filters.

b. Sampling of purified air was for six hours at 20 lpm and  $21 \pm 1^\circ\text{C}$ . Except as noted results are mean values for two trials.

c. An  $\text{NaCl/W41}$  after-filter collected the nitrate lost from the loaded Teflon filter.

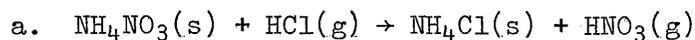
d. Initial loadings based on analysis of one of three filters loaded simultaneously with  $\text{NH}_4\text{NO}_3$ . Earlier studies indicated loadings should be equivalent for the three filters with a C.V. of 2%. The precision of the analytical method is ca. 3%. Accordingly the precision of the initial loading is estimated at 4%.

e. Based on both calculated  $\text{NO}_3^-$  loss and  $\text{NO}_3^-$  on after-filter.

stream may not be saturated on passing through the loaded filters, this is a lower limit value. It compares to the value ca. 10 (ppb)<sup>2</sup> at 20°C for pure NH<sub>4</sub>NO<sub>3</sub> based on extrapolated dissociation pressure values.<sup>7</sup>

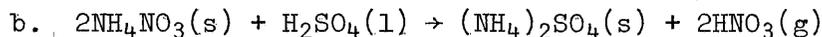
### 3. Loss of Nitrate by Reactions with Gaseous and Particulate Acids

Loss of nitrates from inert prefilters may result from reaction of any nitrate salt leading to HNO<sub>3</sub> formation. Reactions of NH<sub>4</sub>NO<sub>3</sub> with gaseous and particulate strong acids were evaluated since this salt may often be the dominant nitrate form present in atmospheric particulate matter. The reactions considered include:



$$\Delta F_{298^\circ\text{K}} = +1.98 \text{ Kcal/mole}^2$$

$$K_{298^\circ} = 3.53 \times 10^{-2}$$



$$\Delta F_{298^\circ\text{K}} = +4.14 \text{ Kcal/mole}^2$$

$$K_{298^\circ} = 9.21 \times 10^{-4}$$

Loss of NO<sub>3</sub><sup>-</sup> by reaction with H<sub>2</sub>SO<sub>4</sub> has been previously observed or inferred.<sup>8,9</sup> The reaction is irreversible under conditions in which HNO<sub>3</sub> is permitted to escape. Based on standard free energy of formation calculations<sup>10</sup> neither reaction is favored thermodynamically. However, under conditions in which the equilibrium concentration of HNO<sub>3</sub> is not permitted to build up (e.g., in a moving stream of air passing through a filter loaded with NH<sub>4</sub>NO<sub>3</sub> particles), NH<sub>4</sub>NO<sub>3</sub> loss might still occur.

To evaluate the loss of NH<sub>4</sub>NO<sub>3</sub> with gaseous HCl, ammonium nitrate particles of  $\leq 0.2 \mu\text{m}$  diameter particle size were generated with a nebulizer system previously described.<sup>11</sup> Particles in the range  $\geq 0.1 \mu\text{m}$  were measured with a Royco Model 226 optical particle counter.

Teflon filters loaded with 80-130  $\mu\text{g}$  of the salt (as NO<sub>3</sub><sup>-</sup>) were exposed for two hours to clean air or to about 20 ppb HCl in air at 50% R.H. The HCl concentration was established with bubbler samples collected in 0.01M NaOH and analyzed by a colorimetric procedure using mercuric thiocyanate.<sup>14</sup> Other conditions and results are summarized in Table 8. In the absence of HCl, the nitrate loss due to volatilization was about 18%, which compares to  $19.5 \pm 0.3\%$  calculated from Table 7 assuming a constant loss

Table 8

PERCENT LOSS OF  $\text{NH}_4\text{NO}_3$  FROM TEFLON FILTERS BY  
REACTION WITH HCl IN AIR AT 50% R.H. a,b

Mean $\text{NH}_4\text{NO}_3$ Loadings ( $\mu\text{g NO}_3^-/\text{filter}$ )	% Loss at HCl level		
	0	$17 \pm 1$ ppb	$23 \pm 1$ ppb
128	$18.1 \pm 0.7$	$87 \pm 4$	
80			$90 \pm 8$

a.  $0.2 \pm 0.1 \mu\text{m}$   $\text{NH}_4\text{NO}_3$  particles on 47 mm, 2  $\mu\text{m}$  pore size Zefluor filters.  
Flow rate = 20 Lpm, T =  $21 \pm 1^\circ\text{C}$ . Sampling time = 2 hours.

b. Results are mean values for two filters run side-by-side.

rate with time. When 17 to 23 ppb HCl was added, the nitrate loss increased to about 90% of the particulate nitrate sample. Thus the effect of HCl on nitrate loss from Teflon filters was dramatic.

Few data on atmospheric HCl levels are available. Existing data indicate levels up to about 8 ppb with highest values in seacoast cities.<sup>15</sup> HCl at or above this level are possible for many areas in California and might, therefore, profoundly influence particulate  $\text{NO}_3^-$  values obtained in sampling with inert filters.

To evaluate nitrate loss due to  $\text{H}_2\text{SO}_4$  reactions employing Teflon filters previously loaded with  $\text{NH}_4\text{NO}_3$ ,  $\text{H}_2\text{SO}_4$  aerosol ( $\leq 0.1 \mu\text{m}$ ) was added using the generator previously described.<sup>11</sup> Loading time to add about 100  $\mu\text{g}$   $\text{H}_2\text{SO}_4$  was ten minutes. The R.H. during  $\text{H}_2\text{SO}_4$  loading was  $\leq 1\%$ . Loss of  $\text{NO}_3^-$  during and subsequent to  $\text{H}_2\text{SO}_4$  loading was judged by the  $\text{NO}_3^-$  collected on NaCl/W41 after-filters. Half of the samples were subject to additional exposure to clean air for six hours at 90% R.H. at flow rates equivalent to that used in atmospheric  $\text{NO}_3^-$  sampling. Sample loadings and results are summarized in Table 9.

During the ten minutes required to load the  $\text{H}_2\text{SO}_4$  aerosol, loss of nitrate averaged 9 to 14%, more than twice the loss ascribable to volatilization. When exposed to a clean air stream for an additional six hours at 90% R.H., the loss observed was close to 95%, about three times the loss of  $\text{NO}_3^-$  observed from filters without  $\text{H}_2\text{SO}_4$ . Thus the reaction of  $\text{NH}_4\text{NO}_3$  with  $\text{H}_2\text{SO}_4$  on the filter surface is not immediate at  $\leq 1\%$  R.H. At 90% R.H., wherein the  $\text{NH}_4\text{NO}_3$  deliquesces to liquid droplets which are likely to dissolve the  $\text{H}_2\text{SO}_4$  as well, the reaction is nearly complete after six hours.

We conclude that because of the significance of loss of  $\text{NH}_4\text{NO}_3$  by volatilization as well as reactions with particulate strong acids (e.g.,  $\text{H}_2\text{SO}_4$ ) and gaseous strong acids (e.g., HCl) particulate  $\text{NO}_3^-$  values obtained with Teflon filters represent lower limits to the true  $\text{NO}_3^-$  levels.

## C. A Potential Reference Method for $\text{HNO}_3$ and Particulate Nitrate Sampling

### 1. Introduction

In the preceding sections it was demonstrated that particulate nitrate measurements by collection on inert filters are subject to both positive and negative errors. These lead to the complementary error in  $\text{HNO}_3$  measurements by  $\text{HNO}_3$  collection with an after-filter. Nevertheless, the sum of the nitrate retained by the prefilter and an efficient after-filter should equal the total inorganic nitrate (i.e.,  $\text{HNO}_3$  plus particulate nitrate).

Table 9

Loss of  $\text{NH}_4\text{NO}_3$  from Inert Filters Due to Reaction with  $\text{H}_2\text{SO}_4$  Aerosol

	Conditions for $\text{H}_2\text{SO}_4 - \text{NH}_4\text{NO}_3$ Reaction			
	10 min at room temp. $\leq 1\% \text{ R.H.}^{\text{c,g}}$		6 hours at room temp. 90% R.H. <sup>h</sup>	
	<u>Trial I</u>	<u>Trial II</u>	<u>Trial I</u>	<u>Trial II</u>
Initial $\text{NO}_3^-$ , $\mu\text{g}^{\text{a}}$	101.1 $\pm$ 5.4	113.7 $\pm$ 2.8	91.9 $\pm$ 2.6	71 $\pm$ 2.7
Initial $\text{H}_2\text{SO}_4$ , $\mu\text{g SO}_4^{\text{=b}}$	66.5 $\pm$ 3.5	63 $\pm$ 5	91.2 $\pm$ 4.1	89.3 $\pm$ 9.6
Nitrate lost by $\text{H}_2\text{SO}_4$ reaction, $\mu\text{g}^{\text{d}}$	9.0 $\pm$ 0.6	15.8 $\pm$ 0.4	86.3 $\pm$ 0.8 <sup>e</sup>	67.0 $\pm$ 3.1 <sup>e</sup>
Nitrate lost by volatilization, $\mu\text{g}^{\text{f}}$	< 5	< 5	29.0	35.1

a. From  $0.2 \pm 0.1 \mu\text{m}$   $\text{NH}_4\text{NO}_3$  particles.

b. From  $\leq 0.1 \mu\text{m}$   $\text{H}_2\text{SO}_4$  particles added following initial loading with  $\text{NH}_4\text{NO}_3$ .

c. Reaction time was the period during which  $\text{H}_2\text{SO}_4$  was loaded on the filters at a flow rate of 10 Lpm with 47 mm filters.

d. Collected by NaCl-impregnated W41 filters.

e. Includes the  $\text{NO}_3^-$  lost during 10 min. loading of  $\text{H}_2\text{SO}_4$  at 1% R.H., and flow rate of 28.3 Lpm.

f. Filters initially contain the  $\text{NO}_3^-$  level shown above as "initial  $\text{NO}_3^-$ " but without added  $\text{H}_2\text{SO}_4$ .

g. Initial ratio of equivalents  $\text{H}^+/\text{NO}_3^- = 0.77 \pm 0.1$ .

h. Initial ratio of equivalents  $\text{H}^+/\text{NO}_3^- = 1.4 \pm 0.2$ . Flow rate 20 Lpm.

R. Shaw et al. recently proposed<sup>16</sup> use of such a total inorganic nitrate (TIN) sampler in parallel with a particulate nitrate sampler as shown schematically in Figure 3. For the latter, the ambient air mixture of HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup> passes first through a diffusion denuder coated on its inner walls with powdered MgO. The relatively rapid diffusion of gases permits removal of HNO<sub>3</sub> (and other acidic gases) while permitting non-volatile particulate matter to penetrate with high efficiency. The nitrate reaching the Teflon prefilter in this case should be true particulate nitrate. The after-filter collects any of this nitrate lost by volatilization or reactions liberating HNO<sub>3</sub>. If particulate NO<sub>3</sub><sup>-</sup> is not lost in the denuder, the total of the NO<sub>3</sub><sup>-</sup> on these two filters equals the total particulate nitrate (PN) in the atmosphere. The difference between TIN and PN should equal the ambient HNO<sub>3</sub> level.

The efficiency of HNO<sub>3</sub> removal in such a denuder, under conditions of laminar flow (Reynolds number < 2000), can be calculated by the Gormley-Kennedy equation:<sup>37</sup>

$$\frac{\bar{C}}{C_0} = 0.82 \exp(-15\Delta) + 0.098 \exp(-89\Delta) + 0.033 \exp(-228\Delta)$$

where

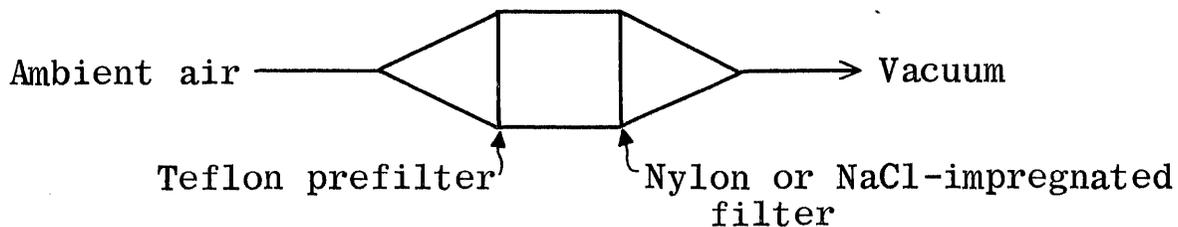
- $\Delta = DL\pi/4Q$
- D = diffusion coefficient (cm<sup>2</sup>/sec)
- L = total length of tube (cm)
- Q = flow rate through tube (cm<sup>3</sup>/sec)
- C<sub>0</sub> = concentration entering tube
- $\bar{C}$  = average concentration exiting tube
- (1 -  $\bar{C}/C_0$ ) x 100 = percent removal

At the time this work was initiated a diffusion coefficient for HNO<sub>3</sub> was not available. Accordingly, a value of D = 0.4 cm<sup>2</sup>/sec was employed, as previously used for NH<sub>3</sub>. It should be noted that tube diameter is not critical as long as the Reynolds number is maintained below 2000. The most compact denuder configuration consists of an array of parallel tubes, the sum of whose lengths yield the desired total tube length. Based on this value for D, a denuder with eleven, 30 cm tubes should provide > 99% removal of HNO<sub>3</sub> at 20 Lpm (Reynolds number < 500) while removing < 6% of the  $\geq 0.01 \mu\text{m}$  particles by diffusion. The data in Section V are based on a denuder of this design. More recently a diffusion coefficient of 0.15 cm<sup>2</sup>/sec was measured for HNO<sub>3</sub>.<sup>17</sup> With this value and the above equation, the denuder employed for the present work has an expected efficiency for HNO<sub>3</sub> removal of 85.7%.

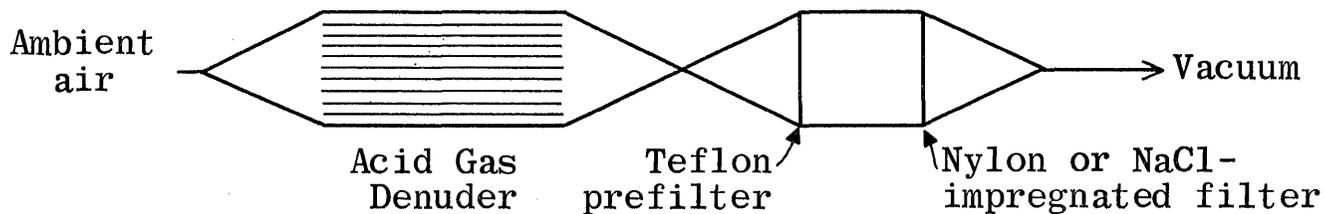
## 2. Laboratory Evaluation of the Efficiency of the Denuder for HNO<sub>3</sub> Removal

The efficiency of the denuder with eleven, 30 cm tubes was measured by sampling laboratory-generated HNO<sub>3</sub> in parallel with

### TOTAL INORGANIC NITRATE (TIN) SAMPLER



### PARTICULATE NITRATE (PN) SAMPLER



$$\text{TIN} - \text{PN} = \text{Ambient HNO}_3$$

Figure 3. SCHEMATIC DIAGRAM OF NITRIC ACID MEASUREMENT BY A DIFFERENCE TECHNIQUE

NaCl/W41 filters. The  $\text{HNO}_3$  penetrating the denuder was collected on an NaCl/W41 filter with or without a Teflon prefilter. Figures 7 to 10 (pages 39 to 42) illustrate the design for the trials with both clean and pre-soiled Teflon prefilters. The results summarized in Table 10 indicate that for temperatures in the range 21 to 32°C and relative humidities from 20 to 80%, the efficiency for 85 to 135 ppb  $\text{HNO}_3$  averaged about 88%. This result was equal, within experimental error, to that predicted by the Gormley-Kennedy equation employing the measured diffusion coefficient for  $\text{HNO}_3$ .

Penetration of  $\text{HNO}_3$  through the denuder would yield apparent particulate nitrate values which are too high with a corresponding negative error in  $\text{HNO}_3$  by difference. Any loss of particulate nitrate in the denuder would produce the reverse. It will be shown in Section V that the expected 12% penetration of  $\text{HNO}_3$  through the denuder was apparently more than offset by opposing sources of error in atmospheric sampling.

### 3. Loss of Particulate Nitrate in the Denuder

The denuder is designed to permit passage of non-volatile particles  $> 0.01 \mu\text{m}$  in diameter with high efficiency, based upon losses by diffusion to the walls. However, loss of particulate nitrates may occur by either or both of two additional mechanisms. Relatively large-particle nitrate (e.g.,  $\text{NaNO}_3$ ) may be lost by impaction near the entrance of the denuder tubes and on the rough MgO coating. In addition, ammonium nitrate, the most likely submicron size nitrate compound in ambient air, might be lost by initial dissociation to gaseous  $\text{HNO}_3$  followed by diffusion of  $\text{HNO}_3$  to the walls:



Since the air stream is denuded of  $\text{HNO}_3$  by the denuder, dissociation of  $\text{NH}_4\text{NO}_3$  may be enhanced within and downstream of the denuder tubes.

To measure losses of  $\text{NH}_4\text{NO}_3$  particles, a nebulizer-type aerosol generator system<sup>1</sup> was employed to prepare  $\text{NH}_4\text{NO}_3$  particles in the ranges 0.1 - 0.4  $\mu\text{m}$  and 1 - 3  $\mu\text{m}$ . A denuder with eleven freshly prepared 30 cm MgO-coated tubes was employed, oriented vertically. A Royco Model 226 optical particle counter counted particles  $\geq 0.1 \mu\text{m}$ . If volatilization was involved in particle loss, loss should be more evident in the smaller particles because their higher surface area per unit mass would increase their volatilization rate. To minimize experimental bias, identical sampling probes and tubing were used upstream and downstream of the denuder.

Table 10 EFFICIENCY VALUES OF DIFFUSION DENUDER FOR  
 220 - 345  $\mu\text{g}/\text{m}^3$  (85 - 135 PPB) NITRIC ACID

<u>Trial</u>	<u>Temp. °C</u>	<u>R.H. (%)</u>	<u>Flow Rate, Lpm</u>	<u>Efficiency of HNO<sub>3</sub> Removal, %<sup>a</sup></u>
5A	21	50	20	97.3
5B	21	80	20	96.9
16C	32	30	20	87.3 ± 2.2
16D	32	30	20	85.6 ± 1.1
16E	21	50	20	85.4 ± 3.3
16F	21	50	20	83.5 ± 0.4
Overall mean:				87.8 ± 5.1

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a. Calculated assuming that all nitrate penetrating the denuder is HNO<sub>3</sub> and the mean TIN values (corrected for atmospheric nitrate, if present) are to equal to the input concentration of HNO<sub>3</sub>.

Table 11 summarizes the experimental conditions studied. The average residence time of a particle within a denuder tube at 20 Lpm is 0.3 sec. Both the flow rate and R.H. were varied. However, in all cases the downstream particle count remained equal, within experimental variability, to that upstream for the size ranges 0.1 to 0.2, 0.2 to 0.3 and 0.3 to 0.4  $\mu\text{m}$ . Thus no loss of particles was observed.

In studies with 1 to 3  $\mu\text{m}$  particles, results were obtained both by filter collection and real-time particle counting. The denuder was attached to one of three equivalent positions in the  $\text{NH}_4\text{NO}_3$  generator system manifold. Nitrate penetrating the denuder was compared to that at the other two positions. Since the airstream penetrating the denuder should be nearly free of  $\text{HNO}_3$ , dissociation of  $\text{NH}_4\text{NO}_3$  on an inert filter would be expected. Accordingly, Teflon prefilters and NaCl/W41 after-filters were used at this position.

Because of the limited flow capacity of the  $\text{NH}_4\text{NO}_3$  generator, the three samplers operated at 10 Lpm rather than the 20 Lpm employed for field sampling with the denuder. However, the average residence time of particles and the air velocity within denuder tubes was maintained approximately equal to that in atmospheric sampling by using 6 denuder tubes in place of the 11 employed in field sampling.

Losses were judged by comparing nitrate levels on the two filters sampling at the manifold with the total  $\text{NO}_3^-$  on the filters downstream of the denuder. In addition, a Climet Model 206 optical particle counter (OPC) was used for repeated measurements of nitrate particles upstream and downstream of the denuder. The results shown in Table 12 indicate that losses are nil based on filter collection. Similarly, the OPC data showed no difference between upstream and downstream values.

We conclude that loss of 0.1 to 3  $\mu\text{m}$  particulate nitrate in the denuder was not measurable. However, since atmospheric nitrate can be present in particles  $> 3 \mu\text{m}$ , and impaction of such particles is likely, loss of particulate nitrate in the denuder cannot be discounted. Unfortunately, the presently available system did not permit experiments with  $> 3 \mu\text{m}$  nitrate particles.

#### D. Modified Chemiluminescent $\text{NO}_x$ Analyzer Method

##### 1. Introduction

The dual channel  $\text{NO}_x$  analyzer, Monitor Labs Model 8840E, relies on the chemiluminescent reaction between NO and ozone to detect and measure NO. In one flow system, NO is measured selectively, while a second flow system reduces  $\text{NO}_2$  (and  $\text{HNO}_3$ ) to NO to give

Table 11

CONDITIONS STUDIED FOR LOSS OF 0.1-0.4  $\mu\text{m}$   
 $\text{NH}_4\text{NO}_3$  PARTICLES IN THE ACID GAS DENUDE<sup>a</sup>

<u>Trial</u>	<u>Conditions</u>
1	20 % R.H. 40 Lpm (0.15 sec residence time)
2	20% R.H. 20 Lpm (0.3 sec residence time)
3	60% R.H. 20 Lpm (0.3 sec residence time)
4	60% R.H. 10 Lpm (0.6 sec residence time)

- 
- a. The Royco Model 226 OPC provided particle counts in the ranges 0.1-0.2, 0.2-0.3, and 0.3-0.4  $\mu\text{m}$ . Typical particle counts were 150,000, 60,000 and 8,000 per minute for the three ranges.

Table 12

LOSS OF  $2 \pm 1 \mu\text{m}$   $\text{NH}_4\text{NO}_3$  PARTICLES IN ACID GAS DENUDER  
 BASED ON PARTICULATE NITRATE COLLECTION<sup>a</sup>

<u>Trial</u>	Nitrate Levels ( $\mu\text{g}/\text{filter}$ )	
	<u>Upstream</u>	<u>Downstream of Denuder</u>
A	$2759 \pm 300$	$2586^b$
B	$2774 \pm 201$	$2952^b$

- 
- a. Nitrate collected upstream with Zefluor (Teflon) filters. Nitrate collected downstream with a Zefluor and NaCl/W41 in series. The latter retained  $\text{HNO}_3$  lost by volatilization from the Teflon filter.
- b. The nitrate on the NaCl/W41 after-filter was  $< 0.1\%$  of the total in 6-minute loading periods.

a measure of total  $\text{NO}_x$  (Figure 4A). The total  $\text{NO}_x$  signal minus the NO signal yields the approximate  $\text{NO}_2$ , since  $\text{HNO}_3$  levels are normally small by comparison to  $\text{NO}_2$ .

The analyzer was modified as described by Joseph and Spicer<sup>18</sup> to provide a continuous measure of atmospheric  $\text{HNO}_3$  (Figure 4B). The nylon filter ahead of the second catalyst bed selectively removes  $\text{HNO}_3$  but allows passage of NO and  $\text{NO}_2$ . Thus this channel provides a measure of total  $\text{NO}_x$  less  $\text{HNO}_3$ . Since the other channel measures total  $\text{NO}_x$  (i.e.,  $\text{NO} + \text{NO}_2 + \text{HNO}_3$ ),  $\text{HNO}_3$  is measured by the difference signal between the two channels.  $\text{HNO}_3$  in ambient air is usually  $\ll \text{NO} + \text{NO}_2$ , so the difference value is obtained between two relatively large numbers. The modifications made include:

- a. installation of an additional  $\text{NO}_x$  to NO converter, a heated molybdenum catalyst, in what was originally the NO flow system,
- b. installation of a 47 mm nylon filter in a glass fiber-filled polypropylene holder (Millipore 43 047 00)\* in line ahead of this second catalyst,
- c. increasing the temperature of both catalysts' beds from  $315^\circ\text{C}$  to  $350^\circ\text{C}$ , to increase the efficiency of  $\text{HNO}_3$  conversion to NO,
- d. moving the flow control orifices ahead of the catalysts and nylon filter to place both flow channels under partial vacuum and thereby minimize  $\text{HNO}_3$  losses on surfaces,
- e. increasing the sampling rate from 250 mL/min to 720 mL/min for faster response, and
- f. increasing the system vacuum from 24 inches Hg to the maximum attainable (28.5 inches Hg), to further minimize  $\text{HNO}_3$  loss.

## 2. Evaluation Procedure

The performance of the modified analyzer was determined with NO,  $\text{NO}_2$  and  $\text{HNO}_3$ . Dilute NO was generated by quantitative dilutions of 5 or 50 ppm NO in  $\text{N}_2$  with synthetic air or filtered ambient air.  $\text{NO}_2$  was obtained by gas phase titrations of the NO with  $\text{O}_3$ .  $\text{HNO}_3$  concentrations were obtained by quantitative dilution with dry cylinder or filter ambient air of 10 to 40 ppm  $\text{HNO}_3$  in dry  $\text{N}_2$  from a 30 ft Teflon bag.<sup>1</sup> The concentration of the  $\text{HNO}_3$  in the Teflon bag was determined by a nitrate specific electrode following bubbler collection in 0.1N NaOH and adjustment of electrolyte.

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\*Used in place of a Teflon holder employed by Joseph and Spicer.

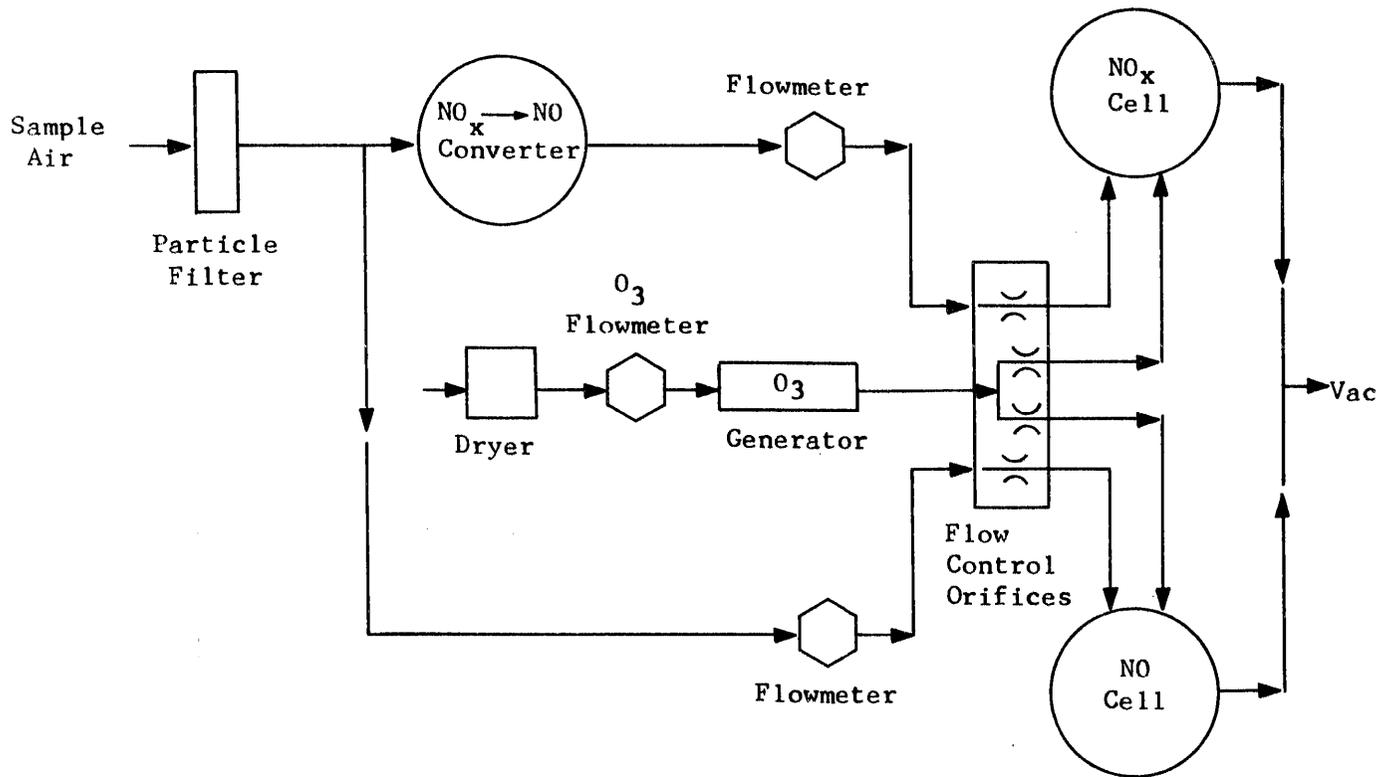


Figure 4A Schematic of Unmodified Monitor Labs  $\text{NO}_x$  Analyzer.

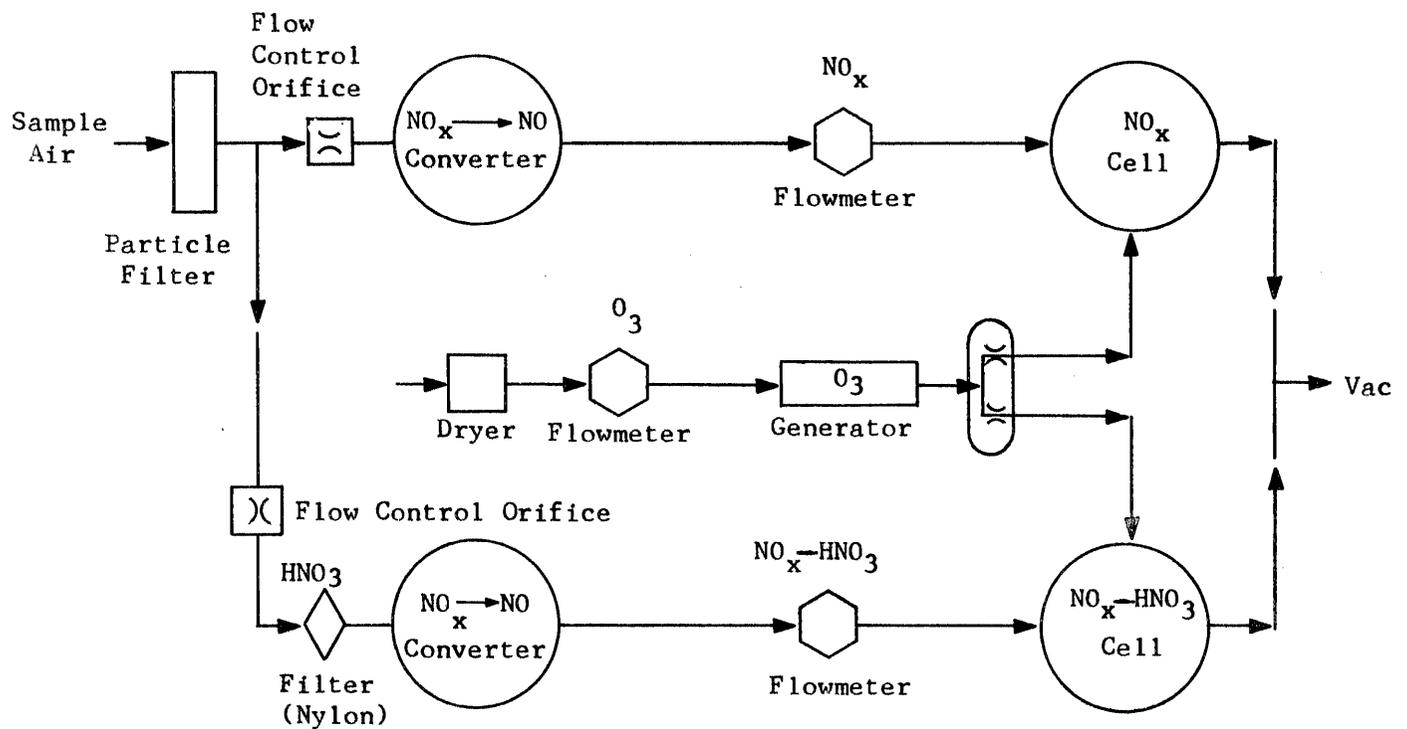


Figure 4B Schematic of Monitor Labs Analyzer Modified For  $\text{HNO}_3$  Analysis.

Converter efficiency for  $\text{NO}_2$  was evaluated by bypassing each converter, in turn, and adding ozone to the  $\text{NO}$  stream gas phase titration and looking for changes in the  $\text{NO}_x$  channel, while the decrease in the  $\text{NO}$  channel was used to determine the  $\text{O}_3$  added.

### 3. Results

The response of the modified analyzer to  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{HNO}_3$  are shown in Figures 5 and 6 for  $\text{NO}$  and  $\text{HNO}_3$ . The addition of  $\text{O}_3$  to the  $\text{NO}$  resulted in no reduction in  $\text{NO}_x$  signal until the  $\text{O}_3$  concentration exceeded that of  $\text{NO}$  (56 ppb) indicating 100% conversion in each case. The response of the instrument to  $\text{HNO}_3$  in dry air differed from that for  $\text{NO}$  by about 10% at the upper end of the range.

The lower limit of detection of  $\text{HNO}_3$  was estimated to be 6 ppb based on twice the instrument noise. This compares to 1 to 2 ppb presently claimed by Spicer.<sup>19</sup> The instrument's rate of response is a function of the time-constant setting. On the 20 sec setting, the time to 90% of final response to  $\text{NO}$  and  $\text{NO}_2$  was 46 sec. However with  $\text{HNO}_3$  at 50 to 60% R.H. an initial lag time of between 0.75 and 8 minutes was observed, increasing with decreasing  $\text{HNO}_3$  concentration apparently due to conditioning of the tubing. The time to 90% of final response ranged between 20 minutes to over 1.5 hours varying inversely with concentration.

We conclude that the continuous  $\text{HNO}_3$  analyzer, as described here, is a very useful device for laboratory application. However, successful application in the atmosphere must be preceded by additional efforts to decrease the response time and limit of detection to values similar to those reported by Spicer. The higher limit of detection probably reflects the greater electronic noise in the photomultiplier tube. The reason for the greater response time remains unknown.

#### E. Intermethod Comparison of Techniques for $\text{HNO}_3$ Measurement

##### 1. Objectives

The objectives of this series of experiments were: 1) to compare  $\text{HNO}_3$  measurements by the difference technique to  $\text{HNO}_3$  by filter collection (the Okita method) and to the modified Monitor Labs chemiluminescent  $\text{HNO}_3$  analyzer, and 2) to obtain additional evaluations of the efficiency of the  $\text{HNO}_3$  diffusion denuder for  $\text{HNO}_3$  removal. Efficiency results from these experiments were discussed in Section III.

Experiments were planned to simulate the meteorological extremes encountered in the atmospheric sampling described in Section V. Experiments employed either clean Teflon (Zefluor) prefilters or Teflon filters preloaded with atmospheric particulate matter to

Figure 5  
MONITOR LABS RESPONSE TO NITRIC OXIDE ON 100ppb RANGE

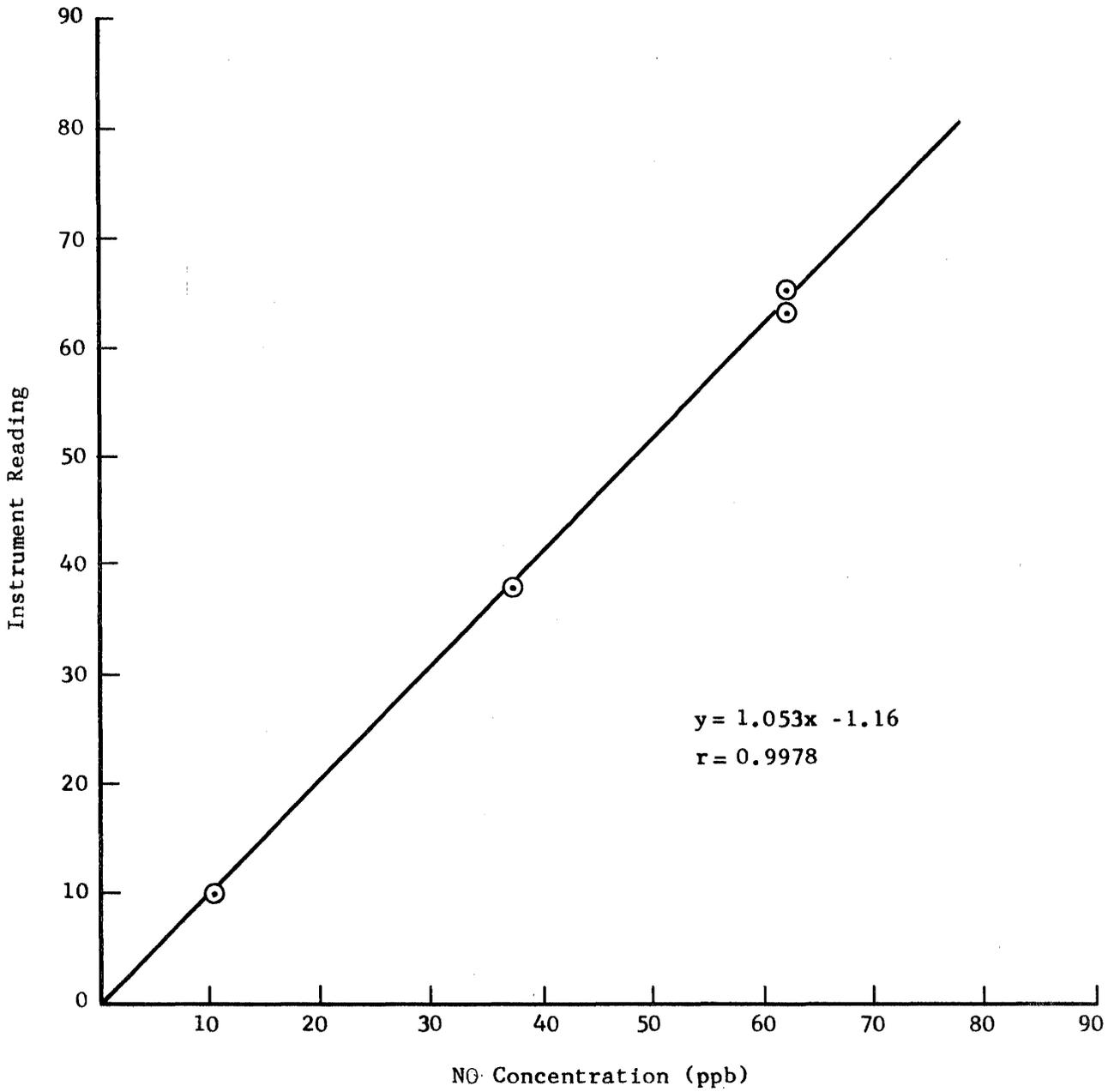
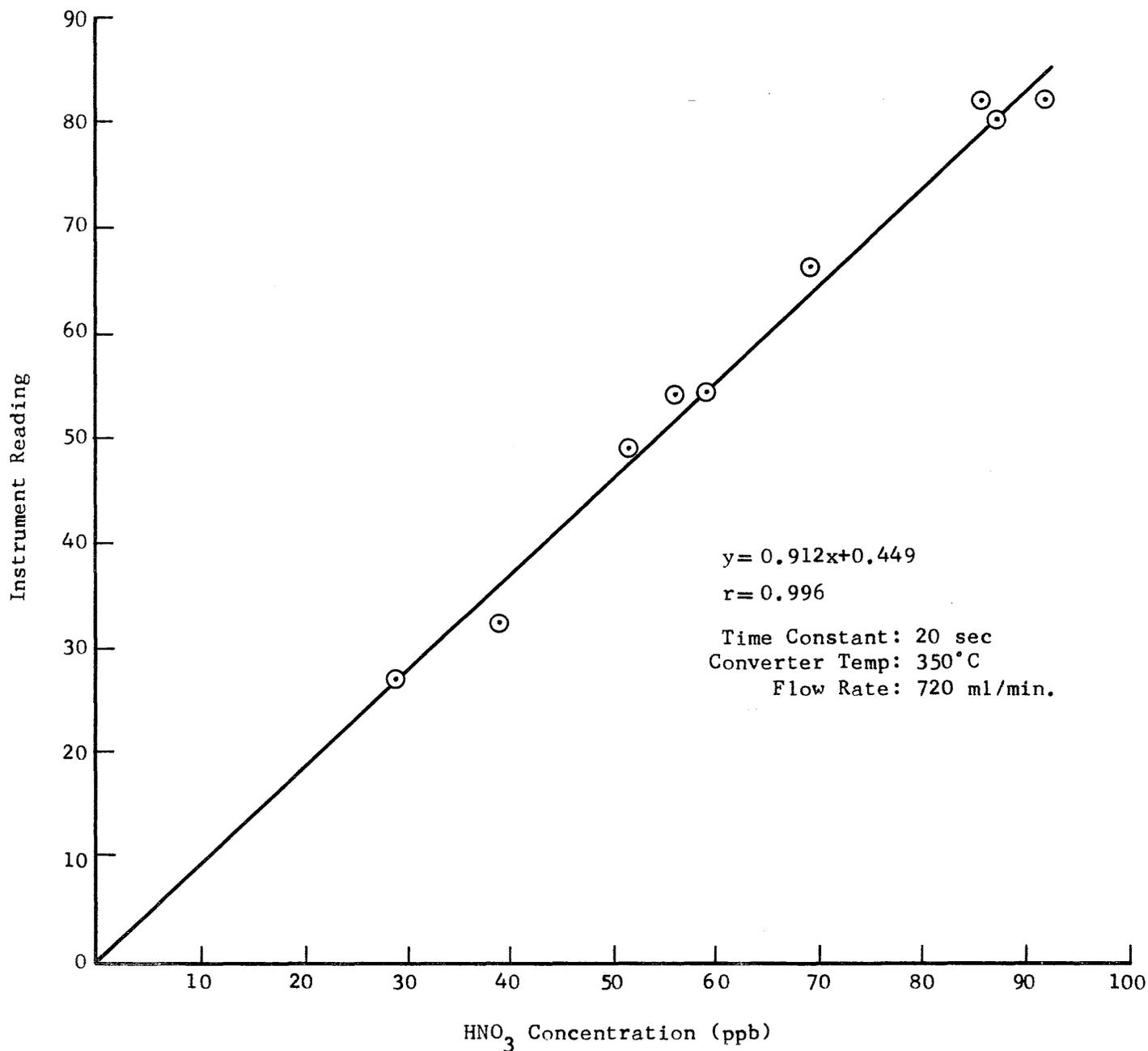


Figure 6  
MONITOR LABS RESPONSE TO HNO<sub>3</sub> ON 100ppb RANGE



assess the effect of particulate matter on the observed  $\text{HNO}_3$  levels by the Okita procedure.

## 2. Results

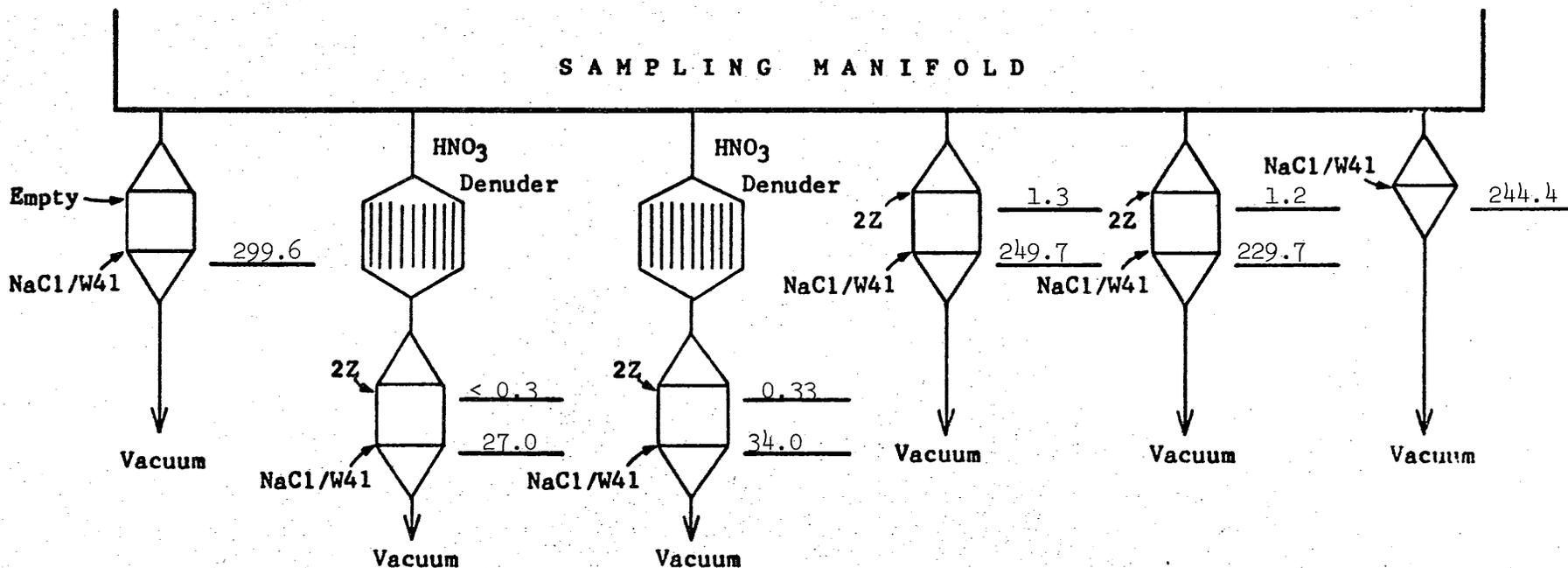
Figures 7 through 10 show schematically the design for the four experiments which yielded useful data, 16 C - F, together with individual filter results. Two denuder plus after-filter systems as well as two units for  $\text{HNO}_3$  collection by the Okita method sampled in parallel. In addition, two NaCl/W41 samplers were operated without prefilters. One of the NaCl/W41 samplers had an empty holder (a stacked Nuclepore filter holder) in the pre-filter position. Based on the experience gained in atmospheric sampling (Section V), no filter heating was employed. Experiments 16 C and E used clean prefilters while D and F used prefilters loaded with about 300 and 800  $\mu\text{g}$  atmospheric particulate matter, respectively.\* For trials D and F the reported nitrate values for the prefilters include atmospheric nitrate. The atmospheric nitrate values are expressed in units of  $\mu\text{g}/\text{filter}$  and  $\mu\text{g}/\text{m}^3$  based on the volume of air sampled in the subsequent laboratory exposure.

Nitric acid values obtained by the three techniques are shown in Table 13. Results discussed in Section III C indicate that the diffusion denuder was about 88% efficient for  $\text{HNO}_3$  removal. The method of  $\text{HNO}_3$  generation as well as the absence of significant  $\text{NO}_3^-$  levels on clean Teflon prefilters suggest that the 12% average  $\text{NO}_3^-$  penetration through the denuder was indeed  $\text{HNO}_3$  and not particulate nitrate. Accordingly, particulate nitrate and "HNO<sub>3</sub> by difference" values are shown calculated with apparent particulate nitrate (PN) values (i.e., equating all nitrate penetrating the denuder with particulate nitrate) and with results corrected assuming  $\text{PN} = 0$  except when atmospheric particulate-loaded Zefluor filters were employed. Apparent "HNO<sub>3</sub> by difference", while generally lower than  $\text{HNO}_3$  by the Okita method, agrees relatively well with  $\text{HNO}_3$  by the Monitor Labs chemiluminescent analyzer. However, our experience suggests the Monitor Labs unit tends to give low results in laboratory trials because of  $\text{HNO}_3$  losses to tubing walls in excess of those experienced by the other techniques. Corrected "HNO<sub>3</sub> by difference" agrees well with  $\text{HNO}_3$  by the Okita method. Significant difference occurs only when the prefilter is relatively heavily loaded with atmospheric particulate matter. The ratios of means, relative to the corrected  $\text{HNO}_3$  by difference, show agreement by the three techniques within 11%. Relative to uncorrected  $\text{HNO}_3$  by difference, results agree, on average, within 17%. In trial 16F with 768  $\mu\text{g}$  TSP per pre-filter, the Okita method is 13 to 18% lower than the other techniques reflecting the retention of  $\text{HNO}_3$  on the prefilter.

Future atmospheric trials sampling nitric acid by the difference method will employ a denuder with sufficient total MgO tube length to insure > 99%  $\text{HNO}_3$  removal. Under these conditions the present

\* Samples for each trial collected simultaneously in Berkeley.

Figure 7 SCHEMATIC COMPILATION OF HNO<sub>3</sub> FILTER COLLECTION RESULTS, TRIAL 16C ( $\mu\text{g}/\text{m}^3$ )



Experimental Conditions:

R.H. (%) 30

Temp., °C 32

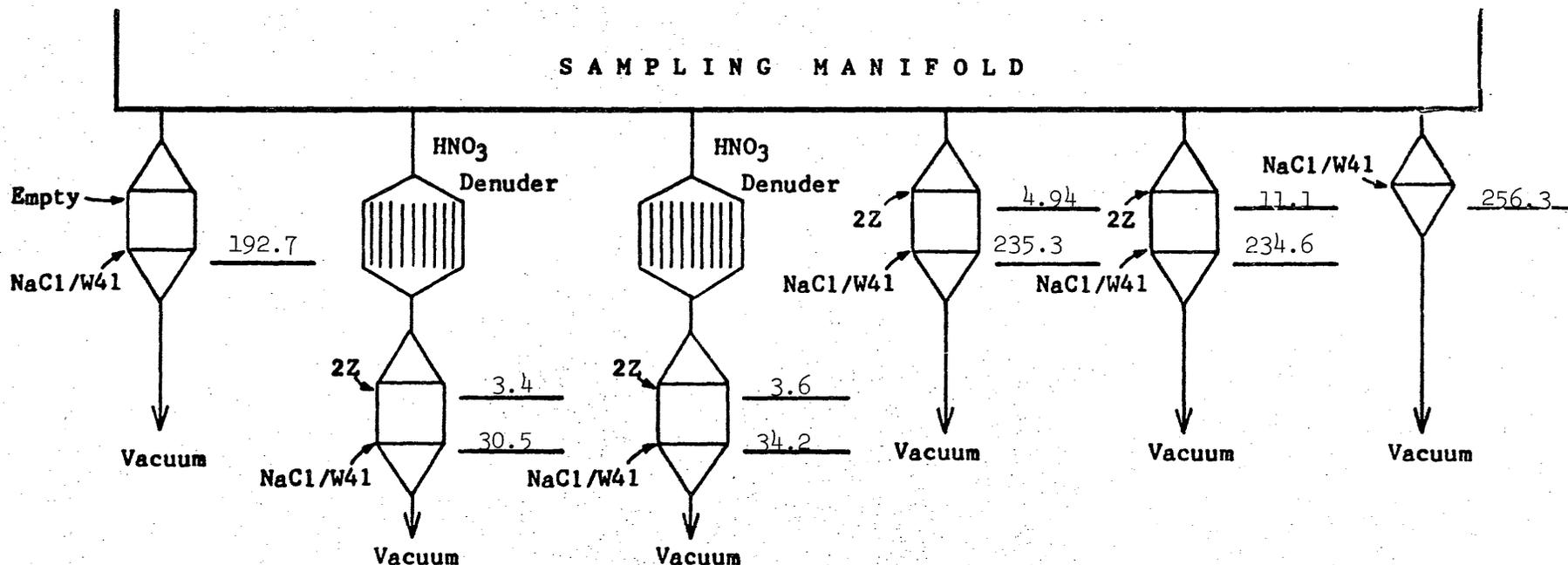
Prefilter Atm. Partic. Loading none

Sampling Time, hrs. (flow rate) 4.0 (20 Lpm)

Abbreviations: 2Z = 2 $\mu\text{m}$  pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 8 SCHEMATIC COMPILATION OF HNO<sub>3</sub> FILTER COLLECTION RESULTS, TRIAL 16D ( $\mu\text{g}/\text{m}^3$ )



07

Experimental Conditions:

R.H. (%) 30

Temp., °C 32

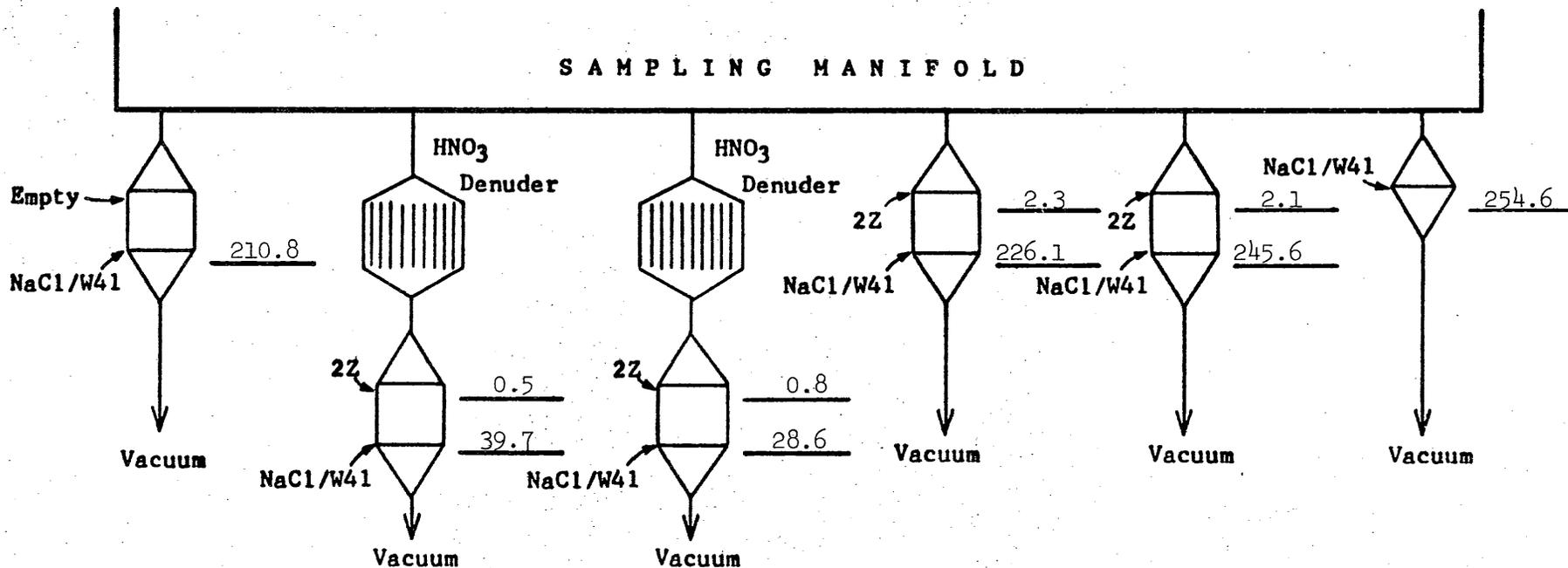
Prefilter Atm. Partic. Loading 271 ± 87  $\mu\text{g}$  (Atm. Partic. contributes 1.0  $\mu\text{g}/\text{m}^3$  to observed values on 2Z filters)

Sampling Time, hrs. (flow rate) 4.5 (20 Lpm)

Abbreviations: 2Z = 2 $\mu\text{m}$  pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 9 SCHEMATIC COMPILATION OF HNO<sub>3</sub> FILTER COLLECTION RESULTS, TRIAL 16E ( $\mu\text{g}/\text{m}^3$ )



17

Experimental Conditions: R.H. (%) 50

Temp., °C 21

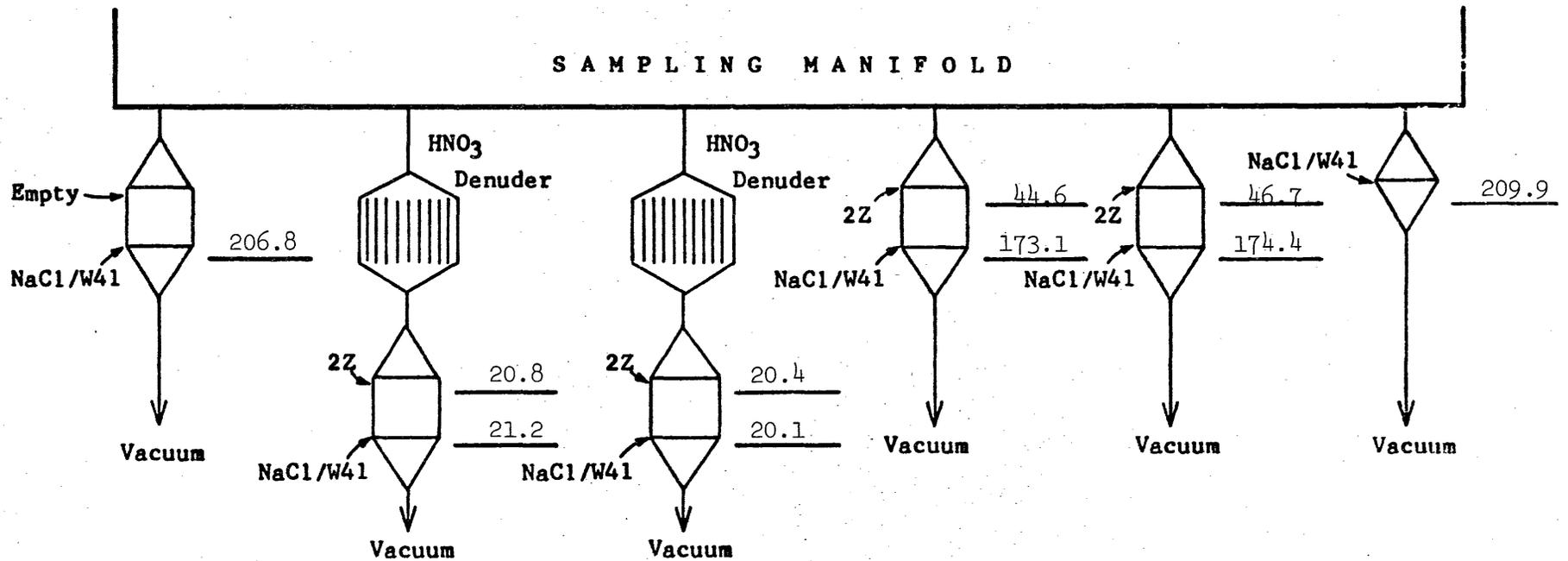
Prefilter Atm. Partic. Loading none

Sampling Time, hrs. (flow rate) 4.0 (20 Lpm)

Abbreviations: 2Z = 2 $\mu\text{m}$  pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 10 SCHEMATIC COMPILATION OF HNO<sub>3</sub> FILTER COLLECTION RESULTS, TRIAL 16F ( $\mu\text{g}/\text{m}^3$ )



42

Experimental Conditions:

R.H. (%) 50

Temp., °C 21

Prefilter Atm. Partic. Loading 768 ± 5 μg (Atm. Partic. contributes 6.1 μg/m<sup>3</sup> to observed values on 2Z filters)

Sampling Time, hrs. (flow rate) 4.0 (20 Lpm)

Abbreviations: 2Z = 2μm pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Table 13 INTERMETHOD COMPARISON OF HNO<sub>3</sub> SAMPLING TECHNIQUES UNDER LABORATORY CONDITIONS (μg/m<sup>3</sup>)

Trial	Temp. °C	R.H. (%)	Prefilter Loading, μg	TIN <sup>a</sup>	PN		HNO <sub>3</sub> by Difference <sup>c</sup>		HNO <sub>3</sub> by Okita Method <sup>d</sup>	HNO <sub>3</sub> by Monitor Labs Analyzer <sup>e</sup>
					Apparent <sup>b</sup>	Corrected <sup>f</sup>	Apparent	Corrected <sup>f</sup>		
16C	32	30	none	241 ± 14	30.5 ± 4.9	0	211 ± 16	241 ± 14	239 ± 14	215 ± 11
16D	32	30	271 ± 87	243 ± 4	35.9 ± 2.8	1.0	207 ± 5	242 ± 87	235 ± 0.5	212 ± 9
16E	21	50	none	238 ± 14	34.8 ± 7.6	0	203 ± 16	238 ± 14	236 ± 14	206 ± 4
16F	21	50	768 ± 5	219 ± 2.4	41.3 ± 1.1	6.1	178 ± 3	213 ± 2.4	174 ± 1	201 ± 7
Ratio of Means:							0.85	1.0	0.95	0.89
							1.0	1.17	1.11	1.04

a. Total inorganic nitrate.

b. The apparent particulate nitrate assuming all nitrate penetrating the denuder to be particulate nitrate (see Table and text).

c. TIN less PN.

d. The nitrate on NaCl/W41 filters downstream of Teflon prefilter.

e. Continuous readings averaged over the four-hour sampling time.

f. Correction assumed nitrate penetrating denuder was HNO<sub>3</sub>. Thus corrected values are either zero or the nitrate contributed by the atmospheric particles on the Teflon filter.

method comparison employing the "corrected" results should be more relevant.

Since the atmospheric particulate matter contains nitrate (in Trial 16F it corresponded to about  $6 \mu\text{g}/\text{m}^3$ ), in principle the  $\text{HNO}_3$  results might err in either direction depending on the dominance of  $\text{HNO}_3$  adsorption on the prefilter or  $\text{NH}_4\text{NO}_3$  dissociation. In the present laboratory trial which maintained  $\text{HNO}_3$  constant at about 80 ppb, such dissociation should be repressed, favoring the observed negative deviations in  $\text{HNO}_3$  (and increase in nitrate retained on the prefilter used to measure particulate nitrate by the Okita method). However, as suggested above, such retention of  $\text{HNO}_3$  may not be observable in atmospheric sampling (where  $\text{HNO}_3$  levels can drop to low levels) especially under conditions of high particulate nitrates.

In addition to trials 16 C - F, two similar experiments were attempted at 80% R.H. and  $16^\circ\text{C}$ . The conditions approach those experienced at night and early morning in atmospheric sampling, for which R.H. values  $> 90\%$  were often found. However, under these conditions losses of about 99% of the  $\text{HNO}_3$  (at a calculated 80 ppb) was experienced ahead of the filter samplers apparently by collection on the walls of the glass dilution system and sampling manifold. The effective scavenging of  $\text{HNO}_3$  by surfaces under these conditions suggests that retention of atmospheric  $\text{HNO}_3$  on particulate matter-loaded Teflon prefilters (and perhaps on suspended particles) at high R.H. should be efficient as well. Conversely, loss of  $\text{NH}_4\text{NO}_3$  by dissociation to  $\text{HNO}_3$  should be repressed.

#### IV. LABORATORY EVALUATION OF SAMPLING TECHNIQUES FOR H<sub>2</sub>SO<sub>4</sub>

##### A. Introduction

Previous atmospheric sampling trials in Pittsburg<sup>1</sup> as well as those for the present study in the Los Angeles Basin included both respirable particulate hi-vol and lo-vol sampling for H<sub>2</sub>SO<sub>4</sub>. The latter used a denuder for removal of atmospheric NH<sub>3</sub> in an attempt to increase the stability of any acidic aerosol collected. However, the use of an ammonia denuder introduces a potentially significant source of error in monitoring the acidity of atmospheric particulates. The system H<sub>2</sub>O-NO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>=</sup>-NH<sub>4</sub><sup>+</sup>-HCO<sub>3</sub><sup>-</sup>-H<sub>2</sub>CO<sub>3</sub> such as might be found in a given aerosol particle, may exist in equilibrium with corresponding materials in gas phase (e.g., HNO<sub>3</sub>, NH<sub>3</sub>, CO<sub>2</sub>). The removal of NH<sub>3</sub> from the air stream might, therefore, induce increased acidity in the particulate by causing dissociation of NH<sub>4</sub><sup>+</sup> to gaseous NH<sub>3</sub> and H<sup>+</sup>. The latter might then react preferentially with the most alkaline material remaining, e.g., HCO<sub>3</sub><sup>-</sup>, forming the weak acid H<sub>2</sub>CO<sub>3</sub>, not measurable as strong acid by the titrimetric method used. However, if the bicarbonate anion is consumed, further NH<sub>3</sub> loss could lead to either H<sub>3</sub>O<sup>+</sup> or HSO<sub>4</sub><sup>-</sup>. In either case, increased strong acid levels would then be observed. Brosset has predicted that, at least for aerosols which resemble aqueous solutions, such NH<sub>3</sub> loss should occur.<sup>20</sup> In addition to NH<sub>3</sub> loss, transfer of phosphorous acid from the tubes of the denuder to the filters would also cause increase in the measured strong acid.

##### B. Experimental Procedure

To assess these possible sources of artifact strong acid, Teflon filters were loaded with  $\leq 0.2 \mu\text{m}$  (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-NH<sub>4</sub>NO<sub>3</sub> aerosol mixtures prepared from a solution of the two salts. The loaded filters were exposed to air purified by removal of NO<sub>x</sub>, ozone and organics heavier than ethane using triethanolamine and charcoal. The purification train is described elsewhere.<sup>35</sup> Atmospheric CO<sub>2</sub> was not significantly removed and CO<sub>2</sub> levels of  $\geq 400$  ppm were expected. Transfer of phosphorous acid to the filter was measured by sampling humidified air through the denuder followed by a clean Teflon filter. Strong acid was measured as previously described.<sup>1</sup>

##### C. Results

Table 14 summarizes the experiments performed running two filters in duplicate. Acidity levels were compared to those of filters loaded

Table 14

Assessment of Artifact H<sup>+</sup> Formation Caused by Use of  
An Ammonia Denuder at 20°C<sup>a</sup>

<u>Particulate Loading</u>	<u>Clean Air Sampling Conditions</u>	<u>Observed H<sup>+</sup> Increase (as <math>\mu\text{g H}_2\text{SO}_4</math> per filter)</u>
None	28 Lpm, 6 hours 80% R.H.	Not detected <sup>b</sup>
400 $\mu\text{g}$ 0.2 $\pm$ 0.1 $\mu\text{m}$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	28 Lpm, 6 hours 50% R.H.	Not detected <sup>b</sup>
416 $\mu\text{g}$ 0.2 $\pm$ 0.1 $\mu\text{m}$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	28 Lpm, 6 hours 90% R.H.	Not detected <sup>b</sup>
370 $\mu\text{g}$ 0.2 $\pm$ 0.1 $\mu\text{m}$ 11:1 w/w (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> :NH <sub>4</sub> NO <sub>3</sub> <sup>c</sup>	28 Lpm, 6 hours 58% R.H.	Not detected <sup>b</sup>
80 $\mu\text{g}$ 0.2 $\pm$ 0.1 $\mu\text{m}$ 0.35 w/w (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> :NH <sub>4</sub> NO <sub>3</sub> <sup>c</sup>	28 Lpm, 6 hours 58% R.H.	Not detected <sup>b</sup>

- 
- a. All results based on filters run in duplicate side-by-side.  
 b. Filter acidity unchanged from that of filters not exposed to clean air.  
 c. Loading estimated from loading rate in other trials.

with equal amounts of the salts but not exposed to the air stream. At 90% R.H.,  $(\text{NH}_4)_2\text{SO}_4$  and the  $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{NO}_3$  mixtures should exist as concentrated solutions (with dissolved  $\text{CO}_2$ )\* in droplets on the filter, conditions which should favor  $\text{NH}_3$  loss as the system strives to establish gas-liquid equilibrium. Nevertheless, no measurable acidity increase was observed. Similarly, no increase in acidity was observed with the blank Teflon filter.

In principle,  $\text{NH}_3$  could be formed from dissociation of  $\text{NH}_4^+$ -containing particles during the 0.2 second calculated residence time within the  $\text{NH}_3$ -denuder tubes. However experiments with  $\text{NH}_4\text{NO}_3$ , described in Section III, did not support the significance of such dissociation making loss of  $\text{NH}_3$  from sulfate salts improbable, as well.

We conclude, therefore, that the use of the  $\text{NH}_3$  denuder does not cause artifact  $\text{H}^+$  formation either from  $\text{NH}_3$  loss from salts on the filter, or by transfer of phosphorous acid.

---

\* The equilibrium concentration of  $\text{H}_2\text{CO}_3$  in water droplets in contact with air is about  $10^{-5}\text{M}$ .21

## V. ATMOSPHERIC SAMPLING

### A. Sampling Strategy

Sampling was performed during July, 1979 for eight days at each of two sites, Lennox and Claremont, California. The sampling strategy is outlined in Table 15. Lennox is in proximity to numerous sulfur oxide emission sites, and might, therefore, be subject to relatively high concentrations of  $H_2SO_4$  (Figure 11). Claremont is about 50 km east of downtown Los Angeles, relatively distant from strong  $SO_x$  emission sources. It was expected to exhibit low acidic sulfate levels but elevated levels of nitric acid and particulate nitrate.

### B. Experimental Procedures

The analytical methods used and their precision, accuracy and limits of detection are shown in Table 16. In general, procedures followed were those described for the preliminary field study in Pittsburg, California.<sup>1,23</sup> However techniques were modified to improve the recovery of  $H_2SO_4$ . It was postulated that some of the loss of  $H_2SO_4$  previously observed resulted from neutralization by ammonia liberated by dissociation of  $NH_4NO_3$  or other  $NH_3$ -containing materials on the filter. To minimize such effects, samples were dried in vacuum to remove weakly bound  $NH_3$ , and stored at low temperature. In addition, four-times larger filter sections were extracted to decrease the limit of detection for  $H_2SO_4$ . Details are as follows.

Immediately following sampling, the samples for  $H_2SO_4$  and  $H^+$  analysis were stored at  $\leq -20^\circ C$ . Samples were held at room temperature for 30 min drying at  $\leq 1$  mm Hg, during sectioning in an  $NH_3$ -free chamber under dry  $N_2$ , and just prior to benzaldehyde addition. With hi-vol samples, 70  $cm^2$  filter sections were extracted in 15 mL benzaldehyde. After 15 min centrifugation at 2000 to 2500 rpm, 10 mL of the extract were recovered from the clear supernatant. Sulfate was transferred by liquid-liquid extraction into 3 mL  $H_2O$  which was analyzed for  $H_2SO_4$  by the ATHL microsulfate method.<sup>26</sup> With lo-vol samples the 47 mm Teflon filter was sectioned in quarters, two quarters being extracted in 10 mL benzaldehyde. Nine mL of the extract were recovered for analysis of  $H_2SO_4$  as  $SO_4^{=}$  following re-extraction into  $H_2O$ . The remaining two quarters were extracted in 10 mL water for  $H^+$  and  $SO_4^{=}$  analysis. Both benzaldehyde and aqueous extractions employed 60 min mechanical shaking with an Eberbach Model 6000 platform shaker. Atmospheric ammonia was sampled on oxalic acid-impregnated Gelman AE filters at 25 Lpm with an unheated sampler.<sup>1</sup> A Gelman type A glass fiber (pH = 7.6) filter removed particulate matter.  $NH_3$  was determined as  $NH_4^+$  using an Orion ion-specific electrode.

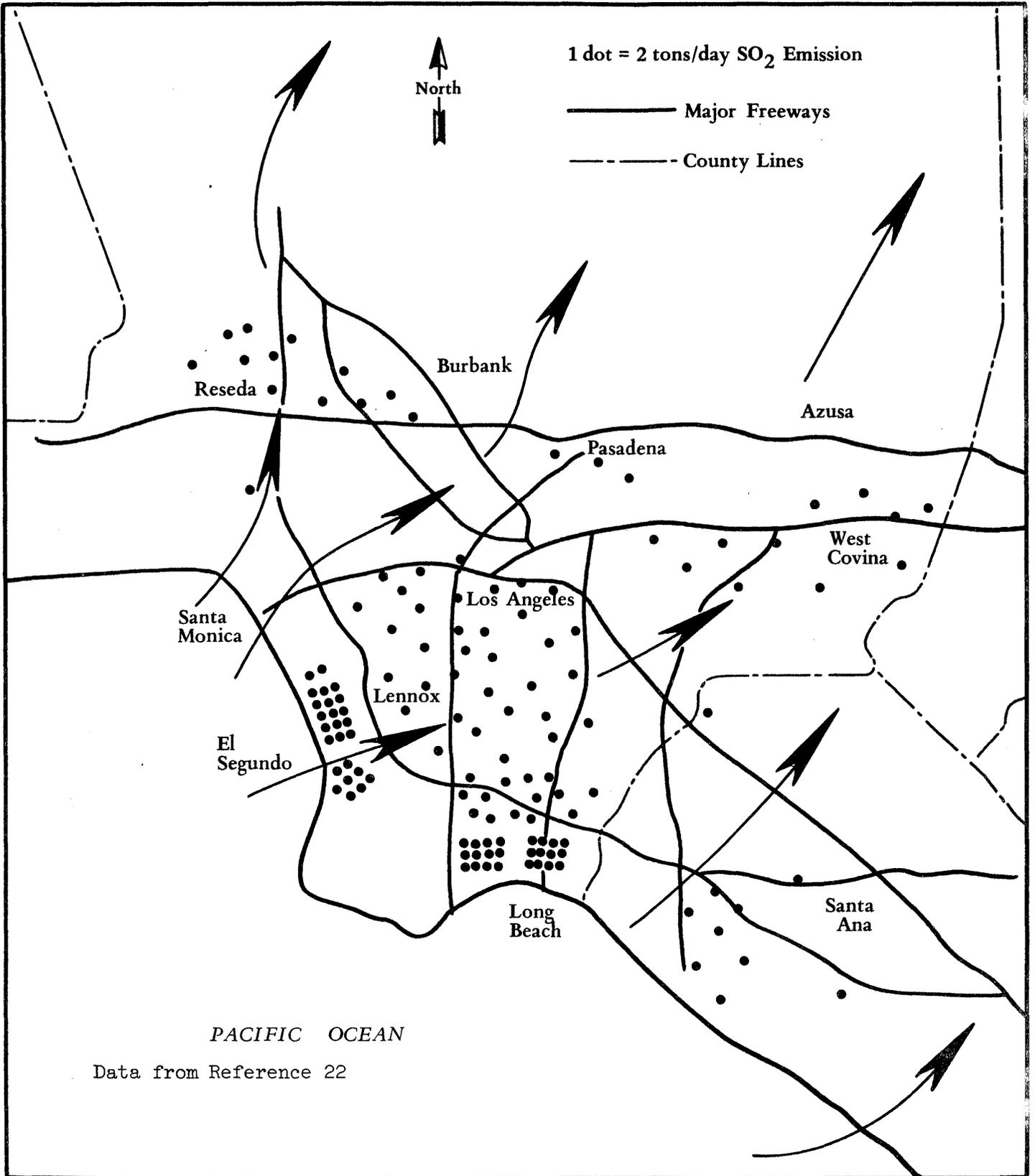
Table 15

## Sampling Strategy at Lennox and Claremont, CA

<u>Sampler</u>	<u>Flow Rate, m<sup>3</sup>/min</u>	<u>Filter</u>	<u>Filter Change Frequency, hrs</u>	<u>Species Measured</u>
Respirable (< 3.5 $\mu$ m) particulate hi-vol	1.1	Acid-washed Pallflex 2500 QAO quartz fiber	2 to 8	H <sub>2</sub> SO <sub>4</sub> , H <sup>+</sup> , SO <sub>4</sub> <sup>=</sup> , NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>
Respirable (< 2.5 $\mu$ m) particulate lo-vol with NH <sub>3</sub> denuder	0.028	Zefluor (Teflon), 2 $\mu$ m pore size <sup>a</sup>	8	H <sub>2</sub> SO <sub>4</sub> , H <sup>+</sup> , SO <sub>4</sub> <sup>=</sup>
Total nitrate sampler	0.020	Zefluor plus NaCl/W41 <sup>b</sup> or Ghia nylon	2 to 8	NO <sub>3</sub> <sup>-</sup>
Total particulate NO <sub>3</sub> <sup>-</sup> sampler using acid gas denuder	0.020	Zefluor plus NaCl/W41 or Ghia nylon	2 to 8	NO <sub>3</sub> <sup>-</sup>
67 Ammonia	0.025	Gelman A glass fiber prefilter plus oxalic acid/Gelman AE	2 to 8	NH <sub>3</sub> as NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> on glass fiber prefilter
Bendix Model 8002 O <sub>3</sub> analyzer		---	continuous	O <sub>3</sub>
Meloy Model 5A160-2 total sulfur analyzer		---	continuous	SO <sub>2</sub> plus H <sub>2</sub> S
Teco Model 14 NO-NO <sub>2</sub> analyzer		---	continuous	NO, NO <sub>2</sub>

a. Ghia Corp., Pleasanton, CA.

b. NaCl-impregnated Whatman 41 (cellulose) filter.



SO<sub>2</sub> EMISSIONS AND PREVAILING WIND PATTERNS  
Figure 11

Table 16

Summary of Analytical Methods and their Precision, Accuracy and Limits of Detection

Species Analyzed	Method	Reference	Precision (C.V.), %	Limit of Detection, $\mu\text{g}/\text{m}^3$	Analytical Accuracy, %
$\text{H}_2\text{SO}_4$ (Hi-vol)	Benzaldehyde Extraction-AIHL $\text{SO}_4$ analysis	24, 1, 23	13% at $< 1 \mu\text{g}/\text{m}^3$ <sup>a</sup> > $1 \mu\text{g}/\text{m}^3$ , see text	-- <sup>d</sup>	Not determined <sup>g</sup>
$\text{H}_2\text{SO}_4$ (Lo-vol)	Same as above	24, 1, 23	Not determined	-- <sup>d</sup>	Not determined <sup>g</sup>
$\text{H}^+$ (Hi-vol) as $\text{H}_2\text{SO}_4$	Titration to pH = 4.0	25, 1, 23	3.6% at $> 1.0 \mu\text{g}/\text{m}^3$ <sup>a</sup> 40% at $0.5 \mu\text{g}/\text{m}^3$	0.5 <sup>c</sup>	Not determined <sup>g</sup>
$\text{H}^+$ (Lo-vol) as $\text{H}_2\text{SO}_4$	Same as above	10, 1, 23	Not determined	Est. 0.3	Not determined <sup>g</sup>
$\text{NH}_4^+$ (Hi-vol)	Selective ion electrode		Mean 13% for 0.4 to $6 \mu\text{g}/\text{m}^3$ samples <sup>a</sup>	0.2 <sup>c</sup>	119 at $0.6 \mu\text{g}/\text{m}^3$ <sup>c</sup>
$\text{SO}_4^{2-}$ (Hi-vol)	AIHL micro $\text{SO}_4^{2-}$ <sup>k</sup>	26	5.8 <sup>b</sup>	0.1 <sup>c</sup>	106 <sup>h</sup>
$\text{SO}_4^{2-}$ (Lo-vol)	AIHL micro $\text{SO}_4^{2-}$ <sup>k</sup>	26	4.0 <sup>b</sup>	0.2	102 <sup>i</sup>
$\text{NO}_3^-$ (Hi-vol)	Automated Cu-Cd reduction-diazotization	27	3.3 <sup>a</sup>	0.7 <sup>c</sup>	98
$\text{NO}_3^-$ (Lo-vol)	Same as above	27	6.0	1.1 <sup>c</sup>	98
$\text{NO}_3^-$ ( $\text{NH}_3$ sampler prefilter)	Gelman A glass fiber (pH = 7.6) <sup>e</sup>		0.9 <sup>b</sup>	1.1 <sup>c</sup>	98
$\text{NH}_3$ as $\text{NH}_4^+$	Oxalic acid on Gelman AE. Selective ion electrode.	28, 1	Not determined	0.8 <sup>c</sup>	119 at $0.6 \mu\text{g}/\text{m}^3$ <sup>j</sup>
$\text{HNO}_3$ (nylon filter)	Particulate removal with Teflon prefilter <sup>e</sup>	3, 1	7 <sup>f</sup>	1.1 <sup>c,d</sup>	See text
$\text{HNO}_3$ (NaCl/W41)	Same as above	2, 1	7 <sup>f</sup>	1.1 <sup>c,d</sup>	See text
$\text{HNO}_3$ (by difference)	See text	16	See text	Not determined	See text

a. Based on analysis of separate filter sections removed and extracted at about the same time.

b. Based on re-analysis of the same filter extracts on a different day.

c. Calculated for 4-hour samples.

d. Subject to positive interference making limit of detection uncertain.

e. Quantitation by the automated Cu-Cd reduction, diazotization method.

f. From laboratory studies in Section III.

g. Recovery studies are described in References 1 and 23.

h. Compared to the mean of analysis of 24 Hi-vol filter extracts by six methods.

i. Compared to the Dionex ion chromatograph for analysis of 24 Lo-vol samples.

j. Based on recovery with standards. Comparison with simultaneous atmospheric  $\text{NH}_3$  measurements by Fourier transform infrared spectroscopy (FTIR) for 7, 2 or 4-hour periods consistently  $2.5 \pm 0.5 \mu\text{g}/\text{m}^3$  lower  $\text{NH}_3$  by the filter technique with atmospheric levels of 4.1 to  $7.8 \mu\text{g}/\text{m}^3$ .

k. Samples were pre-treated with Bio-Rad AG 30W-X8 cation exchange resin to remove cationic interferents.

The precision of  $H_2SO_4$  determinations by benzaldehyde extraction, as measured by duplicate filter sections removed from the same filters, decreased sharply with increasing  $H_2SO_4$  level. Above  $1 \mu g/m^3$  the mean C.V. was 85% ( $n = 3$ ) compared to 13% at  $< 1 \mu g/m^3$  ( $n = 9$ ). Filter sections removed after an additional one-month storage (at  $-10^\circ C$ ) averaged 6% of the initial  $H_2SO_4$  determination. These results reflect, most probably, the extreme sensitivity of  $H_2SO_4$  recovery to details in sample handling (e.g., the cumulative exposure to  $NH_3$ ). The atmospheric  $H_2SO_4$  values are, in general, considered minimum values.

Nitric acid was sampled with 47 mm, NaCl-impregnated Whatman 41 (NaCl/W41) cellulose filters and with Duralon (Millipore Corp.) or Ghia Corp. nylon filters. For a number of sampling periods both NaCl/W41 and nylon filters were run in parallel. Teflon prefilters were used to remove particulate matter. Nitric acid values obtained in this way will be referred to as "HNO<sub>3</sub> by filter collection". Prefilters and HNO<sub>3</sub> collection filters were mounted in series in Nuclepore multiple filter holders with 3.2 cm I.D. 15 cm length polycarbonate inlet tubes. The sum of the nitrate on the Teflon prefilter and nitric acid (as NO<sub>3</sub><sup>-</sup>) on the nylon or NaCl/W41 after-filter equalled the total inorganic nitrate (TIN). The efficiency of the prefilters for collection of particulate matter is  $> 99.9\%$  as measured with room air dust and a condensation nuclei counter.<sup>29</sup> In some cases following each sampling period, ambient air, heated to a temperature which produced a relative humidity of  $< 15\%$  (about  $50^\circ C$ ), was sampled for three minutes at 20 Lpm to desorb nitric acid possibly retained on the prefilter and/or walls of the sampler. In parallel with the Teflon prefilters, particulate nitrate (PN) was sampled following passage of the atmospheric sample through an inlet tube as described above and an acid gas denuder discussed in Section III C. Assuming no loss of particulate nitrate in the denuder, the TIN less PN should equal the gaseous nitrate (i.e., HNO<sub>3</sub>). This is here referred to as "HNO<sub>3</sub> by difference". Nitrate was extracted from filters with 10 mL distilled H<sub>2</sub>O or, for nylon filter, 5 mL 0.1N NaOH, by 60 min agitation using an Eberbach Model 6000 shaker. Basic extracts were neutralized with 5 mL 0.1N HCl prior to NO<sub>3</sub><sup>-</sup> determination.

#### C. Summary of Data

Results obtained with the hi-vol and lo-vol samplers and the nitrate reference sampler are tabulated in Tables 17 through 22, in  $\mu g/m^3$ . The results are discussed in the following sections. To aid in data comparisons, graphical presentations are presented in nano-equivalents per  $m^3$ .

#### D. Particulate Acid Results

##### 1. Lennox

The results for  $H_2SO_4$ ,  $H^+$ ,  $NH_4^+$  and  $NH_3$  are shown in Figure 12. In addition, wind speed and direction are indicated by arrows,

Table i7

Analysis of Respirable Particulate Hi-Vol and NH<sub>3</sub> Sampler Results from Lennox, CA (ug/m<sup>3</sup>)

Date	Time (PDT)	Hi-Vol Sampler <sup>a</sup>					NH <sub>3</sub> Sampler <sup>b</sup>	
		H <sub>2</sub> SO <sub>4</sub>	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>m</sup>	NO <sub>3</sub> <sup>-</sup>	Prefilter NO <sub>3</sub> <sup>-</sup>	NH <sub>3</sub> as NH <sub>4</sub> <sup>+</sup>
7/10/79	6-8	0.2	0.6	< 0.7	3.5	< 1.5	6.6	3.8
	8-10	0.1	< 0.2	< 0.7	3.7	2.0	18.4	3.5
	10-14	0.2	0.3	0.3	5.3	2.6	28.9	0.9
	14-18	0.1	< 0.1	0.7	6.1	0.9	48.1	1.2
	18-22	0.1	< 0.1	< 0.3	3.6	< 0.7	9.8	1.2
	22-06	0.0	0.2	< 0.2	1.3	0.5	2.4	1.7
7/11/79	6-8	0.1	< 0.2	< 0.7	2.5	< 1.7	4.1	1.9
	8-10	0.1	< 0.2	< 0.7	5.6	1.4	8.7	3.0
	10-14	0.1	0.5	< 0.3	3.8	2.1	15.9	3.1
	14-18	0.1	0.5	1.4	8.2	1.8	31.5	1.2
	18-22	0.1	1.1	1.2	7.5	2.2	32.2	< 0.9
	22-06	0.1	< 0.06	2.0	5.1	2.8	17.3	2.1
7/12/79	6-8	0.2	< 0.2	1.6	7.3	2.7	13.2	1.9
	8-10	0.3	< 0.2	1.5	10.1	3.2	17.3	2.4
	10-14	0.1	< 0.1	1.3	7.6	2.3	17.4	4.1
	14-18	0.1	< 0.1	1.1	8.8	1.4	25.5	2.4
	18-22	0.1	< 0.1	0.4	4.7	1.7	10.4	3.4
	22-06	0.1	0.7	2.2	8.9	1.2	13.3	1.0
7/13/79	6-8	0.3	1.6	< 0.7	11.3	< 1.5	14.4	< 1.9
	8-10	0.3	2.4	< 0.7	10.9	< 1.4	17.3	< 1.9
	10-14	0.3	2.4	2.0	13.2	< 0.7	15.9	< 0.9
	14-18	0.3	1.1	2.4	11.8	< 0.7	14.3	0.9
	18-22	0.1	0.3	0.5	6.0	< 0.7	5.3	0.8
	22-06	0.1	0.8	3.0	9.2	< 0.5	16.0	0.6
7/14/79	6-8	0.3	2.1	0.3	13.1	< 1.5	< 2.1	< 1.9
	8-10	0.3	1.6	1.3	12.8	< 1.4	29.2	< 1.9
	10-14	0.3	3.2	1.4	14.1	0.8	25.8	< 0.9
	14-18	0.1	0.2	0.7	6.2	< 0.7	14.7	< 0.9
	18-22	0.1	< 0.1	< 0.3	3.1	< 0.7	4.1	1.5
	22-06	0.1	1.3	0.4	4.7	0.4	6.3	0.5
7/15/79	6-8	7.6	7.5	0.7	10.7	< 1.5	15.8	< 1.9
	8-10	1.1	5.8	2.1	14.8	< 1.5	16.9	< 1.9
	10-14	0.3	4.3	2.1	12.3	< 0.7	22.6	< 1.0
	14-18	0.2	2.0	1.3	8.3	< 0.7	7.6	< 0.9
	18-22	0.3	0.5	0.9	4.5	< 0.7	4.0	< 0.9
	22-06	1.5	2.2	1.3	8.1	< 0.4	8.6	0.7
7/16/79	6-8	0.4	4.4	4.4	20.3	< 1.3	25.3	< 1.7
	8-10	2.0	9.3	1.5	15.2	< 1.7	23.4	< 2.1
	10-14	10.9	4.9	0.7	10.2	< 0.7	16.7	< 0.9
	14-18	0.4	1.5	0.4	5.8	< 0.7	8.1	< 0.9
	18-22	0.1	0.3	1.0	4.8	0.9	6.7	1.3
	22-06	0.2	-- <sup>c</sup>	-- <sup>c</sup>	5.7	1.7	12.1	1.7
7/17/79	6-8	0.2	< 0.2	4.1	8.3	3.9	16.0	4.0
	8-10	0.2	0.5	3.7	7.1	5.3	20.3	3.5
	10-14	0.2	0.9	1.7	7.5	1.0	22.4	2.5
	14-18	9.6	1.1	2.0	10.7	1.0	45.0	< 1.0
	18-22	0.0	0.5	1.1	4.5	1.2	8.5	2.0
	22-06	4.3	1.0	1.6	6.7	1.0	6.3	1.9

a. Collected on acid-washed Pallflex quartz 2500 QAO filters.

b. Samples collected on oxalic acid impregnated Gelman AE glass fiber filters following particle removal with Gelman A glass fiber prefilters.

c. Sample lost.

Table 18

Analysis of Respirable Particulate HI-Vol and NH<sub>3</sub> Sampler Results from Claremont, CA (µg/m<sup>3</sup>)

Date	Time (PDT)	Hi-Vol Sampler <sup>a</sup>					NH <sub>3</sub> Sampler <sup>b</sup>	
		H <sub>2</sub> SO <sub>4</sub>	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup>	Prefilter NO <sub>3</sub> <sup>-</sup>	NH <sub>3</sub> as NH <sub>4</sub> <sup>+</sup>
7/22/79	6-8	0.3	< 0.2	< 0.7	1.4	< 1.5	16.2	4.3
	8-10	0.1	< 0.2	1.6	4.9	6.6	31.0	6.8
	10-14	0.1	1.5	1.9	7.6	1.6	46.0	3.1
	14-18	0.1	0.5	1.4	6.9	1.0	41.6	1.5
	18-22	0.2	< 0.1	1.0	5.6	1.4	18.5	2.1
	22-06	0.7	0.1	1.4	4.5	1.5	16.2	2.5
7/23/79	6-8	0.3	< 0.2	2.5	5.8	5.7	30.2	5.0
	8-10	0.2	< 0.2	6.2	7.3	12.0	55.9	< 1.5
	10-14	0.3	0.3	2.1	7.4	2.6	69.0	3.8
	14-18	1.7	1.2	4.6	12.4	2.2	70.2	0.6
	18-22	3.2	0.4	3.5	9.9	2.6	41.5	0.8
	22-06	0.9	< 0.06	2.7	6.2	2.8	16.2	2.8
7/24/79	6-8	1.9	< 0.2	2.6	7.0	8.1	21.3	7.1 <sup>c</sup>
	8-10	1.5	< 0.2	9.6	11.1	28.2	62.1	---
	10-14	0.6	0.8	2.5	14.5	11.7	80.2	4.0
	14-18	1.6	1.0	0.9	12.5	1.6	65.1	0.8
	18-22	0.2	2.2	5.2	16.4	2.0	46.6	0.8
	22-06	0.1	0.3	7.7	12.8	6.5	22.2	3.4
7/25/79	6-8	4.5	0.5	4.1	9.2	8.1	23.2	4.6
	8-10	1.0	0.7	5.8	15.8	15.5	45.1	4.1
	10-14	0.1	0.7	6.4	14.6	< 0.7	73.0	1.4
	14-18	0.3	1.0	3.0	11.2	1.2	57.3	1.0
	18-22	0.1	< 0.1	---	16.9	1.4	37.5	0.7
	22-06	0.1	0.1	4.7	8.4	6.2	18.4	4.1
7/26/79	6-8	0.2	< 0.2	8.4	14.3	16.5	36.5	9.8
	8-10	0.9	< 0.2	12.8	17.1	13.6	37.3	< 1.5
	10-14	0.7	0.8	10.9	18.5	11.4	82.0	1.5
	14-18	0.5	2.0	6.7	18.7	1.9	60.5	0.7
	18-22	1.5	0.6	3.1	10.0	3.0	36.3	< 0.8
	22-06	0.3	0.4	4.5	7.9	6.0	22.7	2.8
7/27/79	6-8	4.3	0.8	4.4	10.2	12.5	46.5	2.8
	8-10	0.5	1.0	10.8	12.6	27.7	78.2	4.9
	10-14	1.5	0.5	6.7	12.4	11.0	82.3	2.5
	14-18	0.7	1.3	4.3	16.2	1.9	57.8	< 0.8
	18-22	0.2	0.4	2.3	9.0	1.9	38.2	0.8
	22-06	0.1	0.4	2.9	6.1	4.0	89.6	5.4
7/28/79	6-8	0.2	1.6	2.1	6.0	4.5	31.1	< 1.5
	8-10	0.3	1.0	7.4	11.1	18.5	79.3	3.0
	10-14	0.4	0.9	5.6	9.6	7.9	82.3	2.3
	14-18	0.5	1.2	0.9	9.2	2.0	58.4	< 0.8
	18-22	0.2	0.5	2.7	8.8	2.5	41.3	< 0.8
	22-06	0.1	< 0.06	1.9	5.2	1.5	16.7	1.4
7/29/79	6-8	0.2	< 0.2	4.6	9.1	12.1	25.8	5.7
	8-10	0.3	< 0.2	6.5	12.7	19.9	74.6	7.8
	10-14	0.3	0.9	2.8	9.2	3.9	71.2	2.7
	14-18	0.5	0.8	3.4	15.2	1.4	56.3	1.2
	18-22	0.3 <sup>c</sup>	1.3	6.2	17.5	3.8	46.6	< 0.8
	22-06	---	0.4	5.6	12.8	6.2	27.3	1.7

a. Samples collected on acid-washed Pallflex quartz 2500 QAO filters.

b. See footnote b, Table 7.

c. Sample lost.

Table 19

Analysis of Lo-Vol Respirable Particulate Samples (with NH<sub>3</sub> Denuder)  
from Lennox, CA (μg/m<sup>3</sup>)<sup>a</sup>

<u>Date</u>	<u>Time (PDT)</u>	<u>H<sub>2</sub>SO<sub>4</sub></u>	<u>H<sup>+</sup></u>	<u>SO<sub>4</sub><sup>=</sup></u>
7/10/79	6-14	0.8	< 0.3	9.1
	14-22	2.1	< 0.3	14.5
	22-06	0.2	< 0.3	1.9
7/11/79	6-14	0.5	< 0.3	5.8
	14-22	1.7	0.3	10.7
	22-06	1.8	0.3	--- <sup>b</sup>
7/12/79	6-14	0.6	0.6	12.9
	14-22	0.4	0.6	10.3
	22-06	0.6	0.7	17.4
7/13/79	6-14	0.5	4.5	17.9
	14-22	1.5	1.5	14.6
	22-06	0.4	1.9	14.8
7/14/79	6-14	1.3	4.6	21.2
	14-22	0.6	1.3	6.4
	22-06	0.6	2.6	8.4
7/15/79	6-14	2.4	8.6	17.4
	14-22	0.8	1.8	7.4
	22-06	0.6	1.9	14.5
7/16/79	6-14	1.7	8.4	21.1
	14-22	0.4	< 0.3	8.8
	22-06	0.3	< 0.3	7.5
7/17/79	6-14	0.4	< 0.3	9.4
	14-22	0.2	< 0.3	8.9
	22-06	0	10.6	12.0

a. Samples collected on 2.0 μm Teflon (Zefluor) filters.

b. Samples lost.

Table 20

Analysis of Lo-Vol Respirable Particulate Samples (with NH<sub>3</sub> Denuder)  
from Claremont, CA ( $\mu\text{g}/\text{m}^3$ )<sup>a</sup>

<u>Date</u>	<u>Time (PDT)</u>	<u>H<sub>2</sub>SO<sub>4</sub></u>	<u>H<sup>+</sup></u>	<u>SO<sub>4</sub><sup>=</sup></u>
7/22/79	6-14	0.4	< 0.3	10.3
	14-22	0.4	< 0.3	8.7
	22-06	0.3	1.2	6.7
7/23/79	6-14	1.0	0.6	12.1
	14-22	1.2	1.2	19.0
	22-06	0.9	< 0.3	10.0
7/24/79	6-14	1.0	2.3	20.2
	14-22	0.7	3.1	22.4
	22-06	0.7	< 0.3	20.7
7/25/79	6-14	0.4	< 0.3	22.2
	14-22	0.4	0.6	20.9
	22-06	0.8	0.3	13.6
7/26/79	6-14		Samples Lost	
	14-22	1.0	0.9	21.0
	22-06	1.1	1.4	11.5
7/27/79	6-14	1.0	2.0	16.9
	14-22	1.3	1.5	20.1
	22-06	0.8	1.0	10.6
7/28/79	6-14	0.8	0.8	14.7
	14-22	2.5	0.6	14.5
	22-06	1.0	0.3	13.8
7/29/79	6-14	0.6	1.3	17.5
	14-22	0.9	< 0.3	22.1
	22-06	1.3	0.4	21.2

a. Samples collected on 2.0  $\mu\text{m}$  pore size Teflon (Zefluor) filters.

Table 21

Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Lennox, CA ( $\mu\text{g}/\text{m}^3$  as  $\text{NO}_3^-$ )

Date	Time (PDT)	Total Inorganic Nitrate Sampler			Particulate Nitrate Sampler			HNO <sub>3</sub> by Difference <sup>c</sup>
		Pre-filter	After-filter <sup>b</sup>	Total	Pre-filter	After-filter <sup>b</sup>	Total	
7/10/79	6-8	< 2.3	3.9	5.0	< 2.2	4.6	5.7	- 0.7
	8-14	10.9	21.4	32.3	5.9	8.9	14.8	17.5
	14-22	4.5	12.1	16.5	3.4	5.2	8.7	7.8
	22-06	1.6	1.2	2.8	< 0.5	1.1	1.4	1.5
7/11/79	6-14	4.5	3.4	7.9	3.1	2.4	5.4	2.4
	14-22	13.3	11.9	25.2	9.3	5.7	15.0	10.2
	22-06	7.8	6.2	14.1	6.6	6.2	12.8	1.2
7/12/79	6-14	9.2	6.0	15.2	4.4	4.8	9.2	6.0
	14-22	2.0	8.2	10.2	8.5	4.4	12.9	- 2.7
	22-06	5.9	4.8	10.6	4.9	2.9	7.8	2.8
7/13/79	6-14	5.7	7.6	13.3	5.3	3.9	9.2	4.1
	14-22	3.7	6.2	9.9	4.1	3.1	7.2	2.7
	22-06	5.7	7.5	13.2	6.9	3.7	10.6	2.6
7/14/79	6-14	4.9	18.8	23.7	3.2	6.1	9.3	14.4
	14-22	2.0	5.4	7.4	3.4	2.1	5.5	1.9
	22-06	2.8	3.6	6.5	2.3	1.5	3.8	2.7
7/15/79	6-14	3.5	15.1	18.5	2.9	4.5	7.4	11.1
	14-22	1.8	4.3	6.1	1.9	1.6	3.6	2.5
	22-06	2.0	6.3	8.3	2.1	3.3	5.4	2.9
7/16/79	6-14	1.4	18.4	19.8	1.0	6.3	7.3	12.5
	14-22	2.1	5.4	7.5	1.7	2.9	4.6	2.9
	22-06	4.7	5.3	9.9	3.0	5.0	8.0	2.0
7/17/79	6-14	6.2	11.5	17.7	4.7	7.3	12.1	5.6
	14-22	3.9	< 0.5	4.1	2.9	6.5	9.4	- 5.2
	22-06	3.4	3.3	6.6	1.7	3.5	5.2	1.5

a. All samples heated 3 min. at about 50°C following particulate collection.

b. Ghia nylon.

c. Total inorganic NO<sub>3</sub><sup>-</sup> sampler minus particulate NO<sub>3</sub><sup>-</sup> sampler results.

Table 22

Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Claremont, CA ( $\mu\text{g}/\text{m}^3$  as  $\text{NO}_3^-$ )

Date	Time (PDT)	Total Inorganic Nitrate Sampler			Particulate Nitrate Sampler			$\text{HNO}_3$ by Difference <sup>f</sup>
		Pre-filter	After-filter	Total	Pre-filter	After-filter	Total	
7/22/79 <sup>a</sup>	06-14	7.1	22.3 <sup>c</sup>	29.4	4.1	14.1 <sup>c</sup>	18.2	11.2
	14-22	4.6	19.5	24.1	2.7	6.3	9.1	15.0
	22-06	5.3	7.8	13.1	4.0	3.4	9.4	3.7
7/23/79 <sup>a</sup>	0630-1030	13.2	34.4 <sup>d</sup>	47.6	8.4	25.9 <sup>d</sup>	34.3	13.3
	1030-1230	16.0	63.5	79.5	9.4	31.6	41.0	38.5
	1230-1430	14.1	67.1	81.2	6.5	20.9	27.4	53.8
	1430-1630	7.3	67.1	74.4	7.9	21.1	29.0	45.4
	1630-1830	7.7	78.6	86.3	5.6	19.0	24.6	61.7
	1830-2230	7.6	27.7	35.3	5.0	7.1	12.1	23.2
	2230-0630	9.6	4.5	14.1	6.9	1.9	8.8	5.3
7/24/79 <sup>b</sup>	0630-1030	35.3	5.1 <sup>e</sup>	40.4	3.1	4.5 <sup>e</sup>	7.6	32.8
	1030-1230	33.9	34.9	68.8	21.4	27.3	48.7	20.1
	1230-1430	13.4	80.4	93.8	63.4	23.0	86.4	7.4
	1430-1630 <sup>g</sup>	---	---	---	---	---	---	---
	1630-1830	8.1	45.4	53.5	6.4	12.1	21.4	35.0
	1830-2230	8.0	29.3	37.3	5.9	7.1	13.0	24.3
	2230-0630	18.4	4.4	22.8	17.0	2.4	19.4	3.4
7/25/79 <sup>b</sup>	0630-1030	29.5	8.4 <sup>d</sup>	37.9	22.0	12.5 <sup>d</sup>	34.9	3.4
	1030-1230	26.8	48.7	75.5	13.2	14.8	28.0	47.5
	1230-1430	6.8	54.6	61.4	4.4	25.5	30.0	31.4
	1430-1630	6.8	57.1	64.9	3.8	20.9	24.7	39.2
	1630-1830	2.8	45.2	48.1	3.5	8.8	12.4	35.7
	1830-2230	8.9	19.9	28.8	6.3	6.4	12.7	16.1
	2230-0630	16.4	3.2	19.6	14.6	1.6	16.2	3.4
7/26/79 <sup>b</sup>	0630-1030	57.2	7.5 <sup>c</sup>	64.7	45.8	7.1 <sup>c</sup>	53.0	11.7
	1030-1230	32.9	46.5	79.3	19.3	22.1	41.4	37.9
	1230-1430	11.3	80.4	91.7	< 2.1	< 2.1	< 4.2	89.6
	1430-1630	4.6	89.6	94.2	7.3	52.0	59.3	34.9
	1630-1830	5.1	62.5	67.6	3.4	15.0	18.4	49.2
	1830-2230	8.8	19.8	28.6	6.9	6.8	13.7	14.9
	2230-0630	17.6	5.3	22.9	15.4	2.8	18.2	4.7
7/27/79 <sup>a</sup>	06-14	18.5	49.8 <sup>c</sup>	68.2	11.8	36.7 <sup>c</sup>	48.5	19.7
	14-22	4.2	25.4	29.5	3.4	10.4	13.8	15.7
	22-06	6.3	9.4	15.7	3.6	8.7	12.3	3.4
7/28/79 <sup>a</sup>	06-14	22.6	41.5 <sup>c</sup>	64.2	15.8	23.2 <sup>c</sup>	39.0	25.2
	14-22	5.1	28.6	33.7	2.9	4.6	7.6	26.1
	22-06	7.2	9.4	16.6	3.7	4.6	8.4	8.2
7/29/79 <sup>a</sup>	06-14	14.6	44.0 <sup>c</sup>	58.6	10.8	31.0 <sup>c</sup>	41.9	16.7
	14-22	5.5	16.9	22.4	5.2	13.8	18.9	3.5
	22-06	8.3	16.4	24.7	3.8	12.3	16.1	8.6

- a. Samplers heated 3 min. at ca. 50°C following particulate collection.
- b. Samplers not heated.
- c. Ghia nylon used for all after-filters on this day.
- d. NaCl-impregnated Whatman 41 used for all after-filters on this day.
- e. Duralon nylon filters used for all after-filters on this day.
- f. Total inorganic  $\text{NO}_3^-$  sampler minus particulate  $\text{NO}_3^-$  sampler results.
- g. Power failure.

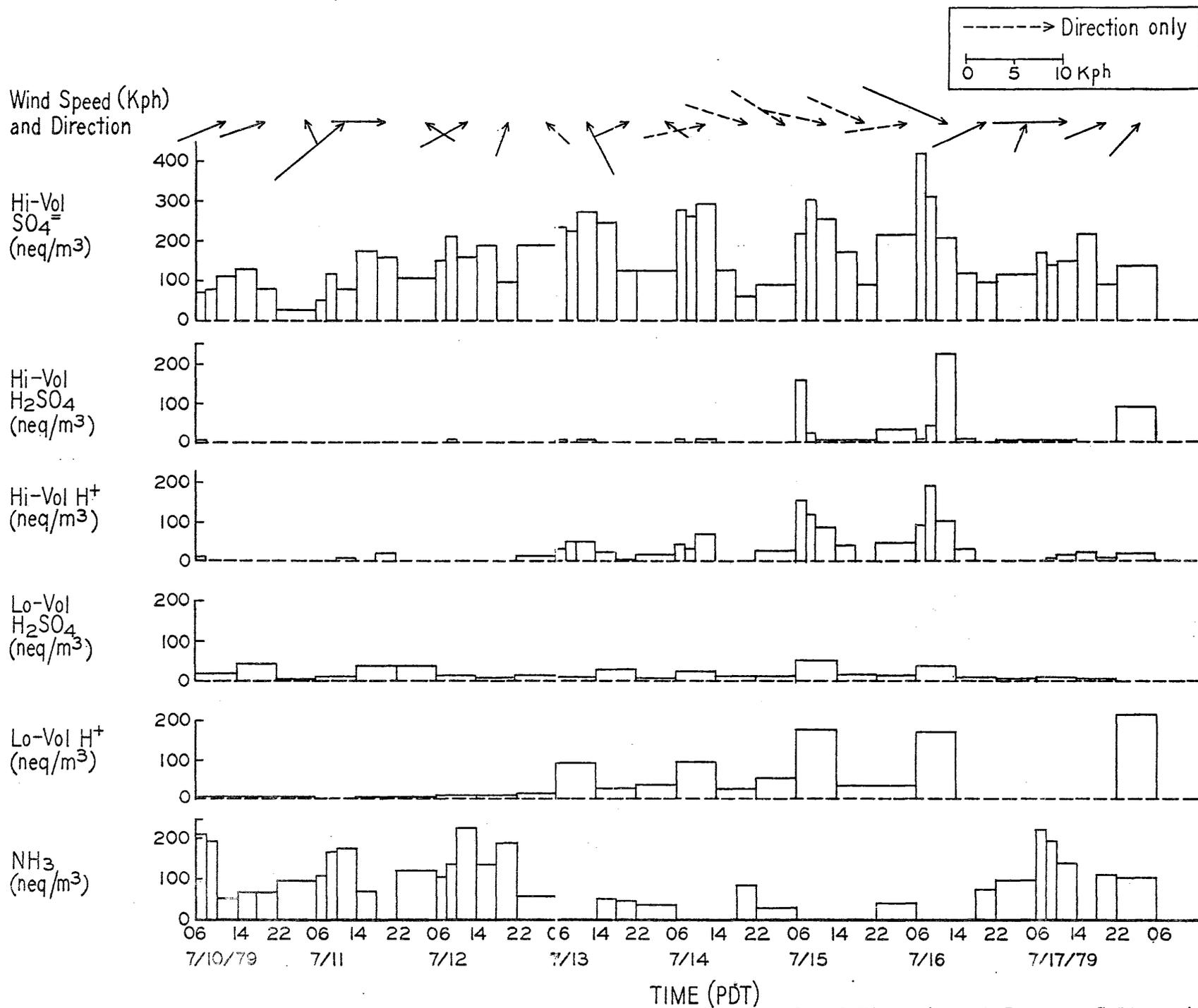


Figure 12 Diurnal Variations of Particulate Acids, Ammonia, Wind Speed and Direction at Lennox, California.

the arrowheads denoting the midpoints for eight-hour average values. Blanks indicate results below limits of detection. Samples showing the highest  $\text{H}_2\text{SO}_4$  levels corresponded to W and NW winds during the preceding night and early morning hours (i.e., from the direction with strong sulfur oxide emissions). On these days, elevated levels of both  $\text{H}_2\text{SO}_4$  and total strong acidity were observed with values up to  $200 \text{ neq/m}^3$  ( $11 \text{ } \mu\text{g/m}^3$  as  $\text{H}_2\text{SO}_4$ ).

Correlation coefficients for linear regression between the aerosol and gaseous constituents are shown in Table 23. For cases with  $r > 0.5$ , the regression equations are given in Table 24. For eight days of sampling the correlation between hi-vol  $\text{H}^+$  and  $\text{H}_2\text{SO}_4$  was relatively low ( $r = 0.45$ ). Gaseous  $\text{HNO}_3$  at Lennox ranged from below detection to  $230 \text{ neq/m}^3$  ( $15 \text{ } \mu\text{g/m}^3$ ). A fraction of this  $\text{HNO}_3$  adsorbed on particulate matter would contribute to the strong acidity measurement. The correlation coefficient between the neq  $\text{H}_2\text{SO}_4$  plus  $\text{HNO}_3$  and strong acid measurements was 0.82, providing limited support for the significance of  $\text{HNO}_3$  in particulate acidity measurements.

The hi-vol and lo-vol  $\text{H}^+$  measurements show moderate linear correlation ( $r = 0.64$ ). The lo-vol samples yielded relatively high strong acid levels but low recoveries of  $\text{H}_2\text{SO}_4$ . Furthermore, the correlation between hi-vol  $\text{H}_2\text{SO}_4$  and lo-vol  $\text{H}^+$  was relatively high ( $r = 0.83$ ). These results are consistent with the conversion of  $\text{H}_2\text{SO}_4$  to  $\text{NH}_4\text{HSO}_4$  on the filters since the acid sulfate is extracted with lower efficiency by benzaldehyde, but titrates as a strong acid. The average recovery of  $\text{H}^+$  on the hi-vol sampler was 50% of that with the lo-vol with  $\text{NH}_3$  denuder. The greater  $\text{H}^+$  values on the lo-vol relative to hi-vol samples may be indicative of the effectiveness of the  $\text{NH}_3$  denuder in preserving samples from neutralization by atmospheric ammonia. However, the negative correlation between hi-vol  $\text{H}^+$  and  $\text{NH}_3$  was only moderate ( $r = -0.54$ ). As shown in Section IV, the denuder does not cause artifact strong acid formation in laboratory trials with  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{NO}_3$  mixture.

Based on the precision data, and decrease in recovery following an additional 30-days storage, the measures taken to preserve the atmospheric filter samples were insufficient to eliminate  $\text{H}_2\text{SO}_4$  loss. One measure of such loss is provided by comparing corresponding  $\text{H}_2\text{SO}_4$  and  $\text{SO}_4^{=}$  levels since the latter represent an upper limit to the  $\text{H}_2\text{SO}_4$  levels. At the  $\text{H}_2\text{SO}_4$  maxima, the  $\text{H}_2\text{SO}_4$  and  $\text{H}^+$  levels were 80 to 110% of the  $\text{SO}_4^{=}$  concentrations, suggesting for these samples, at least, losses are relatively minor. However partial extraction of  $\text{NH}_4\text{HSO}_4$  by benzaldehyde may be influencing these results. In general,  $\text{H}_2\text{SO}_4$  represented 10 to 20% of the sulfate.

Table 23 CORRELATION COEFFICIENTS<sup>a</sup> BETWEEN AEROSOL AND GASEOUS POLLUTANTS SAMPLED AT LENNOX, CALIFORNIA

	Hi-Vol H <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	Hi-Vol H <sup>+</sup>	Hi-Vol SO <sub>4</sub> <sup>=</sup>	Hi-Vol NO <sub>3</sub> <sup>-</sup>	Hi-Vol NH <sub>4</sub> <sup>+</sup>	Lo-Vol H <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	Lo-Vol H <sup>+</sup>	Lo-Vol SO <sub>4</sub> <sup>=</sup>	NH <sub>3</sub>	SO <sub>2</sub>	HNO <sub>3</sub> <sup>d</sup>	Hi-Vol H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub>
Hi-Vol H <sub>2</sub> SO <sub>4</sub>	1.0	0.45	0.23	- 0.43	- 0.21	0.19	0.83	0.31	- 0.22	0.24	0.17	--
Hi-Vol H <sup>+</sup>		1.0	0.67	- 0.38	- 0.04	0.70	0.64	0.69	- 0.54	0.03	0.69	0.82
Hi-Vol SO <sub>4</sub> <sup>=</sup>			1.0	0.10	0.45	0.38	0.47	0.91	- 0.12	0.23	--	--
Hi-Vol NO <sub>3</sub> <sup>-</sup>				1.0	0.65	0.48	- 0.38	0.32	0.53	0.16	0.14	--
Hi-Vol NH <sub>4</sub> <sup>+</sup>					1.0	0.01	0.19	0.24	0.37	0.32	0.07	0.17
Lo-Vol H <sub>2</sub> SO <sub>4</sub>						1.0	0.22	0.55	- 0.30	- 0.12	0.64	--
Lo-Vol H <sup>+</sup>							1.0	0.41	0.02	0.54	0.45	0.71
Lo-Vol SO <sub>4</sub> <sup>=</sup>								1.0	- 0.26	0.03	0.58	--
NH <sub>3</sub>									1.0	0.20	0.18	0.05

a. Pearson's product moment correlation coefficient, r.

b. "Hi-Vol" indicates high volume respirable particulate sampler.

c. "Lo-Vol" indicates low volume respirable particulate sampler.

d. Measured by the difference technique.

Table 24 LINEAR REGRESSION ANALYSIS OF AEROSOL AND GASEOUS POLLUTANTS

SAMPLED AT LENNOX, CALIFORNIA\*

<u>y</u>	<u>x</u>	<u>units of y</u>	<u>units of x</u>	<u>b</u>	<u>a</u>	<u>r</u>	<u>n**</u>	<u>p+++</u>
LV H <sup>+</sup> †	HV H <sub>2</sub> SO <sub>4</sub>	μg/m <sup>3</sup>	neq/m <sup>3</sup>	0.074	1.78	0.84	14	1.00
HV H <sup>+</sup> ††	HV SO <sub>4</sub> <sup>=</sup>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.35	- 1.16	0.66	34	1.00
LV H <sub>2</sub> SO <sub>4</sub>	HV H <sup>+</sup>	μg/m <sup>3</sup>	neq/m <sup>3</sup>	0.013	0.46	0.70	18	1.00
HV H <sup>+</sup>	LV H <sup>+</sup>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.35	0.58	0.64	12	0.98
LV SO <sub>4</sub> <sup>=</sup>	HV H <sup>+</sup>	μg/m <sup>3</sup>	neq/m <sup>3</sup>	0.11	8.66	0.69	19	1.00
HV H <sup>+</sup>	NH <sub>3</sub>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	- 0.23	1.30	- 0.54	12	0.93
HNO <sub>3</sub>	HV H <sup>+</sup>	neq/m <sup>3</sup>	neq/m <sup>3</sup>	1.36	36.8	0.69	15	1.00
HV H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub>	HV H <sup>+</sup>	neq/m <sup>3</sup>	neq/m <sup>3</sup>	2.04	35.5	0.82	16	1.00
LV SO <sub>4</sub> <sup>=</sup>	HV SO <sub>4</sub> <sup>=</sup>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	1.41	1.23	0.91	23	1.00
HV NO <sub>3</sub> <sup>-</sup>	NH <sub>3</sub>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.60	0.56	0.53	22	0.99
LV H <sub>2</sub> SO <sub>4</sub>	LV SO <sub>4</sub> <sup>=</sup>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.068	0.04	0.55	22	0.99
LV H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.09	0.50	0.64	23	1.00
LV H <sup>+</sup>	SO <sub>2</sub>	μg/m <sup>3</sup>	ppm	206	- 0.29	0.54	10	0.89
LV H <sup>+</sup>	HNO <sub>3</sub>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.35	1.92	0.50	14	0.93
LV H <sup>+</sup>	HV H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub>	μg/m <sup>3</sup>	neq/m <sup>3</sup>	0.025	1.00	0.71	14	1.00
LV SO <sub>4</sub> <sup>=</sup>	HNO <sub>3</sub>	μg/m <sup>3</sup>	μg/m <sup>3</sup>	0.62	9.14	0.58	23	1.00

\*  $y = a + bx$ 

\*\* number of data pairs

† LV = low-volume sampler

†† HV = high-volume sampler

††† Significance of the difference of the correlation coefficient, r, from zero.

## 2. Claremont

As shown in Figure 13, the maximum  $\text{H}_2\text{SO}_4$  levels observed at Claremont were about half those at Lennox. There is no correlation between  $\text{H}^+$  and  $\text{H}_2\text{SO}_4$  levels ( $r = -0.24$  and  $0.09$  for hi-vol and lo-vol samples, respectively). Gaseous  $\text{HNO}_3$  at this site ranged up to  $1200 \text{ neq/m}^3$  ( $76 \mu\text{g/m}^3$ ). The diurnal variations for the  $\text{HNO}_3$  concentration, measured by the difference method, are also shown in Figure 13. The addition of  $\text{HNO}_3$  to the  $\text{H}_2\text{SO}_4$  level improves the correlation with particulate  $\text{H}^+$ , but the correlation coefficient remains relatively low ( $r = 0.44$ ).

The concentration of gaseous  $\text{NH}_3$  at Claremont exceeded that at Lennox exhibiting a pronounced diurnal maximum during early morning hours. Negative correlations between  $\text{NH}_3$  and  $\text{H}^+$  or  $\text{H}_2\text{SO}_4$  with the unprotected respirable particulate hi-volume sampler might be expected. The observed correlation coefficients were  $r = -0.52$  and  $r = -0.05$  for  $\text{H}^+$  against  $\text{NH}_3$ , and  $\text{H}_2\text{SO}_4$  against  $\text{NH}_3$ , respectively. Thus, while neutralization of airborne  $\text{H}_2\text{SO}_4$  aerosols by atmospheric  $\text{NH}_3$  is highly likely, no correlation between the  $\text{NH}_3$  level at the sampling site and the  $\text{H}_2\text{SO}_4$  concentration is seen.

The sum of the equivalents of sulfate and nitrate may be compared to the total of  $\text{H}^+$  and ammonium ions at both sites. For 16 sampling periods the cation:anion ratio of equivalents averaged  $0.68 \pm 0.21$ . Even during periods of elevated  $\text{H}_2\text{SO}_4$  and/or  $\text{H}^+$ , the ratio remained within the variation shown. Thus other water-soluble cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ) contribute to the particulate matter.

## E. Measurement of Nitric Acid

Atmospheric sampling was done by the Okita and Spicer methods with and without filter heating. Figure 14 compares atmospheric  $\text{HNO}_3$  results on heated, NaCl/W41 and nylon filters. Consistent with the laboratory findings for samples with  $< 500 \mu\text{g NO}_3^-/\text{filter}$  (Section III), results on the NaCl/W41 filters (i.e., the Okita method) are slightly higher than on nylon.

Measurement of  $\text{HNO}_3$  by filter collection is subject to positive error if particulate nitrate is lost from the Teflon prefilter. However,  $\text{HNO}_3$  measured by TTN minus PN ("HNO<sub>3</sub> by difference") should be independent of such error. Figure 15 compares "HNO<sub>3</sub> by difference" and  $\text{HNO}_3$  by unheated filter collection. The results show high correlation. The higher values by filter collection are consistent with the loss of nitrate from the prefilters. The same comparison, but with heated filters, is shown in Figure 16. Again, results correlate well, with higher values by filter collection. However, there is greater average deviation from "HNO<sub>3</sub> by difference" compared to results without heating, implying increased  $\text{NO}_3^-$  loss from the prefilter.

49

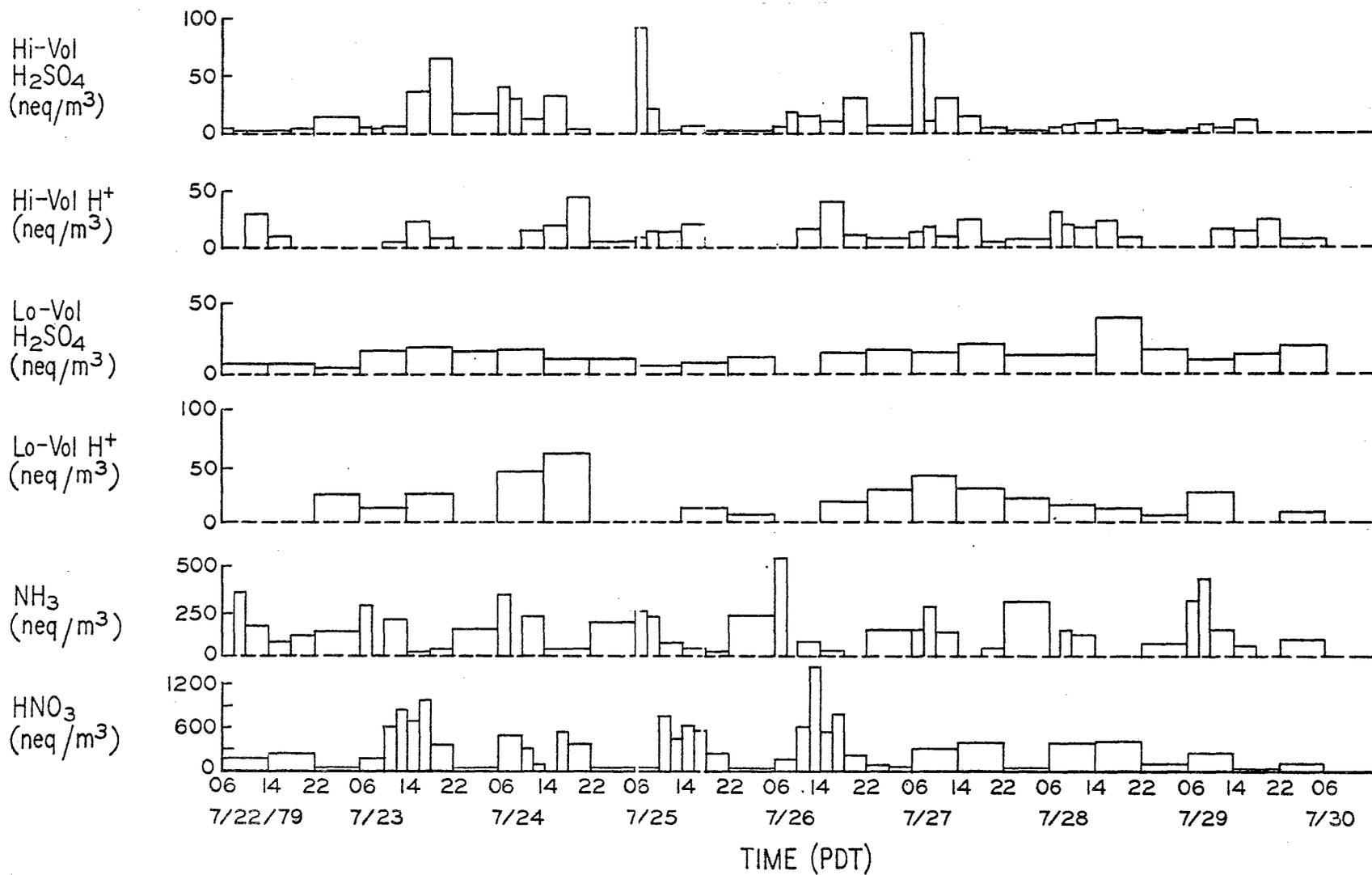


Figure 13 Diurnal Variations of Particulate Acids, Ammonia and Nitric Acid at Claremont, California

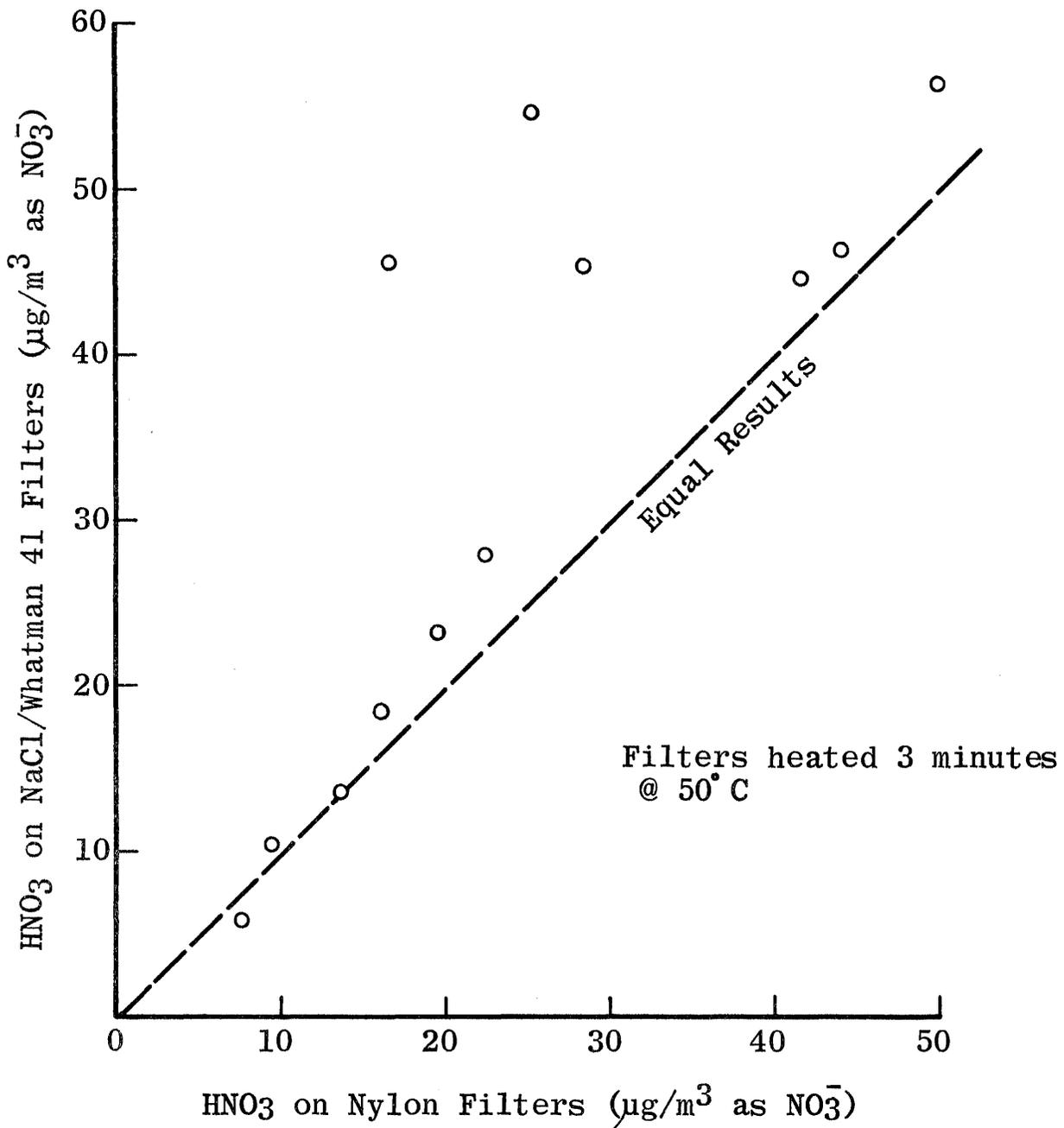


Figure 14 Atmospheric HNO<sub>3</sub> Collection on Nylon vs. NaCl/Whatman 41 Filters

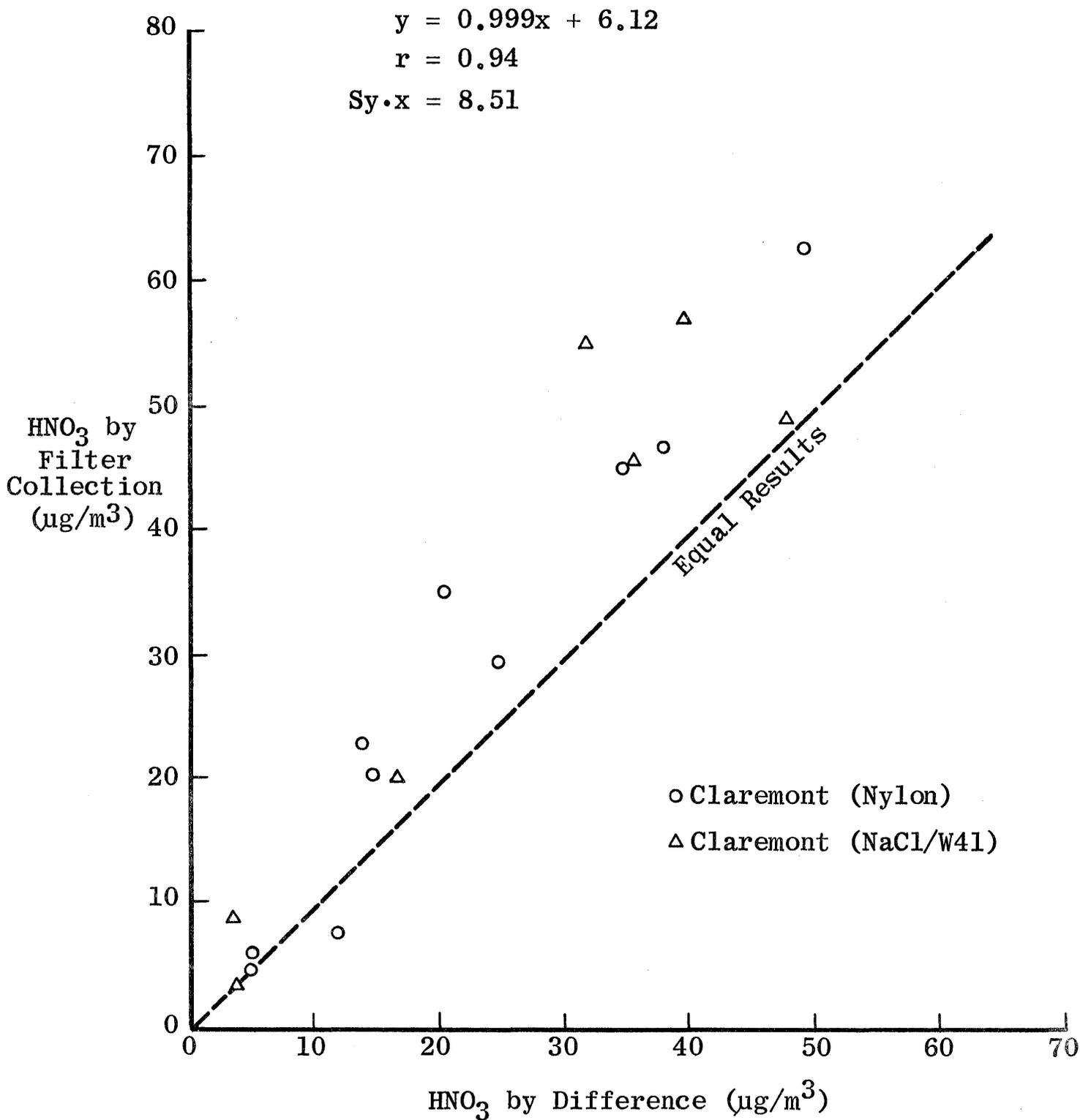


Figure 15 Comparison of HNO<sub>3</sub> by filter collection and "by Difference" Using Unheated Samplers

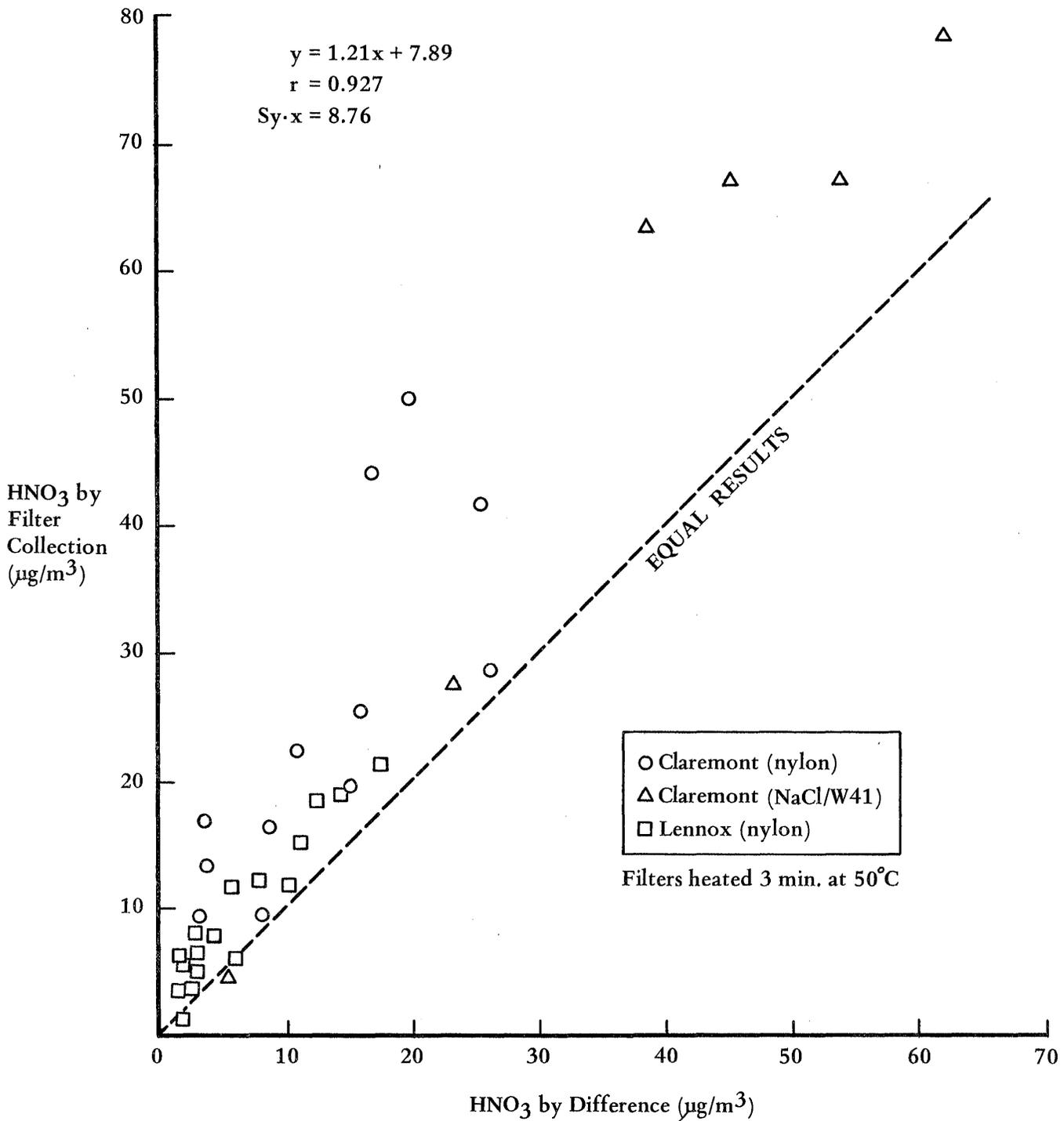


Figure 16 Comparison of HNO<sub>3</sub> by Filter Collection and "by Difference" Using Heated Samplers

In Section III losses of  $\text{HNO}_3$  up to about 25% were shown on Teflon prefilters bearing atmospheric particulate matter, the level increasing with particulate loading. This produced a corresponding negative error in nitric acid measurements by the filter collecting technique using these prefilters. In the present atmospheric trials, while TSP measurements were not made, such negative errors appear to be offset by losses of volatile particulate nitrate from the prefilter. Assuming a TSP of  $100 \mu\text{g}/\text{m}^3$ , the atmospheric particulate matter collected in 2, 4 and 8-hour samples equals 240, 480 and 960  $\mu\text{g}/\text{filter}$ . From Figure 1, only the eight-hour samples would show retentions  $> 10\%$ . However, in locations with relatively high  $\text{HNO}_3$  levels but low particulate nitrate, errors in  $\text{HNO}_3$  measurement due to retention of the acid on particulate matter may be detectable.

Figure 17 compares " $\text{HNO}_3$  by difference" to simultaneous  $\text{HNO}_3$  by measurements by a long-path Fourier transform infrared (FTIR) technique, here considered to be the reference method. FTIR data were obtained by averaging results obtained at 15 to 30-minute intervals. The ratio of means,  $\text{HNO}_3$  by difference :  $\text{HNO}_3$  by FTIR was 1.2, implying an average accuracy of 80% for the difference method. However, the linear correlation coefficient was low ( $r = 0.2$ ). Because of the generally higher results for " $\text{HNO}_3$  by difference" only lower limit estimates of the error in the  $\text{HNO}_3$  values by filter collection can be inferred from comparisons with " $\text{HNO}_3$  by difference" as in Figures 15 and 16.

These results may be considered viz-a-viz the 88% efficiency measured for the denuder for  $\text{HNO}_3$  removal. A 12% penetration of  $\text{HNO}_3$  should yield high PN values. Since PN represented, on average, nearly 50% of the TIN, this should yield about 12% low " $\text{HNO}_3$  by difference" values. Comparing " $\text{HNO}_3$  by difference" to FTIR results, results with the former suggest that opposing sources of error (e.g., loss of particulate nitrate) more than offset that caused by  $\text{HNO}_3$  penetration. While laboratory studies could not demonstrate loss of 0.1 to 3  $\mu\text{m}$  PN particles in the denuder, loss of  $> 3 \mu\text{m}$  nitrate-containing particles remains a possible explanation for the high " $\text{HNO}_3$  by difference" results.

#### F. Negative Errors in Particulate Nitrate Sampling

Although Teflon and quartz filters yield low levels of artifact particulate nitrate, particulate nitrate sampling with such inert filters is subject to negative error because of volatilization of  $\text{NH}_4\text{NO}_3$  and reactions liberating  $\text{HNO}_3$ . Figure 18 is a scatter diagram of nitrate against  $\text{H}^+$  results both obtained from two to eight-hour samples collected with the respirable particulate hi-vol sampler and acid-washed quartz filters. No correlation is evident suggesting that other factors control the observed  $\text{NO}_3^-$  levels.

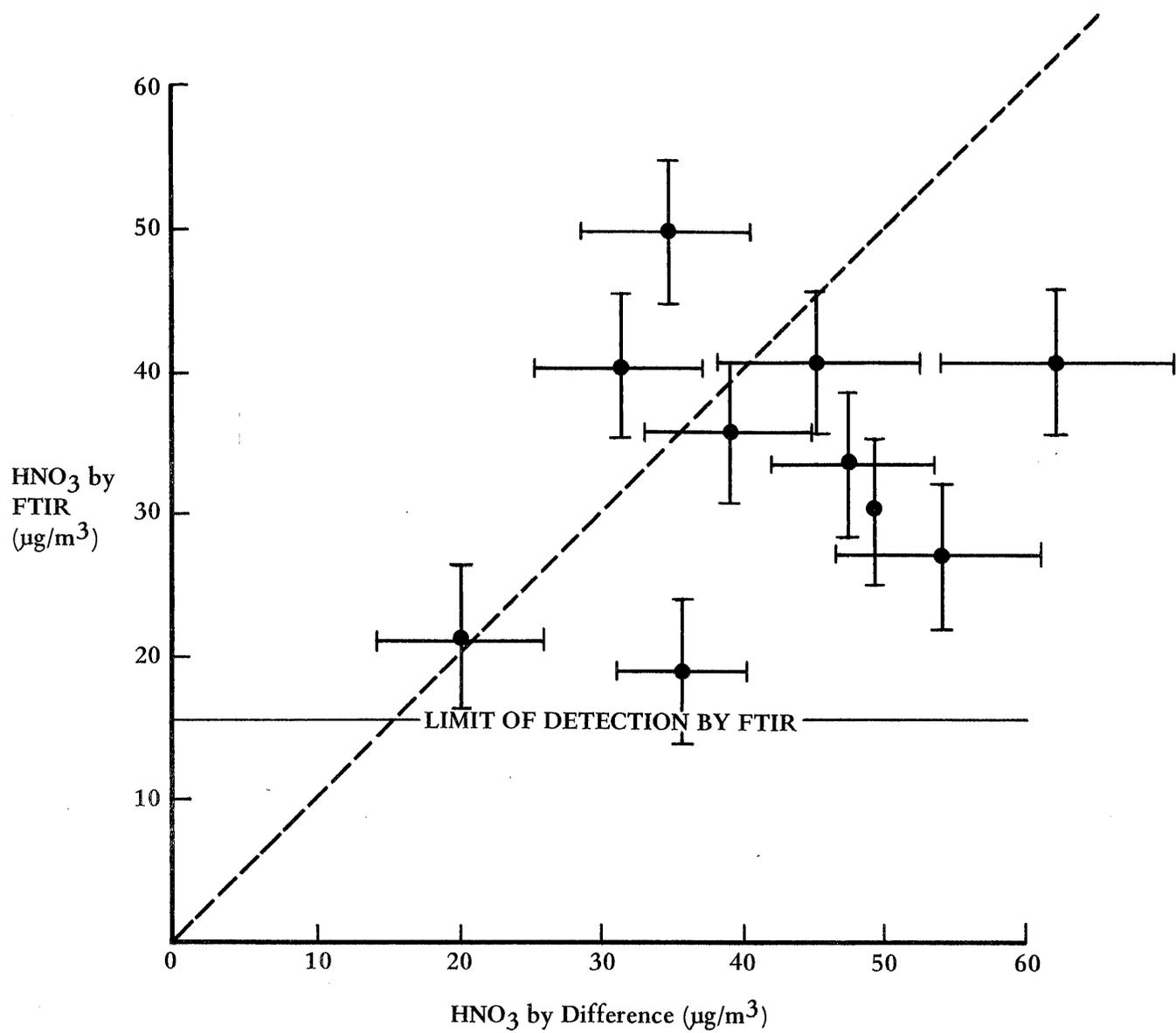
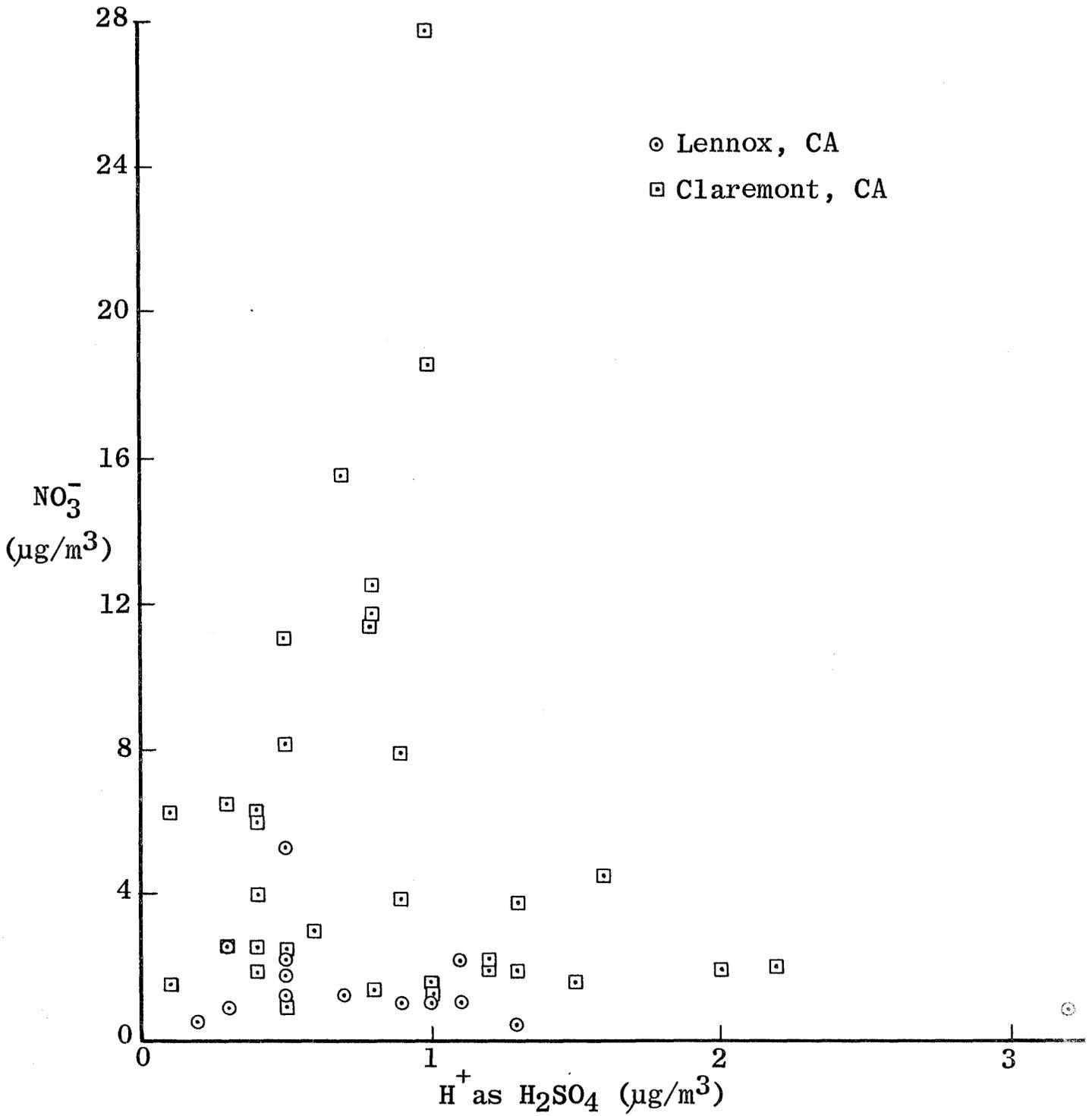


Figure 17 Comparison of HNO<sub>3</sub> by Long Path Fourier Transform Infrared (FTIR) and "by Difference"

Figure 18

SCATTER DIAGRAM OF NITRATE AGAINST STRONG ACID CONCENTRATIONS FOR HI-VOL SAMPLES COLLECTED ON QUARTZ FIBER FILTERS



A somewhat more specific evaluation of the effect of particulate acids on nitrate loss is provided by examining the results obtained with the particulate nitrate sampler. The nitrate collected on the Teflon filter downstream of the acid gas denuder is subject to losses both from volatilization and particulate acid-nitrate salt reactions. Gaseous acid-nitrate salt reactions would be negligible because of the use of the acid gas denuder. The nitrate lost by either mechanism was collected on the reactive after-filter. The proportion of the total 8-hour average total particulate nitrate retained on the Teflon filter is plotted against simultaneous strong particulate acidity values in Figure 19. Only data from Lennox, California were examined because of the high particulate acidity levels observed at that site. For concentration of strong acid which reached nearly  $11 \mu\text{g}/\text{m}^3$  (expressed as  $\text{H}_2\text{SO}_4$ ) and nitrate levels up to  $9 \mu\text{g}/\text{m}^3$  on the prefilters, a correlation coefficient of  $-0.75$  was observed, providing some support for the significance of this loss mechanism. By contrast the analogous plot against  $1/T$  ( $^\circ\text{K}$ ) showed no correlation ( $r = -0.15$ ) implying that volatilization was not the dominant source of particulate nitrate loss at this site.

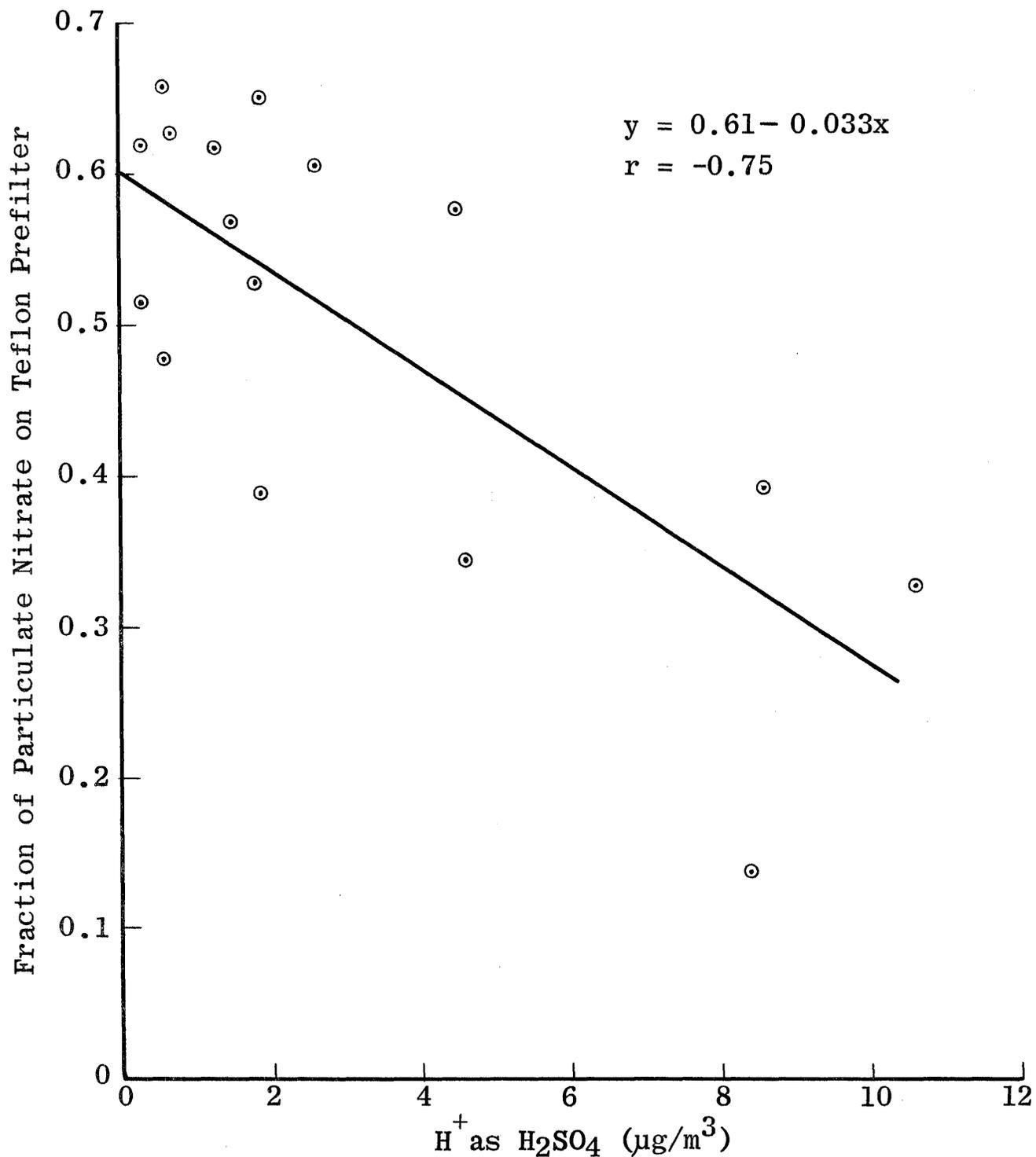
The extent of the loss of particulate nitrate from Teflon filters during atmospheric sampling was estimated by comparing the nitrate results on Teflon prefilters with those from simultaneously collected PN samples using the acid gas denuder (i.e., the sum of the  $\text{NO}_3^-$  on the Teflon filter and reactive after-filter). With unheated samples, the results (Figure 20) fall into two sets, one with reasonable agreement between techniques and the second, with much lower prefilter results. The first set corresponds to samples collected during night and morning hours. The samples deviating badly were collected with ambient temperatures in the range  $29$  to  $35^\circ\text{C}$  and relative humidities about  $30\%$ . Under these conditions, more than  $50\%$  of the nitrate appears to be lost from the Teflon prefilters. Figure 21 makes the same comparison using heated samplers. The results for all samples are similar to those in Figure 20 when the ambient temperature was high, indicating that most of the nitrate on the prefilter has been lost. Because of possible loss of PN in the denuder, errors inferred for the prefilters are minimum values. We conclude that the PN sampler (Figure 3) gives a more reliable measure of particulate nitrate than collection on Teflon filters.

#### G. Positive Errors in Particulate Nitrate Sampling with Glass Fiber Filters

Artifact particulate nitrate formation can be a major source of interference with glass fiber, cellulose, and cellulose ester filters. Earlier studies comparing atmospheric nitrate collection with six filter types to the results from laboratory exposures of these filters to nitrogen oxides, suggested that retention of nitric acid, rather than  $\text{NO}_2$ , was the dominant source of artifact particulate nitrate formation.<sup>30</sup> Atmospheric sampling of nitrates

Figure 19

SCATTER DIAGRAM OF THE PROPORTION OF PARTICULATE NITRATE  
RETAINED BY A TEFLON FILTER AGAINST THE PARTICULATE  
STRONG ACID CONCENTRATION AT LENNOX, CA



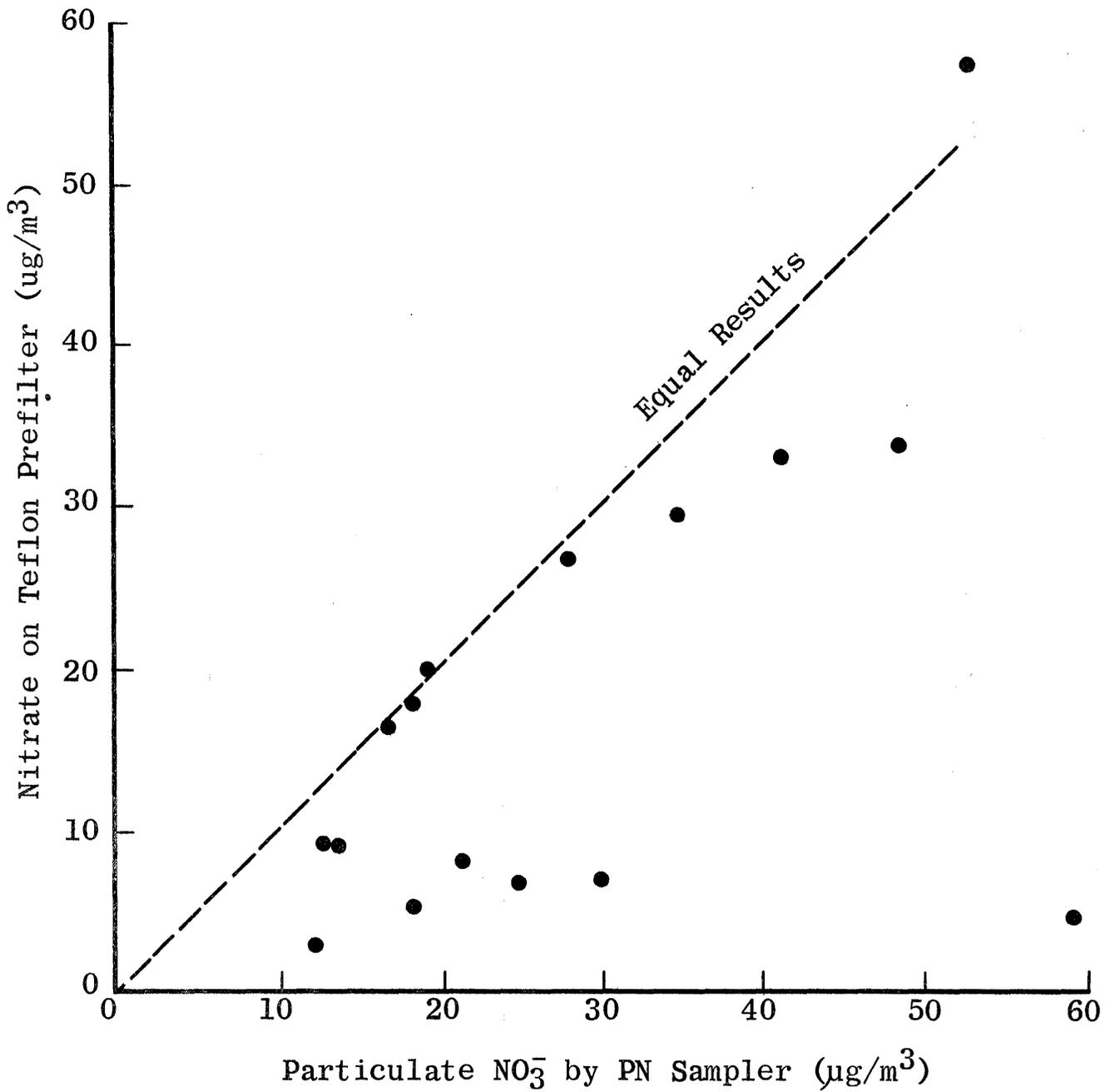


Figure 20 Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Unheated)

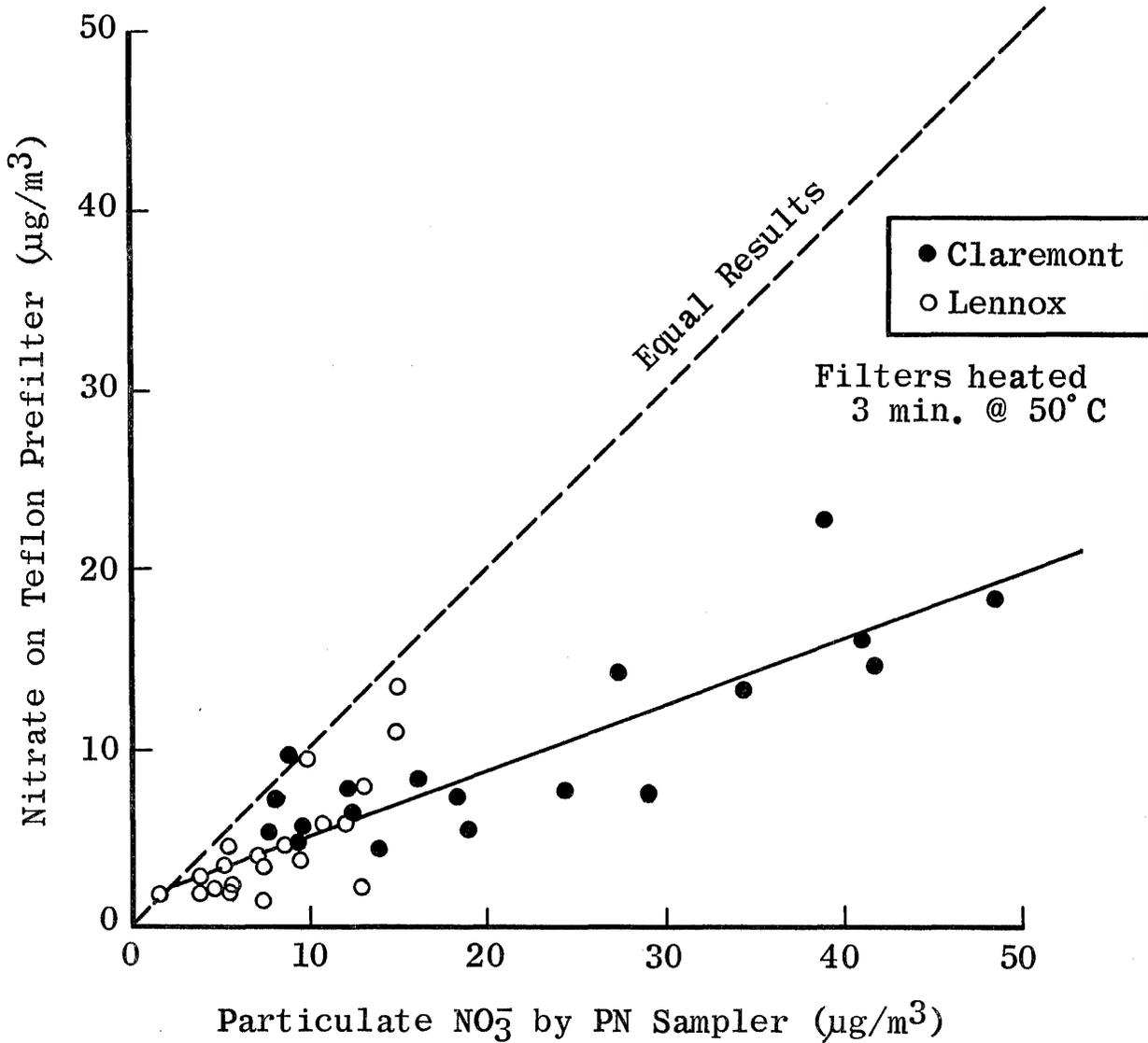


Figure 21 Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Heated)

with Gelman A (pH = 7.6) glass fiber filters demonstrated that the concentrations measured were equal to the TIN at low ( $< 4 \mu\text{g}/\text{m}^3$ )  $\text{HNO}_3$  levels.

In the present study this evaluation was extended to higher  $\text{HNO}_3$  and TIN levels. Figure 22 compares TIN values to nitrate concentrations obtained with 47 mm Gelman A (pH = 7.6) glass fiber filters sampling for two to eight hours at 25 Lpm. Again, the results are not significantly different. Since  $\text{NO}_2$  at ambient levels is not collected on nylon or NaCl/W41 filters,<sup>1,13,31</sup> these findings confirm that nitric acid is the principal source of artifact particulate nitrate on glass fiber filters, at least at the locations studied. Similar behavior would be expected with 24-hour samples using the more alkaline (pH  $\geq 9$ ) glass fiber filters typically employed in high-volume samplers.

#### H. Atmospheric Nitrate and $\text{HNO}_3$ Levels at Claremont, California

Figure 23 compares the diurnal variations of PN with those for  $\text{HNO}_3$  (by difference) and  $\text{O}_3$  at Claremont.  $\text{HNO}_3$  and  $\text{O}_3$  show similar diurnal patterns consistent with previous reports using real-time analyzers.<sup>32</sup> The diurnal maximum for particulate  $\text{NO}_3^-$  occurred earlier in the day, compared to those for  $\text{HNO}_3$  and  $\text{O}_3$ , again consistent with earlier results.<sup>33</sup>

#### I. Intermethod Comparison of Techniques for Atmospheric Ammonia Determination

Atmospheric  $\text{NH}_3$  results obtained by the oxalic acid-impregnated filter technique are compared to those by FTIR in Figure 24. FTIR data are averages of results obtained at 15 to 20-minute intervals for comparison with the two-hour integrated values by the filter method. The results are highly correlated, but FTIR values are consistently higher. The mean difference in the data sets is  $2.5 \pm 0.5 \mu\text{g}/\text{m}^3$  (as  $\text{NH}_4^+$ ). Assuming the FTIR results to be correct, the present comparison suggests that 1)  $\text{NH}_3$  may be lost by adsorption and/or reaction on the glass fiber prefilter and its particulate matter, and 2) that such loss dominates over the opposing source of error, reactions of ammonium salts on the prefilter liberating  $\text{NH}_3$ . Alternatively, the impregnated filters may be inefficient for  $\text{NH}_3$  collection at very low concentrations.

#### J. The Role of Ammonia in Nitrate Chemistry

Atmospheric ammonium nitrate is believed to exist in equilibrium with  $\text{NH}_3$  and  $\text{HNO}_3$ :



$$K = (\text{NH}_3)(\text{HNO}_3)$$

The equilibrium "constant" is dependent on temperature and, perhaps on relative humidity as well.<sup>7</sup> High concentrations of ammonia

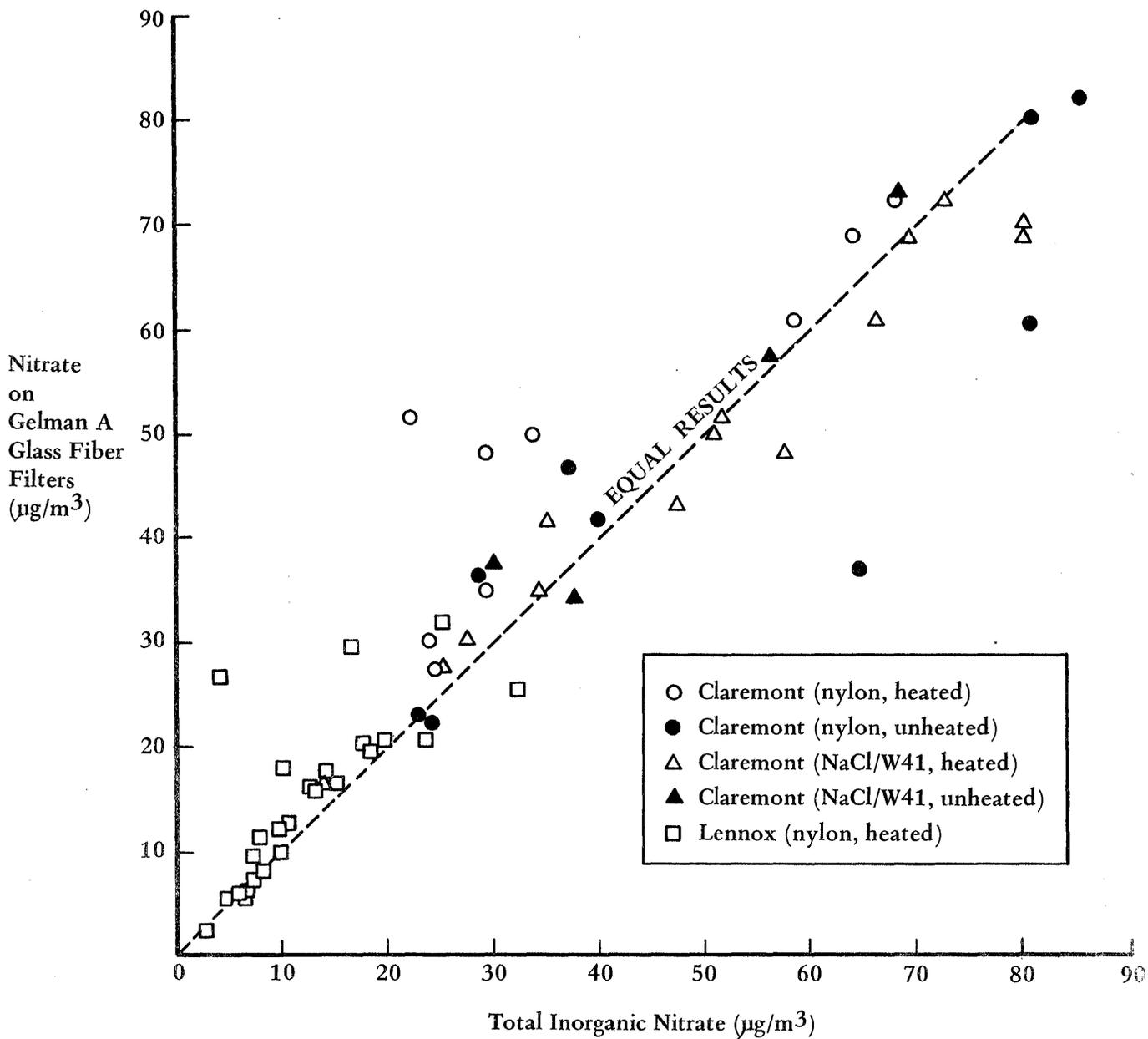


Figure 22 Glass Fiber Filters as Total Inorganic Nitrate Samplers

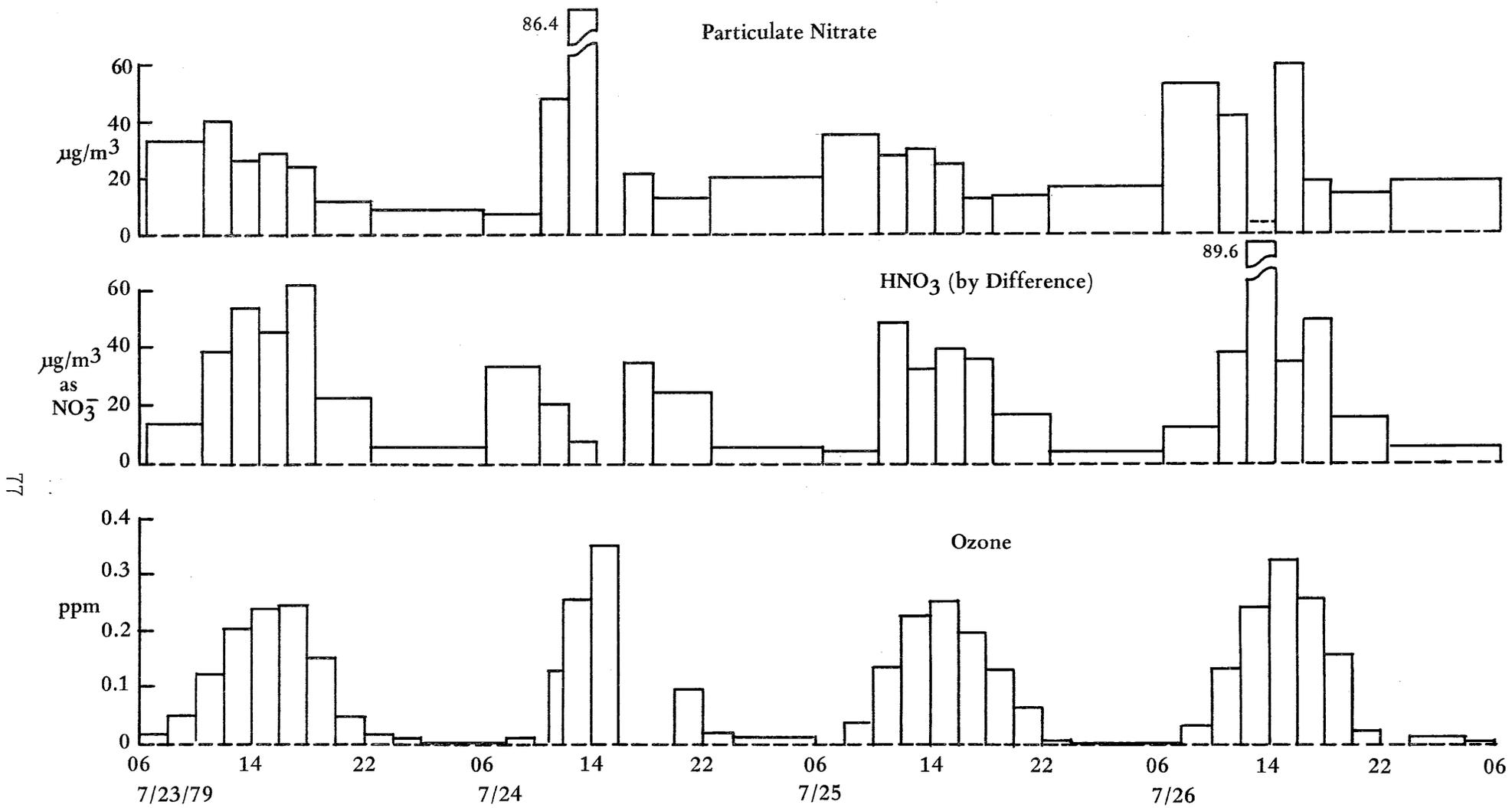
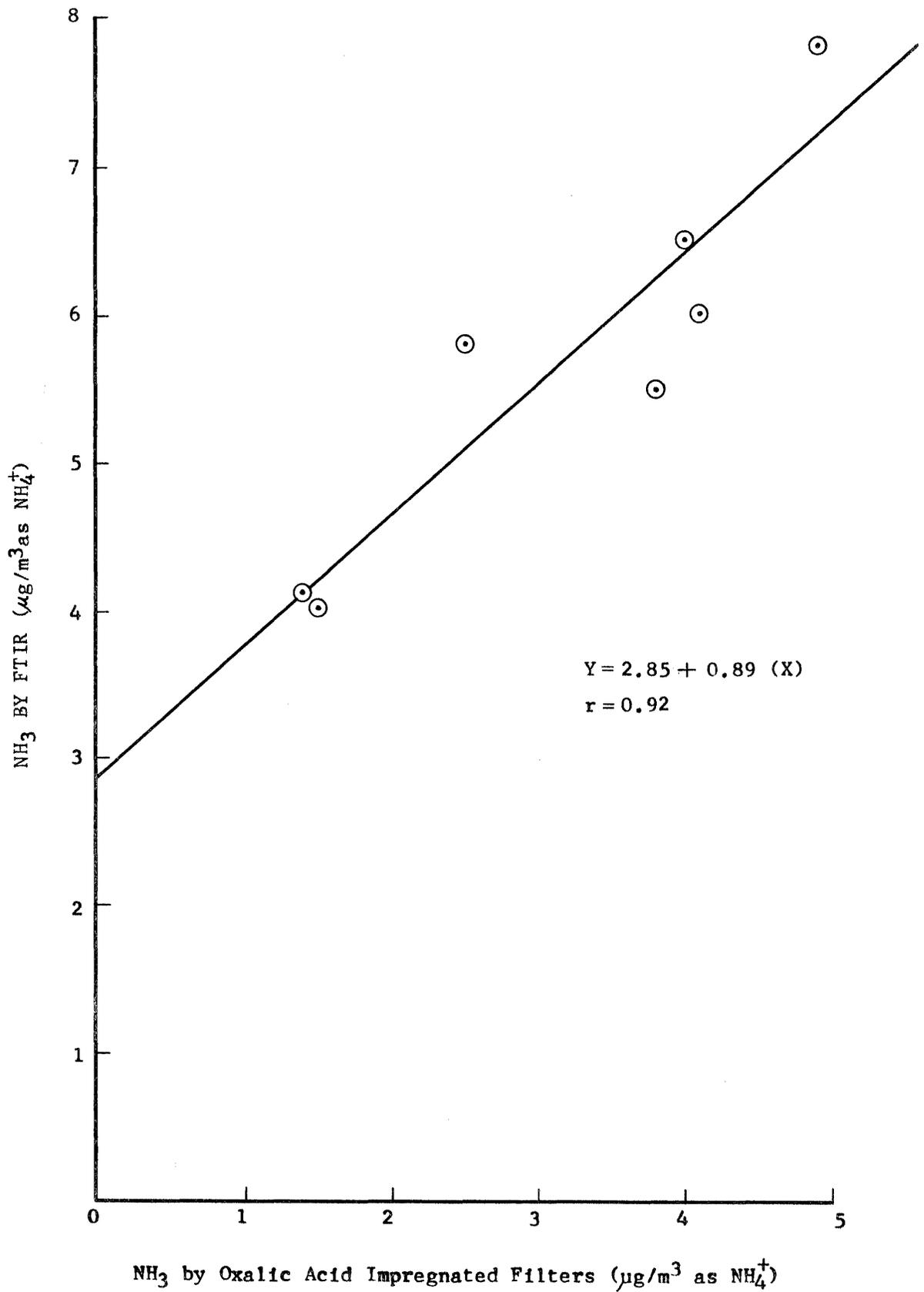


Figure 23 Diurnal Variations of HNO<sub>3</sub>, Particulate Nitrate and Ozone at Claremont, California

Figure 24 COMPARISON OF NH<sub>3</sub> BY LONG PATH FOURIER TRANSFORM INFRARED (FTIR) AND BY OXALIC ACID-IMPREGNATED FILTERS



should lead to low observed  $\text{HNO}_3$  levels. Figure 25 is a scatter diagram of  $\text{HNO}_3$  concentration against  $\text{NH}_3$ . While the negative correlation coefficient is relatively low,  $-0.47$ , the trend supports expectations.

The  $\text{NH}_3$  and  $\text{HNO}_3$  data may be used to calculate the above equilibrium constant. Since at low concentrations the  $\text{NH}_3$  and  $\text{HNO}_3$  are probably below the equilibrium concentration based on saturation with respect to  $\text{NH}_4\text{NO}_3$  dissociation, the resulting concentration product would provide only lower limit values for K. Figures 26 and 27 plot the concentration product against relative humidity and  $1/T$  ( $^\circ\text{K}$ ) for cases with products  $> 5(\text{ppb})^2$ . The dissociation constant is highest at low R.H. and high temperature. These findings are consistent with the preceding results which showed the greatest loss of  $\text{NO}_3^-$  from prefilters at the highest temperatures and lowest R.H. Figure 25 also shows results segregated by R.H. range. At constant temperature, lower R.H. seems to favor higher K values. The median concentration product for the data plotted was  $15.8 (\text{ppb})^2$ . This value is similar to those reported by Stelson et al.<sup>2</sup> and compares to the value  $\geq 21 (\text{ppb})^2$  reported in Section III for volatilization of pure  $\text{NH}_4\text{NO}_3$  at 50 and 80% R.H. and  $21^\circ\text{C}$ .

Figure 13 noted elevated early morning levels of  $\text{NH}_3$ . It follows that the observed diurnal variation for  $\text{HNO}_3$ , with its midday maximum, might reflect, at least in part, the decreased concentration of  $\text{NH}_3$  rather than a photochemical origin for  $\text{HNO}_3$ .

#### K. The Composition of Atmospheric Particulate Nitrate

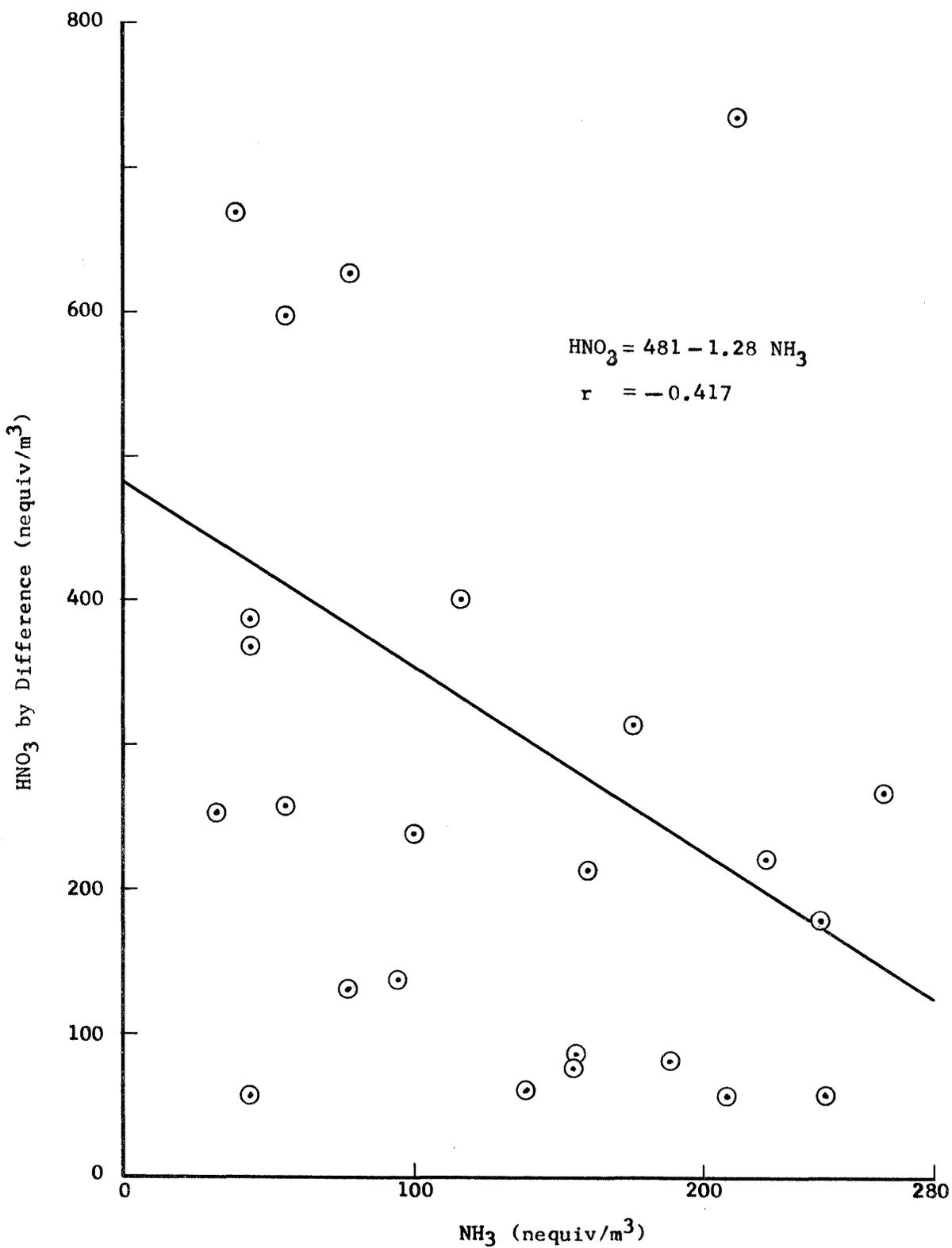
The preceding discussion of the role of  $\text{NH}_3$  in particulate nitrate formation provides support for the significance of  $\text{NH}_4\text{NO}_3$  in atmospheric particulate matter. In addition to this salt, nitrate may be present as the sodium (or other metal) salt,\* as adsorbed  $\text{HNO}_3$  or as addition compounds, e.g.,  $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$ .<sup>36</sup> The latter two would contribute to particulate acidity. It was shown in Section V D that the correlation between total strong particle acids and the sum of particulate  $\text{H}_2\text{SO}_4$  and gaseous  $\text{HNO}_3$  was substantially better than between strong acid and  $\text{H}_2\text{SO}_4$  alone. This was interpreted as support for the significance of adsorbed  $\text{HNO}_3$ . Additional support was previously reported using temperature-programmed electron spectroscopy for chemical analysis (ESCA).<sup>36</sup> Volatilization rates for nitrate and ammonium from atmospheric samples were greatly in excess of those from pure  $\text{NH}_4\text{NO}_3$ .

The chemical nature of particulate nitrate may also be revealed by the pattern of nitrate collection following passage through the diffusion denuder. If this nitrate were non-volatile, all

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\* Reference 34 discusses techniques to distinguish  $\text{NH}_4\text{NO}_3$  from  $\text{NaNO}_3$  and their application in atmospheric sampling.

Figure 25. ATMOSPHERIC NITRIC ACID  
AGAINST AMMONIA CONCENTRATIONS AT CLAREMONT



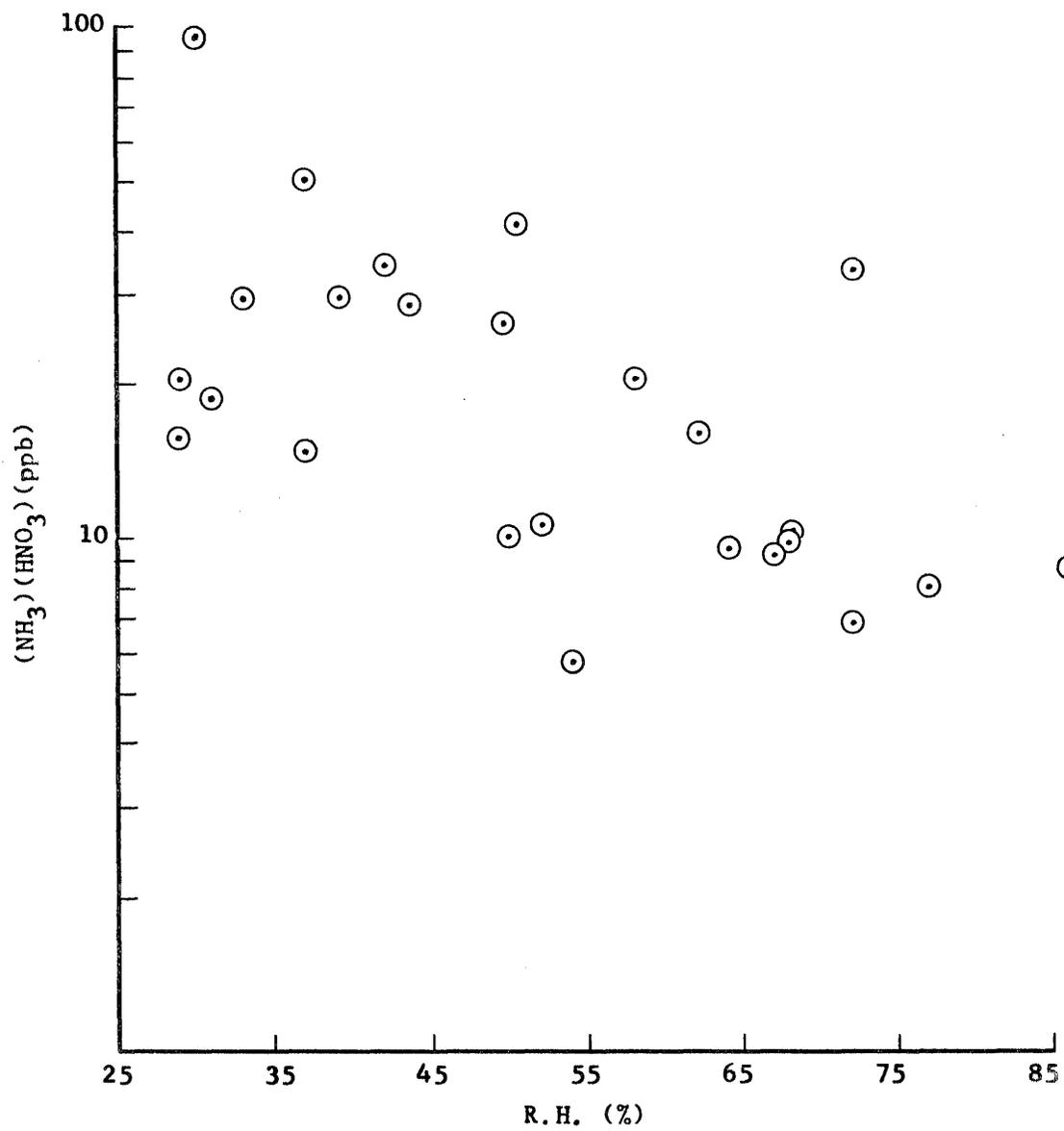
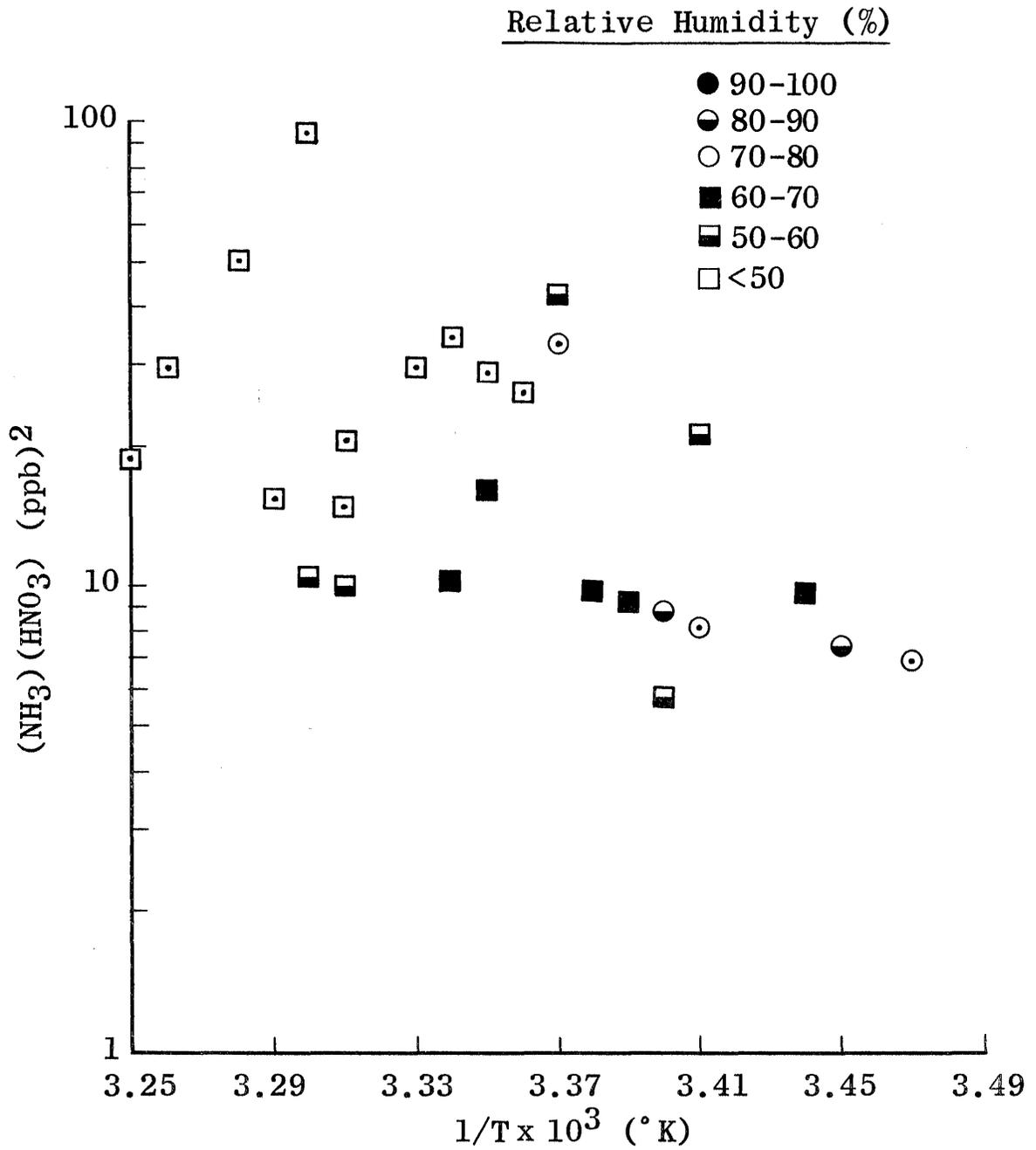


Figure 26 RELATIVE HUMIDITY DEPENDENCE OF THE CALCULATED  $\text{NH}_4\text{NO}_3$  DISSOCIATION CONSTANT.

Figure 27  
 TEMPERATURE DEPENDENCE OF THE  
 CALCULATED  $\text{NH}_4\text{NO}_3$  DISSOCIATION CONSTANT



would remain on the Teflon filter (excepting the  $\text{HNO}_3$  liberated by reaction of the nitrate salts with particulate acids). Figure 28 plots the fraction of the nitrate retained by the Teflon prefilter against the ambient  $\text{HNO}_3$  concentration measured by the difference method. The data plotted are for the three episodes, 7/24, 7/25, and 7/26/80 when no filter heating was employed. In spite of the removal of 88% of the  $\text{HNO}_3$  by the denuder, the fraction of nitrate retained on the prefilter is negatively correlated with the  $\text{HNO}_3$  level. Assuming 12% penetration of  $\text{HNO}_3$  through the denuder (see Section III), the mean nitrate expected on the after-filter due only to the  $\text{HNO}_3$  is  $2.9 \mu\text{g}/\text{m}^3$ , compared to an observed mean of  $14.4 \mu\text{g}/\text{m}^3$  ( $n = 19$ ). Thus, on average, the observed  $\text{NO}_3^-$  on the after-filter is five times that explainable by atmospheric  $\text{HNO}_3$  penetration. These results are consistent with the significance of particulate-bound  $\text{HNO}_3$  which is easily desorbed when gaseous  $\text{HNO}_3$  is removed.

However, these observations lend themselves to alternate interpretations. Figure 29 shows a similar plot against average ambient temperature for the same episodes. Data points are also coded for R.H. range. Clearly high temperature and low R.H. can also be related to low retention of nitrate on the filters. Such an observation is qualitatively consistent both with loss of adsorbed  $\text{HNO}_3$  (or dissociation of  $\text{HNO}_3\text{-NH}_4\text{NO}_3$  adducts) and  $\text{NH}_4\text{NO}_3$  dissociation on the prefilter. The latter should also be favored by elimination of  $\text{HNO}_3$ . Further work is needed to elucidate the contributions of the various nitrate compounds to atmospheric particulate matter especially as regards the role of particle-bound nitric acid.

#### L. Conclusions

1. Significant levels of  $\text{H}_2\text{SO}_4$  and particulate acidity have been observed for the first time in California ambient air. The highest level of  $\text{H}_2\text{SO}_4$  found was  $220 \text{ neq}/\text{m}^3$  ( $11 \mu\text{g}/\text{m}^3$ ) for a four-hour period. This compares to California's 24-hour standard of  $25 \mu\text{g}/\text{m}^3$  for total water soluble sulfate.
2. Particle bound  $\text{HNO}_3$  appears to contribute to the observed particulate acidity.
3. The strong dependence of  $\text{H}_2\text{SO}_4$  levels on wind direction at Lennox suggests that stationary emissions of  $\text{H}_2\text{SO}_4$  and/or  $\text{SO}_3$  were the source of the observed  $\text{H}_2\text{SO}_4$ .
4. Short-term sampling is useful in minimizing losses of  $\text{H}_2\text{SO}_4$ .
5. Glass fiber filters approximate total inorganic nitrate samplers, collecting both atmospheric particulate nitrates and nitric acid.
6. In California's South Coast Air Basin, (as well as in Pittsburg, California as shown in Phase I), nitric acid is the only

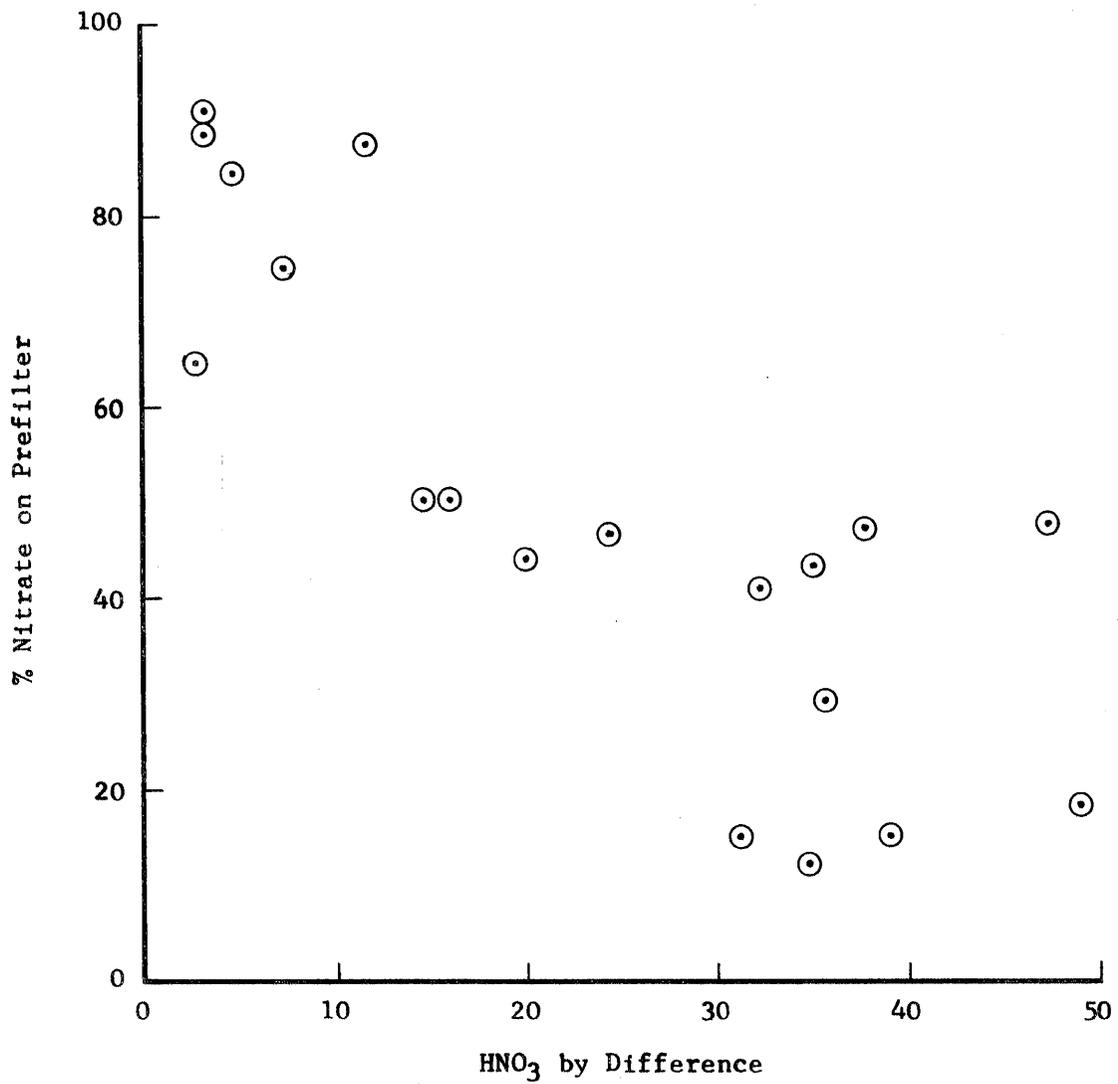


Figure 28 THE PERCENT OF NITRATE ON THE PREFILTER OF THE PARTICULATE NITRATE SAMPLER vs HNO<sub>3</sub> CONCENTRATION

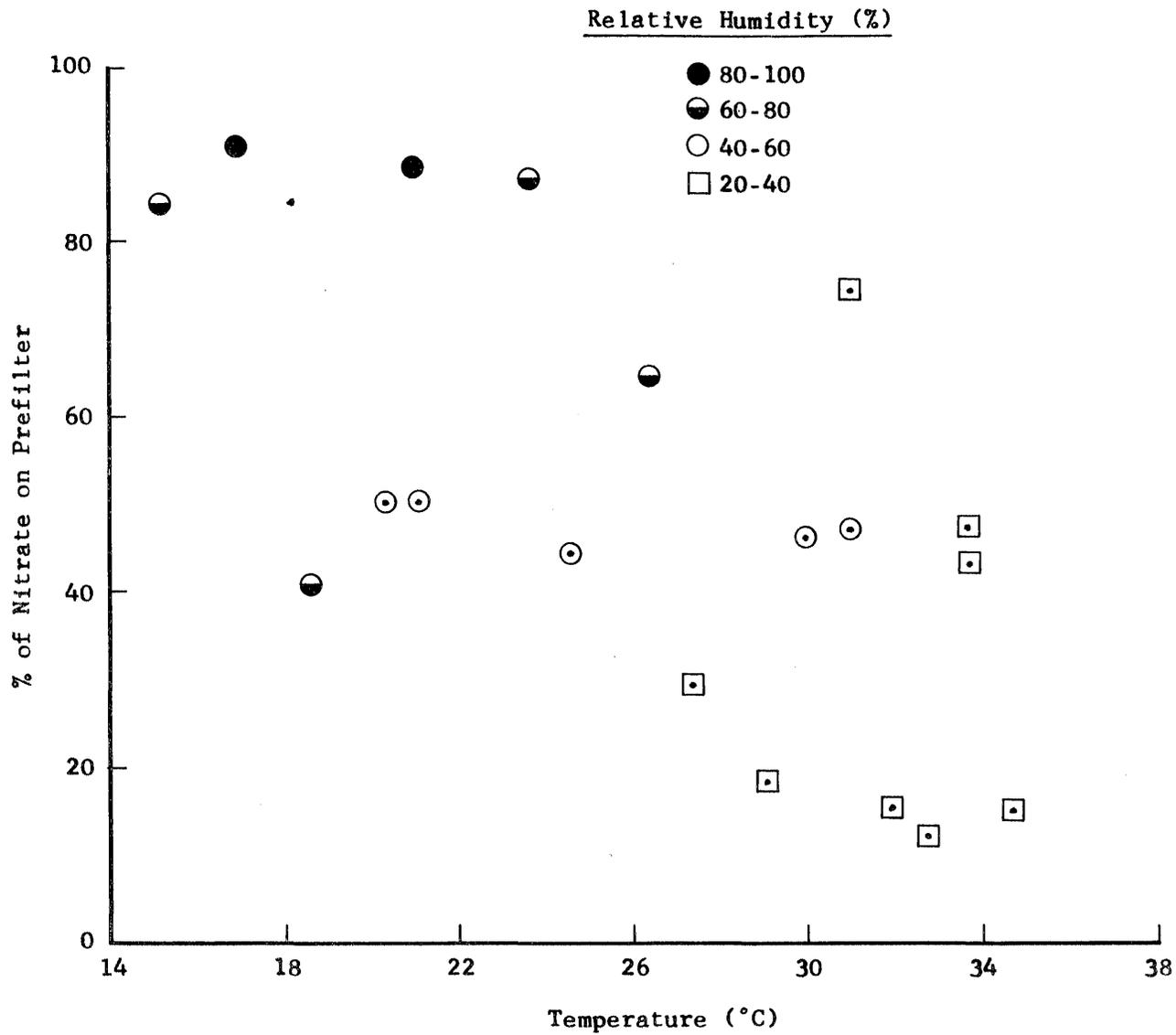


Figure 29 THE PERCENT OF NITRATE ON THE PREFILTER OF THE PARTICULATE NITRATE SAMPLER vs TEMPERATURE.

observable contributor to artifact particulate nitrate formation in atmospheric sampling with glass fiber filters.

7. The heating of filter samplers for particulate nitrate and  $\text{HNO}_3$  causes increased error. Even without heating, > 50% losses of particulate nitrate from the Teflon prefilter can occur with corresponding positive errors in  $\text{HNO}_3$  measurement.
8. Nitric acid values obtained by difference between total inorganic nitrate and particulate nitrate measurements are too high. Nevertheless, these results are more accurate than those by simple filter collection techniques.
9. Sampling of particulate nitrate with an acid gas denuder, Teflon prefilter and  $\text{HNO}_3$  trap provides improved sampling accuracy compared to collection with Teflon filters.

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